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# GENERAL INFORMATION

# CONCERNING HYDROXIDES

By

Mary E. Lee




OAK RIDGE NATIONAL LABORATORY

OPERATED BY

CARBIDE AND CARBON CHEMICALS COMPANY

A DIVISION OF UNION CARBIDE AND CARBON CORPORATION

OAK RIDGE, TENNESSEE

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# GENERAL INFORMATION CONCERNING HYDROXIDES

Mary E. Lee

April 21, 1952

AIRCRAFT NUCLEAR PROPULSION DIVISION

OAK RIDGE NATIONAL LABORATORY
Operated by
CARBIDE AND CARBON CHEMICALS COMPANY
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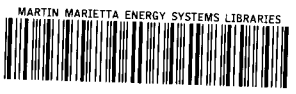



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## ABSTRACT

This report is a compilation of abstracts taken from Chemical Abstracts (1907 thru Sec. 4, 1952) containing information concerning the hydroxides of barium, calcium, cesium, lithium, magnesium, potassium, rubidium, sodium and strontium.

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## GENERAL INFORMATION CONCERNING HYDROXIDES

CA 1,262-6

KOH Production
Ettore Crudo, Rome
173,901, Dec. 18, 1904

Process of prodg. KOH by means of the reaction between alkali sulphate and mono-calcium phosphate, consisting in causing an alkali bisulphate solution to react upon dicalciumphosphate for the purpose of forming a solution of monoalkali phosphate and free $H_3PO_4$, which solution is then treated for the elimination of the free $H_3PO_4$ with pptd. $Ca_3(PO_4)_2$, then with so much KOH as to change the monoalkali phosphate into dialkali phosphate with the sepn. of the dicalcium phosphate which can be again used in the process, whereupon the KOH is recovered from the resulting solution of the dialkali sulphate by further treatment with CaO, with the sepn. of $Ca_3(PO_4)_2$, which can be used again in the process.

CA 1,379-3

Dehydration of Caustic Alaklies
Badische Analin and Soda Fabrik, Ger.
352,076, March 6, 1905

Process of dehydrating caustic alkalies, consisting in heating the alkaline liquors under pressure, the NaOH to 180° and the KOH to 260°, about, that is to a temperature below the point of fusion.

CA 1,381-9

Electrolysis of Alkali Chlorides
Granier
353,304, May 18, 1905

Apparatus for the electrolysis of alkali chlorides, characterized by non-filtering diaphragms, completely separating the positive and negative solutions. The caustic solution resulting from the electrolysis being formed alone in the negative liquid, while the positive liquid gives rise to the formation of chlorine.

CA 1,474-8

Rendering $Na_2CO_3$ and $K_2CO_3$ Caustic by Means of CaO
LeBlanc, K. Navotny
Z. anorg. Chem. 51, 181-201

$$Na_2CO_3 + CaO + H_2O \longrightarrow 2NaOH + CaCO_3$$

| Temp. | Soly. $CaCO_3$(mg/1000 cc.) In $H_2O$ | In NaOH | | Hydrolysis Calc. | |
|---|---|---|---|---|---|
| | | Cal. from Cond. | Dir. Detn. | Cond. | Dir.Detn. |
| 18° | 12.8 | 2.7 | 4.2 | 80% | 67% |
| | | 5.3 | | | |
| 95-100° | 20.7 | --- | 5.7 | --- | 72% |

Velocity of reaction more important than temperature or pressure upon yield. Excess CaO, vigorous agitation, high temperature with 2.5N $Na_2CO_3$ solution in 1/2 hour gave 93.6% yield.

CA 1,1168-5

Causticizing of $Na_2CO_3$
Rud. Wegscheider
Ann. 351, 87-89

$$Na_2CO_3 + Ca(OH)_2 \longrightarrow 2NaOH + CaCO_3$$

$$\xrightarrow{40°} CaNa_2CO_3 \cdot 2H_2O$$

$$K_{reaction} = \frac{(NaOH)^2}{Na_2CO_3} \text{ at } 80°, 108°$$

equil. reached in $2\frac{1}{2}$ - 3 hr. at 108°
12 hr. at 80°
not in 40 hr. at 62°

The hydrated double salt is soluble at low temperatures and the $Na_2CO_3$ may be recovered.

CA 1,2290-5

The Working Up of Alkaline Lyes Including Those Obtained by Electrolysis, I. Caustic Lyes

H. Voss

Chem. Ztg. 31, 496-98

$Na_2CO_3 + Ca(OH)_2 \longrightarrow CaCO_3 + 2NaOH$

$Q_2 = Q\,(1 - g/g_1)$

$Q_1 = Q - Q_2$

$g_1 = \frac{Q_1 g}{Q - Q_2}$

$Q$ = initial wt. of liquor in Kg.
$Q_1$ = final wt. of liquor in Kg.
$Q_2$ = quantity of water to be evap.
$g$ = initial strength in °Bé
$g_1$ = final strength in °Bé

$p$ (vapor tension) $= \frac{(N+n)p'}{N}$

$A = \frac{C}{60ktE}$

$t$ = diff. in temp. of boiling liquor and heating vapor

$E = \frac{\text{act. efficiency}}{\text{theor. efficiency}} = 0.80 - 0.93$

$p'$ = aqueous vapor tension at temp. of vapor given off by the liquor

$N = \frac{W}{M} = \frac{\text{Wt. of solvent}}{\text{Mol. wt. of same}}$

$n = \frac{W}{M} = \frac{\text{Wt. of Solutes}}{\text{Mol. wts. of same}}$

$a$ = heating area

$A$ = heating surface in sq. meters

$C$ = cal/hr.

$k$ = coeff. for transmission of heat = 8 cal(wrought iron), 3 cast iron or 1°/sq. in./min.

CA 1, 2291-5

Working Up of Alkaline Lyes, Including Those Obtained by Electrolysis II. Electrolytic Lyes.
H. Voss
Chem. Ztg. 31, 528-29.

$vs = x + y + z$

$v_1 s_1 = x_1 + y_1 + z_1$

$x_1 = x - wv_2$

$Y_1 = y$ = constant

$z_1 = z - v_2$

$v_1 = v - v_2$

$$v_1 = v - v_2 - \frac{n}{S_2} v_2$$

$$v_2 = \frac{v(S_1 - S)}{S_1 (1 + \frac{n}{S_2}) - (1+n)}$$

$$v_2 = \frac{v(S_1 - S)}{1.127 S_1 - 1.28}$$

$$v_2 = \frac{v(S_1 - S)}{1.133 S_1 - 1.36}$$

$$S_1 = \frac{vS - v_2(1+n)}{v - v_2 (1 + \frac{n}{S_2})}$$

$v$ = init. vol. in liters
$v_1$ = final vol. in liters
$v_2$ = vol. of water evap.
$S$ = sp. grav. of init. liquor
$S_1$ = sp. grav. of final liquor
$S_2$ = sp. grav. of salt deposited
$x$ = init. % KCl (NaCl) in kg.
$y$ = init. % NaOH (KOH) in kg.
$z$ = init. % $H_2O$ in kg.
$n$ = % NaCl (KCl) of the satd. soln.
Assuming satd. soln. at 100° of NaCl = 28%, KCl = 36% and sp. gr. NaCl = 2.2, KCl = 2.7

CA 1, 2333-3

Patent 182,201, Jan. 5., 1905
Badische Anilin - und-Soda-Fabrik, Ludwigshafen a/Rh.

Process of preparing caustic alkalies free from, and not containing more than 10% of water, consisting in heating caustic soda in vacuo for some time at about 180°, or caustic soda in vacuo at 260° at temperatures at which fusion does not result, whereby the iron vessel is not attacked, with consequent decrease in the content of the product to a mere trace.

CA 1, 2510-8

Patent 6,405, Mar. 16, 1907
Salzbergwerke Neustassfurt and Theilmehner, Zecherndorf, Germany

Process of preparing crystalline KOH, consisting for dry KOH, in allowing very highly concd. KOH solns. to cool and the crystals to separate out from the mother liquor before the concn. has sunk to 85% caustic potash; second, for crystalline mono-hydrated KOH, in allowing concd. KOH solns. containing 59-85% KOH to cool and the crystals to separate out from the mother liquor before a concn. of 58% downwards and 86% upwards is exceeded; third, for a crystalline mixture of dry and mono-hydrated KOH, in allowing highly concd. KOH solns. containing above 85% KOH to cool, and according to the percentage desired the crystallization is interrupted, the crystals being separated from the mother liquor; fourth, for a crystalline mixture of mono- and bi-hydrated KOH, in allowing KOH lyes containing below 75% KOH to cool, the concn. thereby sinking so far below 58% KOH that the crystals separated out have attained the desired content.

CA 1, 3044-9

The Electrolytic Caustic Soda Industry
M. L. Magnot
Mon. Sci. (4) 21, 586

Discussion of various electrolytic processes. Detailed description of Onthenin-Chalandre diaphragm process.

CA 2, 634-9

Interaction of Metallic Sulphates and Caustic Alkalies
Spencer Pickering
Proc. Chem. Soc., 23, 261; J. Chem. Soc. 91-2, 1981

Most metallic sulphates, on treatment with caustic alkali give ppts. which are definite basic salts. Excess of alkali produces in some cases salts still more basic and finally metallic hydroxides. Mn and Mg sulphates are pptd. at once as hydroxides.

CA 2, 1076-1

Patent 189,474, Oct. 23, 1906
Cornelio L. Sagui, Saloniki, Turkei

Apparatus for producing caustic alkali by electrolysis of molten alkali chloride, with the use of a lead cathode, characterized in that a tube siphons the lead-alkali alloy over into another container wherein steam converts it into caustic alkali.

CA 2, 1077-8

Patent 189,835, July 17, 1906
Salzbergwerk Neustassfurt and Teilnehmer, Zscherndorf bei Bitterfeld

Process of producing crystallized caustic potash in various commercial forms, consisting in crystallizing out (1) water-free KOH by cooling highly conc. KOH solns. and separating the crystals before the concn. of the mother liquor has fallen to 85% KOH; (2) monohydrated KOH from conc. KOH solns. of 59-85% KOH, by cooling and separating the crystals before the concn. of the mother liquor has fallen to 58% or increased to 86% KOH; (3) any desired mixture of anhydrous and monohydrated KOH from highly conc. KOH solns. with a content of over 85% KOH, by cooling, and discontinuing the operation at the proper time by separation of the mixed crystals; (4) by cooling, a mixture of mono- and dihydrated KOH from a KOH soln. of under 75% KOH and allowing the concn. to fall below 58% KOH until the desired content is obtained; and (5) obtaining Na-free KOH by separating the crystals from the last-mentioned mother liquor, which is then renewed.

CA 2, 1502-7

Pat. 877,376
Philip B. Sadtler, Samuel P. Sadtler, Phila., Pa.

A method of making alkali hydroxide which consists in intimately mixing finely divided alkali sulphate with at least an equal amount of $Al_2O_3$, heating the same to at least an incipient yellow heat until an alkali aluminate is formed therefrom, decomposing the aluminate and prodg. alkali hydroxide therefrom.

CA 2, 1932-4

Action of Heat on the Hydrates of Lithium
DeForcrand
Compt. rend., 146, 802 (Apr. 15)

In 1888 Dittmar obtained a hydrate of the composition $LiOH \cdot H_2O$. The author has repeated the work and finds that the substance obtained as crystals still contains a little water but that when dried in hydrogen at +33° it has the composition as found by Dittmar. When this substance is heated in dry hydrogen up to +140° it is changed in the course of an hour to LiOH. This substance thus prepared is of the same nature as the hydrate, while if it is heated to a higher temperature polymeric modifications are formed. The commercial product does not contain the same amount of water, it does not lose water at 140° nor a little above this. It reaches a constant weight when heated to 445° and has the composition $LiOH + 0.125\ H_2O$. By continuing the heating for some time and raising the temperature finally to 780° the anhydrous oxide is obtained. The presence of polymeric forms in some of the intermediate stages was confirmed by a study of the heats of solution in the different cases.

CA 2, 2033-3

On the Dissociation Pressure of Certain Hydroxides and Carbonates
John Johnston (Univ. Breslau)
Z. physik. Chem. 62, 330-58 (Mar. 31)

This systematic series of measurements of the dissociation pressure of the hydroxides and carbonates of the alkaline earth metals and of lithium was undertaken with a view of demonstrating regularities in accordance with the periodic arrangement of the elements. Two methods were employed: the first (in which the material in question was kept in an atmosphere in which the partial pressure of the dissociation product was just such that no loss or gain in weight would occur) was given up; the second (a static method) was employed with success. In plotting the results the temperature is taken as abscissa and for ordinate the temperature at which water (or calcium hydroxide) shows the same vapor pressure. The resulting plots are, mostly, nearly straight lines; general equations follow:

| | | | |
|---|---|---|---|
| $t_{Ca(OH)_2} = 1.98\ t_w + 349$ | | $t_{Sr(OH)_2} = 1.82\ (t_c-350) + 420$ | |
| $t_{Sr(OH)_2} = 3.62\ t_w + 416$ | | $t_{Ba(OH)_2} = 2.03\ (t_c-350) + 594$ | |
| $t_{Ba(OH)_2} = 4.0\ t_w + 590$ | | $t_{LiOH} = 1.97\ (t_c-350) + 522$ | |
| $t_{LiOH} = 3.9\ t_w + 530$ | | $t_{Li_2CO_3} = 2.75\ (t_c-350) + 730$ | |
| $t_{CaCO_3} = 1.8\ (t_c-350) + 475$ | | $t_{BaCO_3} = 1.6\ (t_c-350) + 1033$ | |

In which t is the temperature at which the pressure is taken, $t_w$ and $t_c$ are the temperatures at which water and calcium hydroxide resp. show the same pressures. The measurements were carried up to 1000°, at which temperature NaOH and $Na_2CO_3$ showed noticeable dissociation pressures. Measurements were also made of the dissociation pressures of hydrated strontium and barium hydroxides. It was found in general that the elements studied, if arranged according to magnitude of dissociation pressures of their compounds, fall in the order to be expected from the periodic classification. A theoretical basis is shown to underlie the linear character of the curves, and it is also shown that this linear relation between corresponding temperatures is generally applicable for interpolation or even extrapolation.

CA 2, 2608-6

Ger., 198,481, Nov. 17, 1905
Ferd Schacke, Koln

Process of mfg. NaOH and KOH from recent volcanic deposits, by grinding them fine, mixing therewith an amount of finely powdered CaO corresponding to the content of K and Na, adding $H_2O$, and heating for a long time,

with or without pressure, thereby obtaining potash and soda lyes septd. from the calcium silicate.

CA 2, 3178-6

Free Energy Changes Attending the Formation of Certain Carbonates and Hydroxides
John Johnston
J. Am. Chem. Soc., 30, 1357-65 (Sept.)

Hydroxide $\longrightarrow$ oxide + $H_2O$ (vapor)
carbonate $\longrightarrow$ oxide + $CO_2$
$\Delta F = \Delta H + RT\ln p + IT$

| | $\Delta F$ 25°C | | | | | |
|---|---|---|---|---|---|---|
| | Mg | Ca | Li | Sr | Ba | Na |
| Hydroxide $\longrightarrow$ oxide | 3,600 | 16,430 | 18,100 | 19,700 | 23,000 | ------ |
| Carbonate $\longrightarrow$ oxide | 11,700 | 41,450 | 42,000 | 44,900 | 51,400 | 61,000 |

inc. stability $\longrightarrow$

CA 2, 3268-6

Brit., 24,891, November 9, 1907
Claus N. Ruber, 44 Kirkeveien, Christiana, Norway

In the electrolytic treatment of alkali chlorides for the prodn. of alkali metals, caustic alkalies, and alkali carbonates or bicarbonates, transforming this electrolytic Cl into HCl, utilizing the acid for the dissolution of phosphates, and adding $Ca(OH)_2$ or $CaCO_3$ to the soln. thus obtained, the Ca salt being pptd., while the $CaCl_2$ remains in the soln., whereby the Cl electrolytically produced is transformed into $CaCl_2$, and a Ca-P compd. suitable for manure is obtained.

CA 3, 32-3

Cu and Fe Salts in Presence of Alkalies and Acids
H. Frischer, Neussa/Rh
Chem-Ztg. 32, 1005 (Oct. 14)

$$2CuSO_4 + 4NaOH \longrightarrow 2Cu(OH)_2 + 2\,Na_2SO_4$$
$$2FeSO_4 + 2Cu(OH)_2 \longrightarrow Fe_2(OH)_4\,SO_4 + Cu_2SO_4$$
$$Cu_2SO_4 + O + H_2O \longrightarrow CuSO_4 \cdot Cu(OH)_2$$
$$2\,FeSO_4 + 2CuSO_4 + 4NaOH + O + H_2O \longrightarrow 2Fe(OH)_3 + 2CuSO_4 + 2Na_2SO_4$$

In acids, just the reverse.

CA 3, 402-1

Electrolytic Caustic and Chlorine, Theory of the Bell Process
A. Brochet
Compt. rend. 147, 674 (Oct. 19)

C = equivalent concentration
k = conductivity of electrolyte
l = mobility of OH ion
C = $10^3 k/l_{OH}$

| | | | | | |
|---|---|---|---|---|---|
| KCl | 20% | $K_{18}$ = 0.2677 | C = 1.538 | KOH = 86.13 g/l |
| NaCl | 20% | 0.1957 | 1.125 | 45.00 |
| NaCl | satd. | 0.2156 | 1.239 | 49.56 |

CA 3, 1262-9

The Preparation of Carbonate-Free Caustic Solutions
W. P. Jorissen and H. Filippo
Chem. Weekblad., 6, 145-49

The authors utilize the principles of the Castner and Kellner process, in an apparatus consisting of a U-tube, the base of which contains metallic Hg, an outlet for which is provided in the shape of a tube supplied with a stopcock and capable of accommodating itself to different levels. One arm of the U-tube is filled with a strong solution of NaOH or KOH, and is closed by a stopper through which there passes an iron rod, ending in a spiral, and a capillary tube, connected with a separatory funnel, containing Hg, the rod serving as anode. The other arm is similarly closed by a stopper through which passes a Pt wire, to the end of which a piece of foil is attached, to serve as the cathode. There is also a soda-lime tube and a siphon tube, through which latter freshly boiled distilled water is conveyed to the arm from a protected container, and through which also the finished alkali is drawn off. The apparatus is then connected with the poles of an accumulator battery of 2 cells, or a Daniel's cell, the cathode lowered into the Hg, and the circulation of the latter so regulated that a minimum amount of $Hg_2O$ can be formed. When a fair amount of amalgam has been formed, the cathode is again raised, and the circulation of the Hg continued until the formation of alkali is ended. A modification of the apparatus is described by which the formation of any $Hg_2O$ is prevented, as well as a device by which the flow of Hg is automatically regulated.

CA 3, 1841-6

Alkali Chloride Electrolysis in Europe
B. Lepsius
Electrochem. Met. Ind. 7, 189.

Discusses the diaphragm process, Hg cathode process, and gravity process.

CA 4, 237-8

KOH (Purified by Alcohol)
H. J. Henderson
Pharm. J. 83, 564

In response to representations that a lot of this product contained only 82.1% KOH, the maker offered the explanation that the technical product, in which a slight contamination (with Fe) is not objectionable, can be evaporated to a concentration of about 100°, but that the pure product cannot be concentrated beyond about 85% without contamination by the Ag of the evaporating vessel.

CA 4, 871-2

Action of Metals on Fused Sodium Hydroxide. I.
M. LeBlanc and L. Bergmann
Ber., 42, 4728-47

NaOH is dehydrated at 400° in a Au crucible in an atm. of N. At 720° no $H_2O$ is given off, the reaction $2NaOH = Na_2O + H_2O$ not taking place. In a vacuum at this temp. NaOH has no effect on Au, while Ag and Na liberate H; and Pt, Cu, Fe, Ni, Al, Zn, and Mg liberate H and $H_2O$. In the presence of NaOH, the Au crucible when heated to 700° with Cu turnings takes up a not inconsiderable amt. of Cu and forms an alloy with it. Similarly Au formed an alloy with Ag and Mg; with Ni no alloy was observed. In the absence of NaOH the alloys did not form.

CA 4, 999-1

Hydrates of Rubidium Hydroxide and Cadmium Hydroxide
DeForcrand
Compt. rend. 149, 1341-4

RbOH forms two hydrates, $RbOH \cdot H_2O$ the common com. sticks and $RbOH-2.10\ H_2O$ m.p. 45-6°. These hydrates are analogous to those of KOH. CsOH forms $CsOH \cdot H_2O$, the pure sticks of commerce (m.p. 180°), a more stable hydrate than the corresponding ones of KOH and RbOH, but did not form a dihydrate. These facts show again the marked difference of Cs from K and Rb.

CA 4, 1531-3

Can. Pat. 124,797, April 5, 1910, Idem.

In preparing caustic potash KOH lye is concentrated to produce a thick pulp of anhyd. crystals of KOH, a melt of KOH of lower % is then added and the whole treated in a hydro-extractor at a temp. at which the melt is still fluid and at which no sepn. of water-containing KOH crystals takes place.

CA 4, 1531-4

Can. Patent 124,796, Apr. 5, 1910
H. Reitz, Griesheim, Ger.

In preparing caustic soda NaOH lye is concentrated until a copious production of anhyd. NaOH crystals is obtained. To the thick pulp formed NaOH lye of lower % is added, the whole being treated in a hydro-extractor at a temp. at which the added lye is still fluid.

CA 4, 2076-5

Simple Method for the Prepn. of Carbonate-Free Solns. of NaOH and KOH by Electrolysis in the Laboratory
W. P. Jorissen and H. Filippo, Univ. Leyden
Z. angew. Chem. 23, 726-7

This is a description, with fig., of the modified app. by the use of which the formation of $Hg_2O$ is avoided (CA 3, 1262). The modification consists in using a second cathode consisting of a Pt wire which dips into the Hg and is nearly completely insulated from the soln. by means of a glass tube. This second cathode is used until sufficient amalgam is produced to supply the dist. water in the cathode chamber with electrolyte. Then by means of an adjustable resistance the current through it is reduced to not exceed 0.2 amp., thus causing the main current to flow through the large cathode.

CA 4, 2763-5

Alkali Hydroxides. I. The Binary Systems NaOH-KOH, KOH-RbOH and RbOH-NaOH
G. von Hevesy (Zurich)
Z. physik. Chem. 73, 667-84

The cooling curves of NaOH, KOH, RbOH and CsOH were obtained by using a Ag-Ni thermoelement, which successfully resists attack by molten alkalies. All four of these alkali hydroxides show two polymorphic forms, the transformation temperatures of which, as well as the m.p. of the substances were readily obtained from the cooling curves and are as follows: NaOH, m.p. 318.4°, trans. point 299.6°; KOH, m.p. 360.4°,

t.p. 248°; RbOH, m.p. 301°, t.p. 245°; CsOH, m.p. 272.3°, t.p. 223°. The binary systems NaOH-KOH, KOH-RbOH, and RbOH-NaOH were worked out and diagrams plotted. The liquid-solid curves belong in all 3 systems to the mixed crystal type, while the transformation curves belong to the Roozeboom's type I. From the cooling curves, the heat of fusion and heat of transformation were calculated.

CA 4, 3286-6

U. S. 971,144, Sept. 27
Heinrich Reitz, Griesheim A/M, Germany
Assignor to Chem. Fabrik Griesheim-Elek., Frankfort a/M, Germany

Making anhydrous caustic soda by concentrating NaOH soln. until a copious production of anhyd. NaOH crystals is obtained, allowing the mother liquor to form a thick pulp while being stirred, adding to this slowly while stirring a NaOH soln. of lower % and sepg. the solid from the liquid at a temp. (about 170°) at which the added soln. is still fluid.

CA 4, 3286-7

U. S., 971,145, Sept. 27
Heinrich Reitz

Making anhydrous caustic potash by concentrating KOH soln. until, on cooling while being stirred, a copious formation of KOH crystals takes place, then mixing with the thick pulp thus formed, while stirring, KOH soln. of lower % and sepg. the solid from the liquid at a temp. (about 140°) at which no sepn. of KOH containing $H_2O$ takes place.

CA 5, 32-3

U. S., 973,171, October 18
Adolf Clemm, Mannheim, Germany

Making hydroxide and chlorine from barium or strontium chloride by subjecting a soln. of the chloride to partial electrolysis until the soln. is nearly satd. with the hydroxide, withdrawing soln. and cooling to crystallize the hydroxide.

CA 5, 164-4

Brit., 29,491, Dec. 16, 1909
Chem. Fabrik Griesheim Elektron, 51 Gutleutstrasse, Frankfurt a/M, Ger.

In the manuf. of anhydrous caustic soda, conc. ordinary NaOH lye of commerce until a copious production of anhydrous NaOH crystals are obtained, and allowing the mother lye to form a thick pulp while being stirred and adding to this, slowly and with stirring, the NaOH lye

of lower %, the pulp being treated in the hydro-extractor at a temp. at which the added lye is still fluid.

CA 5, 772-6

U. S., 974,993, Nov. 8
Charles Rollin, Newcastle upon Tyne, England

Making anhydrous $Ba(OH)_2$ from crystallized $Ba(OH)_2$ by slowly and uniformly heating to 100-200° in thin layers in a vacuum.

CA 5, 1325-7

Brit. 29,494, Dec. 16, 1909
Chemische Fabrik Griesheim-Elektron, 51 Gutleutstrasse, Frankfurt a/M Ger.

In the manuf. of anhydrous caustic potash, so concentrating KOH that on cooling, while being stirred, copious formations of anhydrous crystals of caustic potash takes place, and then admixing with the thick pulp formed, and while stirring a caustic potash not of lower %, and treating the mass in a hydro-extractor at a temp. at which the additional material is still fluid and no separation of $H_2O$-containing KOH crystals takes place.

CA 5, 2917-4

Brit., 26,696, Nov. 17, 1909
Chas. Rollin, Newcastle on Tyne

Manuf. of amorphous anhydrous barium hydroxide from crystallized $Ba(OH)_2$ by melting the crystallized $Ba(OH)_2$ in its $H_2O$ crystn. at a comparatively low temp. and removing $H_2O$ therefrom by causing dry air or other gaseous fluid, free or practically free from $CO_2$ or other injurious matter, to flow slowly and continuously and at a temp. below, at or only slightly above 220° over the liquified $Ba(OH)_2$ until the mass thereof becomes encrusted or solidified or nearly so, then thoroughly breaking up the mass of partly dehydrated $Ba(OH)_2$ and removing the remainder of the water of crystn. therefrom by further heating.

CA 5, 2918-8

Brit. 5,361, Mar. 3, 1910
L. P. Basset
13 Rue del 'Eglise, Enghein, France

Mfg. caustic soda or sodium salt by mixing lime (when NaOH is to be obtained) with a conc. lye of $(NH)_4SiO_4$, drying the mixt. at about 200° to dehydrate the Ca silicate or the $SiO_2$, lixiviating the mass with $H_2O$, and filtering to obtain a soln. of NaOH or the desired Na salt.

CA 5, 2946-8

Electrolytic Prodn. of Cl and Caustic Soda (in paper mills)
W. Ebert
Papier fabr. 9, 305-8, Wochenbl. Papierfabr. 42, 1721-3

Description of a successful cell for mfg. of Cl and NaOH at Aschersleben. Cells and covers were made of granite and concrete, with Fe cathodes, etc.

CA 5, 3750-4

Dissociation Pressures of Alkali Bicarbonates I. $NaHCO_3$
R. M. Caven, H.J.S. Sand
J. Chem. Soc. 99, 1359-69, Proc. 27, 147

$2NaHCO_3 \rightleftharpoons Na_2CO_3 + H_2O + CO_2$ $\quad \triangle H_{dis.} = 13{,}800$ cal.
$Na_2CO_3 \cdot H_2O \longrightarrow Na_2CO_3 + H_2O$ $\quad \triangle H_{dis.} = 30{,}700$ cal.
v.p. $Na_2CO_3 \cdot H_2O$ $(17.5^\circ - 97.7^\circ C)$ $\quad \log p = 10.824 - 3000/T$
v.p. $NaHCO_3$ $(20^\circ - 110^\circ C)$ $\quad \log p = 11.8185 - 3340/T$

CA 5, 3765-2

U. S., 1,003,041, Sept. 12
E. G. Ekstrom, Los Angeles, Cal.

Making alkali hydroxides and their derivatives by electrolysis of a soln. of an alkali-fluorine compound, such as Na fluosilicate between a C anode and a metallic cathode, e.g., Hg. Graphite electrodes sepd. by a diaphragm may also be used.

CA 6, 174-4

Measurements of Specific Heats at Low Temperatures with the Copper Calorimeter
F. Koref
Ann. Physik, 36, 49-73

....The following substances, for certain temperature intervals (given in parentheses) have the following mean at. or mol. heats: Li, (-191 to -80), 3.61; (0 to -78), 5.15; (+19 to -75), 5.44; Na, (-191 to -83), 5.60; (0 to -77), 6.34; K, (-191 to -80), 6.14; (0 to -78), 6.51; NaF, (-191 to -82), 7.31; (0 to -75), 10.43; KF, (-192 to -82), 9.06; (0 to -76), 11.21; $CaF_2$, (-190 to -84), 9.69; (0 to -73), 14.90; $Ca(OH)_2$, (191 to -80), 11.30; (0 to -78), 17.53; (+18 to -73), 18.41;.....

CA 6, 796-6

U. S., 1,015,345, Jan. 23
C. Rollin

Making amorphous anhydrous barium hydroxide.

CA 6, 919-1

U. S., 1,017,593, Feb. 13
C. Rollin

Making amorphous anhydrous barium hydroxide.

CA 6, 2900-7

Pptns. in Metal Salt Solns. by Alkali Hydroxide and Carbonate Solns.
E. Jordis
Elektrochem. Z., 18, 553-62

Metal contents and mol. relations of 1.0-0.1 mol. solns. of $Na_2CO_3$, NaOH, KOH, $K_2CO_3$, $NH_4OH$, $(NH_4)_2CO_3$ and $NaHCO_3$ with $FeCl_3$, $Fe_2(SO_4)_3$, and $CuSO_4$ are given graphically.

CA 6, 3046-4

Dissociation of Some Salts Contg. Water of Crystallization
H. Bolte, Halle,
Z. physik. Chem. 80, 338-60

| | | |
|---|---|---|
| KOH: | 2 aq. | 3.60 mm. at 27.75°C |
| | 1 aq. | 1.54 mm. at 27.75°C |
| | 1 aq. | 2.13 mm. at 31.75°C |
| | 0.75 aq. | 0.75 mm. at 31.75°C |

CA 6, 3314-7

U. S., 1,034,599, Aug. 5
A. W. Ekstrom

Making alkali hydroxides by reacting alkali fluosilicate with $Ba(OH)_2$.

CA 7, 232-8

Note on the Dissociation of Calcium Hydrate
R. K. Hursh, Univ. Ill.
Trans. Am. Ceram. Soc., 14, 792-800

.....at 375° $Ca(OH)_2$ dissociated forming a lower hydrate which loses its $H_2O$ at 580°.

CA 7, 871-8

U. S., 1,050,453, Jan. 14
H. Haberland

Anhydrous potassium hydroxide in the form of small white opaque crystals m. about 350° and deliquescing very slowly; made by cooling a soln. containing over 86% KOH to obtain crystals and removing the latter before the conc. has dropped to 86%.

CA 7, 946-4

Hydrates of Calcium Oxide and their Molecular Combinations
I. Composition of Amorphous Calcium Hydroxide
Th. Selivanov
J. Russ. Phys. Chem. Soc., 44, 1797-813

When $Ca(OH)_2$ is obtained by slaking CaO and the excess of $H_2O$ removed by a pressure of 300 atm., it contains about 3.5% $H_2O$, while that prepd. by pptg. a soln. of $CaCl_2$ with NaOH and subjected to the same pressure contains about 10.6% $H_2O$. When dried $Ca(OH)_2$ is kept in an atm. satd. with $H_2O$ vapor, it gradually absorbs $H_2O$, but the pptd. sample absorbed much faster than the slaked one. The max. amt. of $H_2O$ $Ca(OH)_2$ is capable of absorbing under ordinary pressure is 16.28%. Even on standing under $H_2O$ for 1.5 years it did not absorb more. However, in vacuo over $H_2O$ it may absorb as much as 23.14%. The absorbed $H_2O$ is only loosely held, about 1/3 being given off again when the temp. rises only a few degrees above 16°, or when placed in an atm. only partially satd. with $H_2O$, as in a desiccator over $ZnSO_4 \cdot 7H_2O$ (vapor tension at 18° 8.5 mm.), but the complete removal of the $H_2O$ is extremely difficult even in vacuo over $H_2SO_4$. The amt. of $H_2O$ absorbed by $Ca(OH)_2$ has no influence on its solubility. Hence amorphous $Ca(OH)_2$ and $H_2O$ behave towards each other like 2 liquids difficulty soluble in each other. As the max. of $H_2O$ $Ca(OH)_2$ is capable of absorbing is less than one mol. per mol. of the hydroxide, a compd. $Ca(OH)_2 \cdot H_2O$ does not exist (cf. Karcz, Chem. Ztg. 22, 39).

CA 7, 2167-1

Reaction of Certain Elements with Fused KOH
M. LeBlanc, O. Weyl
Ber. 45, 2300-15

The substances, heated in an elec. furnace, were held in Au or Ni crucibles, suspended in a vertical tube through which $N_2$ was passed. The issuing gases passed in order over gran. $CaCl_2$, red hot CuO, and again $CaCl_2$. At 400°, KOH became dry. At 660°, there was as yet no dissoc. into $K_2O$ and $H_2O$, although noticeable volatilization. At 550-660°, Au, Al, Mn, and K show little or no action on KOH. Fe, Co, and Ni are noticeably attacked but no $H_2O$, H or K is evolved. Cr, Mo and W act slightly, liberating H and K. C and Mg act in the same way but more vigorously. Even at 400°, Si violently displaces H, even when used in relatively small amounts. In the action of K on NaOH and that of Na on KOH, there is probably first established the equil. $Na + KOH \rightleftharpoons K + NaOH$, followed by $2Na + 2\ NaOH \longrightarrow 2Na_2O + H_2$. K is volatilized.

CA 7, 2325-7

Lye Flasks with Slipped-in Metal Stoppers
F. Michel, Luxemburg
Chem. Ztg. 37, 634

Recommends stoppers of phosphor bronze, Ni, Ag, or silvered phosphor bronze for bottles in which caustic Na or K solns. are kept, and also burets with metal cocks, which are made by Hodes and Gobel, Ilmenau.

CA 7, 3207-5

Ger. 261,103, July 4, 1912
AKT-Ges. Weser

Constructional details of a caustic soda vessel of nickel steel or like high grade steel.

CA 8, 632-9

U. S., 1,082,286, Dec. 23
H. D. Ruhm

Electrolytic diaphragm cell for making caustic soda.

CA 8, 1651-3

Ger., 268,532, June 6, 1909
C. Rollin and the Hedworth Barium Co.

Mfg. practically anhydrous, amorphous, pure barium hydroxide.

CA 8, 1949-8

The Embrittling of Iron by Caustic Soda
J. H. Andrew
Trans. Farad. Soc., 9, 316-29

The change in wt. and in brittleness of polished and unpolished Fe and steel after immersion in NaOH was studied. Wrought Fe became highly cryst. and eventually brittle. It is believed that the original metal contains crystals and an amorphous phase which serve to form an elec. couple. When immersed in NaOH soln. electrolysis starts with Fe going into soln. at the anode and H being liberated at the cathode. The H after being discharged at the cathode, is, to some extent, occluded by the remaining metal and it is the occlusion and diffusion of H which cause the cryst. growth and brittleness. When both the amorphous and cryst. metal have become satd. with H, the e.m.f. between these 2 states of metal will drop and consequently the rate of corrosion will diminish. The passivity produced by NaOH soln. is due to the small e.m.f. between hydrogenized amorphous and hydrogenized cryst. metal. A sample of steel with 0.5% C is affected to a much less degree by NaOH soln.

CA 8, 2041-6

Ger. 268,826, Feb. 27, 1912
E. A. Ashcroft

Manuf. of pure anhydrous caustic alkalies by decomposing molten amide, by steam, into caustic alkali and $NH_3$. In the 1st place an alloy of Pb and alkali metal, prepared with or without the aid of electrolysis, is treated with $NH_3$ to convert the alkali into amide. The $NH_3$ liberated in the decomp. is returned to the process. A suitable app. is specified.

CA 8, 2317-5

Ger. 272,476, July 8, 1913
L. T. S. Madsen

In previously used processes for the manuf. of sodium hydroxide from NaCl, with the employment of a Hg cathode, not more than 0.2% Na metal has been amalgamated with the Hg, so that large amts. of Hg and cumbersome app. have been needed. According to this process, a greater conc. of the resulting alkali amalgam has been secured by using as the

electrolyte a soln. containing the salts of several alkali metals. E.g., if a mixture of KCl and NaCl is electrolyzed, with the employment of a Hg cathode, an amalgam is produced which contains about 0.8% Na or K. The carbonate obtained by satn. with $CO_2$ may be sepd. readily by crystn. or otherwise. This process is applicable especially with the Stassfurt mixt. of KCl and NaCl.

CA 8, 2529-5

The Production of Sodium. II. The Electrolysis of Fused Sodium Hydroxide with the Addition of Other Sodium Salts.
B. Neumann
Z. Angew. Chem., 27, I, 195-200

The m.p. curves of NaOH - $Na_2CO_3$ mixts. were detd. and various like mixts. electrolyzed. The best yields of Na (63%) were obtained on the addition of 12-17% $Na_2CO_3$. Various NaOH-NaCl mixts. were made and their m.ps. detd. Electrolysis of these mixts. gave poorer yields than with pure NaOH or NaOH + $Na_2CO_3$. In the best run only 39% current efficiency was obtained. N. states that higher efficiencies in production of Na in technical practice can be obtained by the careful dehydration of fused NaOH before electrolysis, by the use of NaOH free from NaCl, by the addition of $Na_2CO_3$ to lower the temp. of the bath, by careful temp. measurements which until now are regarded as unnecessary and by greater attention to the anodic sepn. of $H_2O$.

CA 8, 2783-1

U. S., 1,098,825, June 2
H. K. Moore

Apparatus for concentrating caustic soda solns. in vacuo.

CA 8, 3761-6

U. S., 1,111,977, Sept. 29
C. C. Titus

Electrolytic cell for producing chlorine and caustic soda from sodium chloride, having 2 compartments sepd. by a diaphragm and perforated steel cathode, with a gas-tight chamber at the top of the anode compartment in which a partial vacuum is maintained and which has an overflow pipe extending down into the liquid in the other compartment.

CA 9, 698-8

Ger., 276,621, Nov. 16, 1910
C. Rollin and Hedworth Barium Co., Ltd.

Pure, anhydrous, amorphous barium hydroxide. (See Brit., 26,696, 1909 (CA 5, 2917).

CA 9, 986-4

Dissociation of the Alkali Bicarbonates II. $KHCO_3$, $RbHCO_3$, $CsHCO_3$
R. M. Caven, H. J. S. Sand,
J. Chem. Soc. 105, 2752-61 (1914)

When $KHCO_3$ or $NaHCO_3$ is heated $H_2O$ and $CO_2$ are evolved in equi-mol. amts., so the statement that $H_2O$ is retained to form a hydrate is incorrect (cf. Hermann, J. Prakt. Chem. 26, 312 (1842). The dissociation pressures of $KHCO_3$, $RbHCO_3$, and $CsHCO_3$ have been determined by the method previously described for $NaHCO_3$ (CA 5, 3750). The results show that the stability toward heat of the alkali hydrogen carbonates increases with rise of atomic weight of the metal.

CA 9, 1155-4

Electrolysis of a Fused Caustic Alkali
Brit., 25,144, Nov. 4, 1913
E. A. Ashcroft

Electrolysis of a fused caustic alkali, with a cathode containing fused heavy metal such as Pb, at 400-500°, so that the $H_2O$ formed at the anode escapes and loss of efficiency by the production of H at the cathode is checked.

The graphite anode of the primary cell may be replaced by one of Ni or other metal, having a number of points distributed over the cathode area and attached to an annular plate.

CA 9, 2297-9

Ger. 281,792, August 30, 1912
W. Hentschel

Process of dehydrating alkali lyes, depending upon the observation that completely dehydrated KOH has no oxidizing action on Fe heated to redness, and that this is practically true of KOH with 1% $H_2O$, while, on the contrary, alkali of 1-4% $H_2O$ content acts energetically on Fe heated to redness. The dehydration of the lyes is effected by allowing them to flow through a system of Fe retorts of different temps. wherein the

alkali of 96-99% dehydration is maintained at a temp. below red heat, while the residual $H_2O$ is removed in retorts heated to redness. The lye is passed in a thin layer over the flat bottoms of the retorts.

CA 9, 2371-6

The Action of Dilute Solns. of Acids, Alkalies and Salts Upon Certain Metals
A. J. Hale, H. S. Foster
J. Soc. Chem. Ind. 34, 464 (1915)

Cleaned and polished pieces of metal 1 sq. dm. in size were immersed for 7 days in 0.5 l. of soln. renewed every day, for 28 days in 1 l. not renewed, and for 4 hrs. in 0.2 N acid and the loss in wt. detd. The metals studied were commercial Zn, cast Fe, wrought Fe, Al, Pb, Cu, Sn, and Ni, the solvents tested were dil. solns. of $HNO_3$, HCl, $H_2SO_4$, $MgCl_2$, NaOH, $CaCl_2$, NaCl, $NH_4OH$ and $Na_2CO_3$.

CA 9, 2573-4

Obtaining Alkali and Alumina from Leucite
E. E. Dougherty
U. S., 1,148,156 (July 27)

CA 9, 2697-9

The Feasibility of Continuous Causticizing
R. W. S.
Met. Chem. Eng. 13, 514-5 (1915)

Discussion of possible flow-sheet for reaction:

$$Na_2CO_3 + CaO + H_2O \longrightarrow 2NaOH + 3\ CaCO_3$$

CA 9, 2798-9

Obtaining Alkalies and Alumina from Feldspar, Leucite and Similar Minerals
F. A. Rody and H. M. Burkey
U. S., 1,151,498 (Aug. 24)

CA 9, 2799-1

Obtaining Alkalies and Alumina from Feldspar, Leucite and Similar Minerals
F. A. Rody
U. S., 1,151,533

CA 9, 2800-6

Sodium Hydroxide
J. H. Hirt
U. S., 1,152,949

Sodium hydroxide is made by allowing molten $Na_2S$ to flow into $H_2O$ and adding $Ca(OH)_2$ to the hot dil. soln. in small portions.

CA 9, 2828-4

Thermal Analysis of Mixtures of Alkali Hydroxides with the Corresponding Halides. I. Compounds of Potassium
Giuseppe Scarpa
Atti accad. Lincei 24, I, 738-46 (1915)

It has long been known that some metallic oxides can combine with their respective halogen salts to form definite and stable compds. (called hydroxy-halides). Considerable work has been done on these compds. in the wet way but very little has been done at high temps. on the behavior of the oxides with the halides. Ruer (Z. anorg. Chem. 49, 365 (1906) studied the system PbO-$PbCl_2$, Sandonnini (Atti accad. Lincei 23, I, 959 (1914) studied PbO-$PbBr_2$ and PbO-$PbF_2$ and Truthe (CA 6, 2372) studied $Cu_2O$-$Cu_2Cl_2$. The first 2 pairs form well-defined hydroxyhalides while the last two show no formation of compds. S. has extended these data and this paper is a report on the K compds. The system KOH-KF, KOH-KCl, KOH-KBr, KOH-KI were investigated. The study of these systems is made difficult by the fact that it is hard to find a container that is not attacked by KOH and by the fact that KOH tends to absorb large amts. of moisture and $CO_2$ from the air. The mixts. were placed in a Ag crucible (since this material is little acted upon by fused KOH in the absence of O at moderate temps.); this is placed in an Fe cylinder, covered with a porcelain cover and the whole put in a resistance furnace in a current of $H_2O$- and $CO_2$-free N. A Ag-Ni thermoelement made and calibrated in the lab was used to measure the temps. since a Pt-Pt+Rd couple is attacked. The Ag-Ni couple was covered with a small Ag cylinder in making the solidification p. detns. and the slight changes in the Ag and Ni were found to be without appreciable effect on the e.m.f. For temps. above 900° (for KOH-KF mixts. containing much KF) a Pt crucible and Pt-Pt+Rd couple were used with success. The KOH used was 89.53% KOH, 1.47% $K_2CO_3$ and 9% $H_2O$; the latter was removed by heating it 45 min. at 500° in the furnace in an atm. of N. The m.p. of the KOH was 380° (Hevesy (CA 4, 2763) found 360° and Neuman and Bergve (CA 8, 3533) found 345°) and the point of transformation was 260° (Hevesy, 248°). The KF solidified at 857° (Plato (CA 2, 502) found 859.9° and Karandezen (Centr. Min. Geol. 1909) found 867°). The solidification pts. of all the mixts. of KOH and KF stand between those of the two components which are completely miscible in the solid state and give mixed crystals of one kind only. Thus, the point of transformation of KOH that results from the solidification p. curve gradually

falls with the increase of the concn. of KF. The KCl used in the study of KOH-KCl m. 776°. In this system the primary crystn. curve falls from the solidification p. of KCl to that of KOH and shows an elbow at 430° at 67 mol % KOH. The mixts. from 36 to 67 mol % KOH show, besides the primary arrest, a secondary arrest of crystn. at 430°; the mixts. from 0 to 25 and 47 to 100 mol % KOH show an interval of crystn. due to the formation of mixed crystals. This system belongs to the fourth type of Roozeboom since it gives two kinds of mixed crystals and a miscibility break. The point of transformation of KOH is markedly lowered by KCl and at 82 mol % KOH is 120°. The point on the descending crystn. curve limiting the solid soln. of KCl in KOH could not be accurately detd. The KBr used in the system KOH-KBr solidifies at 760°. The solidification diagram of this system shows that the two components, if the formation of mixed crystals in the mixts. containing only small amts. of KOH is disregarded, are completely miscible in the liquid state. The eutectic arrest is at 300° with 75 mol % KOH and disappears at 0 to 85 mol % KOH. The point of transformation of KOH is rapidly lowered at first by the addition of KBr but becomes nearly constant at 205° with 90 mol % KOH. The KI used in the system KOH-KI solidifies at 695°. The primary crystn. curve descends from the m.ps. of the two components and intersects at the eutectic at 250° at 73 mol % KOH. The point of transformation of KOH lies a little above the eutectic arrest. The system KOH-KF gives solid solns. in all proportions; KOH with KCl and KBr gives solid solns. of two kinds with a miscibility break; KOH and KI gives a simple eutectic.

II. Compounds of Sodium. Ibid. 955-61.

In continuing the expts. described above the systems NaOH-NaF, NaOH-NaCl, NaOH-NaBr and NaOH-NaI were studied. The methods and technique were the same. The NaOH attacks Ag less than KOH and since it is stable at high temps., higher temps. could be used without any decompn. taking place. The NaOH used was 97.46% NaOH, 1.65% $Na_2CO_3$ and 0.9% $H_2O$. The m. and solidification points of NaOH are 310° and 290° (Hevesy found 318.4° to 299.5° and Neumann and Bergve found the solidification p. to be 300°); the m.p. of NaF was 1005°. The system NaOH-NaF showed the formation of mixed crystals with miscibility break, while KOH-KF gave two kinds of solid solns. The primary curve of crystn. lies between the solidification ps. of the 2 components and shows a slight break at 90 mol % NaOH. For mixts. from 20 to 90 mol % NaOH, there is a second arrest at 360°. The pt. of transformation of NaOH is somewhat lowered and forms, with the limit of the solid soln. of NaF in NaOH, a eutectic which shows a max. at 80 mol % NaOH and which disappears at 5 and 100 (?) mol % NaOH. In mixts. of 5 to 80 mol % NaOH it was possible to det. the duration of the eutectic arrest, but from 80 to 100 mol % NaOH the arrest due to the transformation was also present. The system NaOH-NaCl shows a diagram similar to the preceding. The NaCl m. 806°. The primary crystn. curve shows a break at 350° and 75 mol % NaOH; from 10 to 75 mol % NaOH there is a second arrest at 360°. The pt. of transformation of NaOH is rapidly lowered by small amts. of NaCl with the solid soln. of NaCl in NaOH as the limit and the formation of a eutectic arrest which is

at a max. at 73 mol % NaOH and disappears at 5 and 100% NaOH. The solidification p. of NaBr is 776°. The system NaOH-NaBr shows complete miscibility in the liquid state. The primary crystn. curve shows two branches which intersect at the eutectic, 260° and 80 mol % NaOH. There is not even a slight tendency to form solid solns. The NaI m. 665°. The system NaOH-NaI gives a decomposable compd. From the solidification p. of NaI the primary crystn. curve descends regularly to 65 mol % NaOH where there is a distinct break; then it descends further and intersects the descending solidification p. curve from the solidification p. of NaOH in a eutectic at 220° and 83 mol % NaOH. In the mixts. up to 65 mol % NaOH there is a second arrest in the solidication p. curve at 300° which has a max. duration at 40 mol % NaOH. This arrest coincides with the formation of a compd. decomposable on melting; 2NaOH • 3 NaI is probably its formula. The pt. of transformation of NaOH in a mixt. containing 3 mol % NaI is practically the same as that of pure NaOH. Thus, the systems NaOH-NaF and NaOH-NaCl give solid solns. of two kinds with a miscibility break; NaOH-NaBr gives a simple eutectic; NaOH-NaI gives a compd. decomposable at fusion (probably 2NaOH • 3NaI).

CA 9, 2831-8

Heats of Dilution of Concentrated Solutions
W. S. Tucker
Trans. Roy. Soc. London (A) 215, 319-51 (1915)

The heat of diln. per mol. of added solvent decreased rapidly but regularly with the diln. for HCl and NaOH.

CA 10, 159-5

Report on Testing Chemical Reagents
J. B. Rather (Referee)
J. Assoc. Official Agr. Chem. I. 317-29 (1915)

Detn. of $Na_2CO_3$ in NaOH
Four methods used. I. Krauch-Merck; II. Sutton; III. Sutton, by pptn. as $BaCl_2$; and IV, The following modification by the referee:

Dissolve 2 g. crude NaOH in $H_2O$ and titrate with approx. 2N HCl and phenolphthalein until the color fades. To another 2 g. portion add 0.5 cc. less of the 2N acid, and titrate with 0.2N acid until the color fades; read the buret, add 2-3 drops Me orange, and titrate until the color changes. The number of cc. of 0.2N acid required to change the Me orange x 1.06 gives the % $Na_2CO_3$. Methods I and II give discordant results both for duplicate detns. and by the two methods.

CA 10, 556-1

Decomposition Potentials of Fused Alkali Hydroxides
B. Neumann, E. Bergvre
Z. Elektrochem. 21, 143-52 (1915)

Attempts to measure directly the potentials of Na against NaOH and K against KOH as well as the cell Na/NaOH/KOH/K were not very successful because of exptl. difficulties. The decompn. potentials have been measured by Le Blanc's method (1902) for NaOH, KOH in the presence of air, NaOH in the presence of $Na_2O_2$, KOH in an atm. of N, and mixts. of NaOH and KOH in both air and N.

| NaOH | | KOH | |
|---|---|---|---|
| Temp. | Decompn. potential | Temp. | Decompn. potential |
| 180 | 2.38 | --- | --- |
| 200 | 2.32 | 200 | 2.4 |
| 230 | 2.29 | 230 | 2.37 |
| 280 | 2.25 | 280 | 2.34 |
| 305 | 2.25 | 305 | 2.36 |
| 335 | 2.22 | 335 | 2.4 |
| 390 | 2.05 | 380 | 2.25 |
| 450 | 1.87 | --- | --- |
| 530 | 1.62 | 530 | 1.8 |
| 640 | 1.32 | --- | --- |

The temp. coeff. above 335° for NaOH was $2.95 \times 10^{-3}$, for peroxide-free KOH, $3.05 \times 10^{-3}$. The potential difference is therefore independent of the temp. The decompn. potential of LiOH gave no values for Li/LiOH, but a value of the order of the decompn. potential for $H_2O$.

CA 10, 588-5

Alkali-Resistant Metal Vessel
B. Strauss
U. S., 1,166,866, Jan. 4

Vessels for boiling alkali solns. are formed of Ni steel alloy containing about 25% Ni and 0.5-2% Cr, with an oxidized surface.

CA 10, 1473-7

Electrolytic Production of Sodium Hydroxide and HCl from NaCl
E. J. O. Werner
Norw. 26,707, Feb. 28, 1916

A charge of neutral $Na_2SO_4$ is electrolyzed in a circulating system. After cooling, the acid soln. in the anode chamber is sepd. from the

crystallized neutral sulfate and concd. to recover bisulfate. This product is heated with NaCl to produce HCl and the neutral sulfate. The mother liquor from the cathode chamber is concd. to recover NaOH.

CA 10, 1477-6

Thermal Analysis of the Mixture of the Alkali Hydroxides with the Corresponding Halides. III. Compounds of Lithium
Giuseppe Scarpa
Atti accad. Lincei 24, II, 476-82 (1915)

In two preceding papers (CA 9, 2828) the behavior of KOH and NaOH with the K and Na halides was described; it was found that the tendency to give compds. increases from K to Na. S. has now extended these expts. to Li to see if with its smaller electroaffinity compared with Na there is a further increase in this tendency. The same methods and app. were used as before. The LiOH used contained 98.5% LiOH, 0.8% $Li_2CO_3$ and 0.7% $H_2O$. The Li salts were dehydrated in a Pt crucible. The m.p. of LiOH was found to be 462° (DeForcrand, Compt. rend. 142, 1255 (1906) found 445°); that of LiF is 840°. The sytem LiOH-LiF shows complete miscibility in the liquid state and gives solid solns. in limited proportions. The primary crystn. curve drops from that of LiF to a eutectic at 430° at 80% LiOH and rises to the f.p. of LiOH. The freezing curve shows the eutectic arrest from 5 to 85 mol % LiOH. LiCl m. 605°. The primary crystn. curve of the system LiOH-LiCl drops from the f.p. of LiCl to a eutectic at about 290°, showing a break at 50 mol % LiOH and then rising to the m.p. of LiOH. The eutectic arrest for mixts. of 45-100 mol % LiOH lies at about 285° and shows a max. duration at about 65 mol % LiOH. Mixts. from 0 to 50 mol % LiOH show another arrest at 315° which has a max. duration at 40 mol % LiOH. This arrest corresponds to the formation of a compd. decompg. on fusion, which is probably 2 LiOH · 3 LiCl. LiBr m. 550°. The diagram of the system LiOH-LiBr is similar to that of LiOH-LiCl. The eutectic lies at 275° with 45 mol % LiOH. Mixts. 0 to 70 mol % LiOH show a eutectic arrest which disappears between 75 and 100 mol %; at the latter compns. there is an arrest at 310° which is max. at 75 mol % and corresponds to the decomposable compd. 3 LiOH · LiBr. LiI m. 440°. The primary crystn. curve of the sytem LiOH-LiI drops from the m.p. of LiOH to the eutectic 180° at 45 mol % LiOH and shows a strong break at 75 mol % LiOH and then rises to a temp. of 310° at 80 mol %, which must be due to the formation of a compd. not stable at the m.p.; it must be 4 LiOH · LiI. The results show that the tendency to give compds. between the alkali hydroxides and the halogen salts of the same metal increases gradually on passing from K to Na to Li or with diminishing electroaffinity of the ion. This agrees with the theory of Abegg and Bodlander (Z. Anorg. Chem. 20, 453 (1903)) on electroaffinity and formation of complexes.

The results of the 3 papers are summarized thus:

| | Fluorides | Chlorides | Bromides | Iodides |
|---|---|---|---|---|
| LiOH | xx | 2 LiOH · 3 LiCl | 3 LiOH · LiBr | 4 LiOH · LiI |
| NaOH | xx | xx | V | 2 NaOH · 3 NaI |
| KOH | x--x | xx | V | V |

xx indicate mixed crystals with a break, x--x mixed crystals in any proportion, V formation of a simple eutectic.

CA 10, 2172-7

Electrolytic Manufacture of Potassium Hydroxide
Charles - Pierre Rolland
Fr. 478,371, Dec. 8, 1915

A soln. of $K_2SO_4$ is electrolyzed in an app. comprising a sol. anode, and preferably an anode and a cathode of Fe, obtaining at the cathode the KOH and H, and at the anode a mixt. of $K_2SO_4$ and Fe $SO_4$ suitable for use as a fertilizer.

CA 10, 2279-7

Vacuum Evaporators for Caustic Soda
Ernest Worsley
Chem. Trade J. 58, 481-2 (1916)

CA 10, 2327-4

The Reduction of Sodium Nitrate and Sodium Nitrite to Ammonia and Sodium Hydroxide
Trygve Valeur
Tid. Kemi Farm. Terapi 13, 125-34, 141-50, 162-8 (1916)

By a series of expts. with cathodes made of highly polished Ni, Pb, Fe, graphite, Cu, Cd, and Hg, it was found that Fe used for both anode and cathode gave uniformly the best results. Soln. strength was: $NaNO_3$ 7.18%, $NaNO_2$ 6.15%, with enough NaOH to make the alkalinity 1.41N. The soln. had a sp. gr. of 1.153. There was no Cl nor $SO_4$. With the Fe anode it was found that no oxidation of $NH_4$ or nitrite took place. When a current of 4.25 amp. at 2 volts was passed through such a soln. (25-30°) for 480 amp. hrs. the following results were obtained: Loss of N as free N 3.3%; amt. of current accounted for by $NH_3$ produced, 86.3%. By using a current of 1.4 amp. at 2.15 - 2.2 v. for 125.5 amp. hrs. the results were 3.7% loss as free N and 91.2% of the entire current accounted for by the $NH_3$ formed. Changing the current to 2 amp. and 2.2 - 2.3 v., enough $NH_3$ was produced to account for 92.2% of the current used.

CA 10, 2849-5

Electrolytic Mfg. of Caustic Alkalies
E. A. Ashcroft
U. S., 1,198,987

Fused alkali metal reacts with $NH_3$ in one cell to produce fused alkali metal amide. The amide reacted in second cell with steam to form anhydrous caustic alkali and $NH_3$, residual amide, $NH_3$, and steam put into third cell to complete reaction and dry $NH_3$ which is returned to first cell.

CA 11, 424-1

Electrolytic Production of Alkalies and HCl
E. J. O. Werner
Swed. 41,610, Nov. 29, 1916

A soln. of neutral $Na_2SO_4$ is subjected to electrolysis. The acid soln. obtained at the anode, after cooling and sepn. of uncrystallized neutral salt and subsequent evap. to bisulfate, is heated with NaCl to produce HCl and neutral sulfate. The alk. soln. obtained at the cathode, after cooling and sepg. uncrystallized neutral sulfate is evapd. to NaOH, or converted to carbonate by the introduction of $CO_2$. The neutral $Na_2SO_4$ produced is again subjected to electrolysis.

CA 11, 2171-4

Purifying Caustic Soda Solutions
H. B. Kipper
U. S., 1,227,453 (May 22)

Solns. containing NaOH equiv. to 50-60% $Na_2O$ are electrolyzed to ppt. metallic impurities, while heated to 80-175°, using a Ni anode and steel cathode and removing the O formed at the anode without allowing it to come in contact with the body of the soln.

CA 11, 2448-2

The Embrittling Action of NaOH on Mild Steel and its Possible Relation to Seam Failures of Boiler Plate
Paul D. Merica
Met. Chem. Eng. 16, 496-503 (1917)

A steel wire contg. 0.18% C, 0.024% P, 0.045% S, and 0.42% Mn was exposed to the action of 13.6 N NaOH at 100°, 180°, and 280°. The time of exposure varied from 5 to 30 d; the wire was then subjected to physical tests. It was found that the metal was attacked by the NaOH soln. and brittleness was produced as indicated by the alternating stress and

impact tests but not noticeably by the tensile tests. The theory advanced is that the brittleness is caused by "nascent" H being absorbed by the steel and forming a less ductile alloy; this is relieved by annealing even at low temperatures. The action of the alkali is to a large extent inhibited by the presence of $Na_2CrO_4$ in the caustic soln. The effect of alkalies on steel is discussed in relation to the failure of boiler plates at the seams in localities where the feed-water contains $Na_2CO_3$ or when the water is treated with boiler compounds.

CA 11, 2759-3

Methods of Analysis of Mixtures of Bicarbonate and Carbonate or of Alkali Carbonate and Caustic Alkali without a Previous Weighing or Titration
J. Clarens
Bull. Soc. Chem. 21, 120-4 (1917)

The app. used is that previously reported (cf. CA 4, 132), the 2 cc. pipet being replaced with a 10 cc. pipet graduated in 0.1 cc. Method: Detn. of the vol. V of acid required to liberate the $CO_2$ from a mixt. The amt. of sample used is detd. by two conditions: (a) 10 cc. of acid (capacity of the pipet) must suffice to liberate all of the $CO_2$; (b) the amplitude of the manometer. Place the sample in the reaction vessel, add a known vol. of $H_2O$ (this will be the same in all detns.) and a drop of Me orange. Connect the app. to the manometer, let stand a few min. in a $H_2O$ bath to attain temp. equil., connect the pipet tip to the glass tube provided for this purpose, read the manometer, and release the pinch cock (on a second tube) so that the acid flows in dropwise till the end point is reached with the indicator. Note the vol. of acid, Vm, and run in the remainder of the acid; place the vessel in the $H_2O$ bath till the temp. equil. is established, and read manometer, = H. A similar detn. is made with pure $Na_2CO_3$, using such an amt. that the final pressure will approx. = H. The vol. of acid used = $V_n$ and the pressure = h; the vol. of acid, $V_n$, required to neutralize an amt. of $Na_2CO_3$, to give a pressure H will be: $V_n = V_nH/h$. This expt. need not be repeated with each detn., as it suffices to multiply H, found in any detn. by $V_n/hx(1+\alpha t')/(1+\alpha t)$, t being the temp. at which H has been detd. and t' that for h. From the above data % $NaHCO_3 = 100\ (V_n-V_m)/V_m$. With acid of known titer and a known wt. of sample, the wts. of $Na_2CO_3$, $NaHCO_3$ and inert material can be calcd. from the vol. used: $N_b = V_n-V_m$ and $N_n = 2\ V_m-V_n$ ($N_b$ = cc. of acid required for $NaHCO_3$, $N_n$ for $Na_2CO_3$). By the above procedure the compn. of a mixt. of NaOH and $Na_2CO_3$ can be detd., the formulas being $N_c/N_n = (V_m-V_n)/V_m$ and % = $100\ N_c/N_n+N_c = 100\ (V_m-V_n)/V_m$; the symbols are as above, $N_c$ being the cc. of acid required for the NaOH. From the vol. of the app., temp., and solubility coeff. of $CO_2$ at this temp., the wt. of $CO_2$ evolved can be calcd.

CA 11, 2946-1

Obtaining Alkalies from Silicates
A. H. Cowles
Brit., 107,640, July 4, 1916

A furnace charge comprising silicates, such as feldspar, leucite, zeolites, clay, etc., or artificial alkali, Al silicates with an alk.-earth compd., such as lime, $CaCO_3$, or $CaCl_2$ and, if necessary, an alkali, such as $Na_2CO_3$, is made up in such a manner that, after sintering, there shall be present 2 moles of alk.-earth oxide to each mole of $SiO_2$ and less than 2, but preferably more than 1, mole of $Al_2O_3$. The sintered product may be used as a fertilizer or may be leached with $H_2O$ or, if the proportion of alkali is low, with a soln. of caustic alkali or alkali aluminate high in alkali. The soln. thus obtained is $NaAlO_2$ suitable for treatment by the Bayer process. An artificial silicate for use in the furnace charge may be prepared by heating a mixt. of clay, $CaCl_2$, and C at 1500-2000°F., steam being blown over or through the mixt., a large surface of which is exposed. The product may contain one or more mols. of CaO and 2 or more mols. of $SiO_2$ to 1 mol of $Al_2O_3$. Another artificial silicate, the prepn. of which is not described has the compn. 1.4 $Na_2O$, 2 $SiO_2$, $Al_2O_3$. Cf. 10,093, 1887; 5,296, 1892; and 20,220, 1902; and U. S. 382,505.

CA 11, 3393-7

Producing NaOH from Zeolites, Lime and NaCl
C. P. Hoover
U. S., 1,238,916

NaOH soln. is formed by passing a clear $Ca(OH)_2$ soln. through a Na zeolite filter until the latter becomes substantially inactive through loss of Na. The zeolite is then regenerated for continuing the process, by washing it with a NaCl soln.

CA 11, 3395-6

Filters for Alkalies and Other Solutions
E. J. Sweetland
U. S., 1,240,385, Sept. 18

A filter for solns. of alkalies is formed of a woven fabric containing steel or Pb wool or other metallic wool.

CA 12, 124-9

Electrolytic Production of Caustic Soda
K. Fukuawa and K. Watanabe
Jap., 31,071, May 15, 1917

The cathode grating is placed beneath a bell jar, and the anode is supported horizontally at the surface.

CA 12, 205-4

Barium Hydroxide
C. Deguide
Fr., 483,044, May 23, 1917

Dibarium silicate is decomposed by means of $H_2O$, with the production of the mono Ba silicate, and $Ba(OH)_2$. The $Ba_2SiO_4$ is obtained by calcining, at 1400-1500° a mixt. of $SiO_2$ and $BaCO_3$, or a mixt. of $BaSiO_3$ and $BaCO_3$.

CA 12, 296-6

Making Oxides and Hydroxides of Barium
B. Peacock
Can., 180,525, Nov. 20, 1917

$BaCO_3$ is mixed with sufficient CaO to form a dry mass at a temp. of fusion of the $BaCO_3$ and heated to 1200° to cause the evolution of $CO_2$ and to convert the $BaCO_3$ into BaO. The heating is interrupted before all the carbonate is decomposed and the product is leached with water to ext. the Ba in the form of $Ba(OH)_2$.

CA 12, 406-5

Manufacture of Caustic Soda by the "Loewig" Process
Anon.
Chem. Trade J. 61, 322 (1917)

$$Na_2CO_3 + Fe_2O_3 \xrightarrow[\text{with heat}]{\triangle} Na_2Fe_2O_4 + CO_2$$

$$Na_2Fe_2O_4 + H_2O \longrightarrow 2NaOH + Fe_2O_3$$

Flow-sheet described.

CA 12, 408-6

Sodium Hydroxide
C. S. Bradley
U. S., 1,249,314, Dec. 11

$BaCO_3$ and $NH_4Cl$ are used for making $(NH_4)_2CO_3$. The $(NH_4)_2CO_3$ is caused to react with NaCl and $CO_2$ to produce $Na_2CO_3$ and regenerate $NH_4Cl$. The $Na_2CO_3$ is causticized with $Ba(OH)_2$, thus regenerating $BaCO_3$ for the first reaction. The $Ba(OH)_2$ required is produced by reacting with a portion of the NaOH obtained in the method, upon the $BaCl_2$ formed in the first reaction.

CA 12, 408-7

Continuous Production of Dry Calcium Hydroxide
W. Eckardt and E. Holop, G.M.B.H.
Ger., 294,234, July 15, 1914

The lime, after absorption of a predetd. amt. of $H_2O$, is carried downwards in a vertical chamber from one grate to another in a series of grates, either by its increased wt., due to absorption of $H_2O$, or by the action of the grate-tilting mechanism provided for that purpose. The process is continuous, the quick lime being supplied from above through a hopper, and the dry "hydrate" being discharged at the bottom.

CA 12, 519-1

Barium Oxide and Hydroxide
B. Peacock
U. S., 1,250,642, Dec. 18 (See Can. 180,525 (CA 12, 296)

CA 12, 519-2

Barium Hydroxide and Silicate
C. DeGuide
Brit., 110,537, July 10, 1917

$BaCO_3$ is calcined with $SiO_2$ at 1400-1500° in the proportions to produce $Ba_2SiO_4$. The product, which is not fused, is treated with hot or cold $H_2O$ when half of the Ba becomes hydroxide, which dissolves, leaving $BaSiO_3$ which is sepd., washed, mixed with $BaCO_3$, and heated to 1400-1500° to obtain $Ba_2SiO_4$ again. The $Ba(OH)_2$ may be used in an industrial process in which it is recovered in the form of carbonate, which may then be used in the main process. (Cf. CA 12, 205)

CA 12, 1617-5

Alkali by Electrolysis of Chloride Solutions
K. P. McElroy
U. S., 1,264,536

In making alkali from a chloride soln., a thin layer of the soln is electrolyzed between a pair of parallel diaphragms sepg. the anode and cathode from this thin layer and the anode is bathed in oil gas during electrolysis to combine with the Cl as formed and produce olefin chlorides and chlorohydrins.

CA 12, 1912-1

Causticizing of $K_2CO_3$
E. Belloni, Milano
Ann. Chim. Applicata 9, 115-49 (1918)

$$K_2CO_3 + CaO + H_2O \longrightarrow 2KOH + CaCO_3$$

$k$ = ratio $C^2_{KOH}/C_{K_2CO_3}$

$K_T = \alpha - \alpha'\phi + \alpha''\phi^2$ where $\phi = C_{K_2CO_3}$ initial

$K_{100^\circ} = 133.2 - 127.85\,\phi + 43.5\,\phi^2$

Causticizing never complete, yield greater for $Na_2CO_3$ than for $K_2CO_3$. $KOH \cdot 2H_2O$ crystals are product. Reasonably stable for deliquescence.

CA 12, 2235-1

A Continuous Process of Causticizing Soda-Ash with Lime
Anon.
Met. Chem. Eng. 18, 376-7 (1918)

Kingsport Pulp Co. causticizes soda-ash with lime by a continuous agitation and continuous counter-current decantation process similar to standard cyanide practice.

CA 12, 2285-2

Electrolytic Cells
F. H. Nickle
U. S., 1,278,723-4, Sept. 10

The cells are adapted for the electrolysis of NaCl to produce NaOH and Cl.

CA 13, 9-5

Electrolytic Production of Alkalies
N. Statham
Brit., 118,355, Sept. 26, 1917

A diaphragm (of asbestos board or paper) between an anode chamber and an empty cathode chamber allows passage of sufficient electrolyte to prevent back diffusion of NaOH.

CA 13, 288-1

Electrolytic Cell
L. D. Vorce
U. S., 1,286,844, Dec. 3

The patent relates to structural features of a cell adapted for electrolysis of NaCl soln. to produce NaOH and Cl.

CA 13, 288-9

Fusion of NaOH with Some Inorganic Salts
M. C. Boswell, J. V. Dickson
J. Am. Chem. Soc. 40, 1773-9 (1918)

Reactions were found to take place involving decompn. of water, one mole of O going to effect oxidation and two moles of H being either evolved or fixed. With $NaAsO_2$ and $FeSO_4$, the extent of oxidation was found equivalent to the H evolved; with $SnCl_2$ and $V_2(SO_4)_3$ much H was evolved; with $Ce_2(SO_4)_3$ a less amt.; with $U(SO_4)_2$ only a small amt. Neither $NaNO_2$ nor $Na_2SO_3$ was oxidized.

CA 13, 289-1

Action of NaOH on CO, HC(=O)-ONa, C(=O)(-ONa)-C(=O)-ONa
M. C. Boswell and J. V. Dickinson
J. Am. Chem. Soc. 40, 1779-86 (1918)

CO heated with excess of NaOH at temps. at which formate is transformed to oxalate was oxidized almost quant. to carbonate with evolution of approx. an equiv. amt. of $H_2$. At temps. far below those at which formate and oxalate alone are decompd. NaOH carries both of them almost quant. to carbonate with evolution of the equiv. amt. of $H_2$. In a discussion of the general reaction involving replacement of carboxyl by H in alk. fusions, e.g., $CH_4$ from AcONa, $C_6H_6$ from BzONa, a probability is shown that simultaneous oxidation and reduction by the elements of water are involved.

CA 13, 689-9

A Physico-Chemical Method of Determining Alkali Carbonates in the Presence of Alkali Hydroxides
R. Dubrisay, Tripier, and Toquet
Compt. rend. 168, 56-9 (1919)

The method is based on the diminution of the coeff. of reciprocal miscibility of $H_2O$ and PhOH by alkali carbonates. Temp.-conc. curves of turbidity points of $Na_2CO_3$-NaOH mixtures in 50 cc. aliquots and 50 g. PhOH (after heating for complete solution).

CA 13, 1055-1

Solubility of $Cu(OH)_2$ in NaOH and KOH
E. Justin-Mueller
Compt. rend. 167, 779-80 (1918)

NaOH (d. 1.345-1.370) and KOH (d. 1.453-1.498) dissolve 0.78 g. $Cu(OH)_2$ per 100 cc. Solns. are stable and do not change on heating. Soln. is incomplete in less concd. lyes.

CA 13, 1569-1

Stabilizing Normal Alkali Solution
Winkler, Pharm. Post 1918, 354; Schweiz. Apoth. Ztg. 57, 140 (1919)

The absorption of $CO_2$ by N alkali may be reduced to a minimum by replacing 30% of the $H_2O$ used by 30% of glycerol. This also prevents sticking of glass stoppers.

CA 13, 1749-2

Caustic Soda and Sodium Sulphate
J. Grossman
U. S., 1,298,334

NaOH and $Na_2SO_4$ are produced by mixing niter cake with $CaSO_3$ to form sol. compds. in soln. and a ppt. and then reacting on the substances in sol. with $Ca(OH)_2$.

CA 13, 1978-5

Action of Alkalies on Pt and Au
L. Quennessen
Bull. Soc. Chim. 25, 237-40 (1919)

In a table reproduced here from Bull. des usines de guerre No. 17, p. 134, the losses sustained by crucibles of pure Pt and of various Au alloys are shown when treated with $K_2CO_3$, $KHSO_4$, fused NaOH, and $H_2F_2$-$H_2SO_4$. By totalling the losses under the four reagents, Pt is supposedly shown to be inferior to the alloys. Q. points out that absurdity and that the table clearly shows the superiority of Pt over any known alloy in resistance to acid reagents.

CA 14, 504-2

Action of Alkalies on Crucible of Platinum and Gold Alloys
P. Nicolardot and C. Chatelot
Bull. Soc. Chim. 25, 4-9 (1919)

In the abstract of this paper in CA 14, 29, NaOH and KOH should be substituted for $Na_2CO_3$ and $K_2CO_3$.

CA 14, 678-679

The Ionization and Activity of Largely Ionized Substances
Arthur A. Noyes and Duncan A. MacInnes, Mass. Inst. Tech.
J. Am. Chem. Soc. 42, 239-45 (1920)

For the degree of ionization of acids, bases and salts it is usual to employ the ratio $\Lambda/\Lambda_0$. This is justified only if the ionic mobility is const. and if the mass-effect of the ions is proportional to their concn., as the mass law assumes. The detn. of activity is, therefore, preferred to the detn. of cond. Activity is defined as "the quantity which when substituted for the concn. of the substance in mass-action expressions, will express its effect in detg. equil." The activities at two concns. of an electrolyte are proportional to the partial vapor pressure of the substance, and relative vapor pressures may be found by e.m.f. measurements. Thus, for KCl, LiCl, HCl and NaOH, the activity coeff., decreases with rising concn. much more rapidly than the degree of dissociation as detd. by cond. (with proper correction for changes in viscosity of the solns.). The activity coeff. for all except KCl passes through a minimum around 0.5 mol. and afterwards increases rapidly at higher concns. Other data show a minimum for KCl around 2N. It is pointed out that conductance ratio does not give even an approx. measure of ion activity; that the activity coeff. of an ion is not proportional to nor mainly detd. by the fraction ionized; that there is no direct evidence of the existence of unionized molecules; and that it is advisable to assume complete ionization to these electrolytes, the decrease in conductance ratio being attributable to a decrease in ion mobility. The change of the activity coeff. is due to some as yet unknown physical cause.

CA 14, 693-5

Electrolytic Process of Siemens-Billiter
J. Billiter
Z. Elektrochem. 24, 255 (1919)

B. claims priority in the following points: (1) Use of a diaphragm consisting of a mixt. of fibrous and pulv. material, (2) A comb. of such a diaphragm with an empty cathode space, (3) Supplying the cathode space entirely with a charge of strong alkali which rests on and penetrates the diaphragm, (4) A high current yield, with prodn. of relatively highly concd. alkali solns. with low tension.

J. Nussbaum, Z. Electrochem. 24, 256 - Kellner is credited with having previously patented the use of $BaSO_4$ in a diaphragm.

CA 14, 872-1

Furnace for Heating Sols. of Caustic Soda
F. H. Nickle
U. S., 1,329,470

CA 14, 1084-3

Equilibria in Solutions Containing Mixtures of Salts. II. The System Water and the Chlorides and Sulfates of Sodium and Magnesium at 25°C.
W. C. Blasdale
J. Ind. Eng. Chem. 12, 164-7 (1920); cf. CA 12, 1152

The data necessary for the complete equilibrium diagram are presented and compared with those of other investigators. Many of the latter were found more or less in error. It is concluded that kieserite, $MgSO_4 \cdot H_2O$, does not constitute part of this system at 25°.

CA 14, 1185-6

Caustic Pot Settings
F. G. Wheeler
Chem. Met. Eng. 22, 372-3 (1920)

The caustic pot is a large semi-spherical cast-iron vessel supported by a concrete column for conc. of NaOH. The furnace design must insure ability to finish the caustic, economy in operation, long life for the furnace and the pot, and protection against severe damage to either furnace or setting in case of pot failure. Securing high furnace temps., placing a combustion chamber behind the grate, and proper arrangements of the ash pit and the flue around the pot increase operating economies. W. favors a three-battery setting, using two fusing pots and a pre-heating pot. Long furnace life is obtained by the use of good firebrick,

properly set. A thin guard wall should protect the pot against blow-torch effect, and the caustic pot should be movable. The bottom should be protected from heat to allow setting of impurities. NaOH can be finished with less than 1000 lbs. (454.5 kg.) of coal per ton of caustic.

CA 14, 1415-2

Evaporating Caustic Potash
C. L. Higgins and United Alkali Co.
Brit., 137,632, Feb. 6, 1919

The evapn. of solns. of caustic potash is effected in app. lined with, or made of Au.

CA 14, 1488-9

Caustic Alkalies by Electrolysis of Chlorides
B. Cataldi
U. S., 1,336,281, April 6

Hg cathodes are employed which are not in direct contact with the electrolyte but are in indirect contact with it by means of very porous diaphragms. $H_2O$ is caused to pass successively over the Hg cathodes and is decomposed by the alkali metal amalgamated with the Hg with the formation of NaOH or KOH. A floating layer of C or graphite particles is placed over the cathodes, which, being a good conductor, facilitates the deamalgamation. The C particles may be provided with metal contact pieces in contact with the cathode. The diaphragms may be formed of asbestos cloth.

CA 14, 2121-1

The Influence of Various Metals on the Decomposition of Sodium Amalgam by Water
E. Muller and A. Riedel
Z. Electrochem. 26, 104-9 (1920)

Results previously published have been employed to show that the outstanding catalytic action of the ferrous alloys of Mo, V, W, and Cr on velocity of decompn. of Na amalgams depends upon a surface increase. The possible application of this action to the Hg process of alkali chloride electrolysis is discussed.

CA 14, 2446-4

The Influence of Superimposed Alternating Current on Anodic Ferrate Formation
G. Grube and H. Gmelin
Z. Elektrochem. 26, 153-61 (1920)

The anodic formation of Na ferrate in NaOH soln. has been investigated, and the influence of different factors on the current yield detd. Increase in temp. and alkali concn. favor the formation of ferrate. The yield depends upon the c.d. and with increase in the latter passes through a max. Above and below this optimum c.d. smaller yields of ferrate are obtained. The current yield of Na ferrate can be markedly increased by superimposing an a.c. on the anode. For a const. d.c. the yield increase brought about by the a.c. reaches a max. at a definite a.c.c.d. With an electrolyte consisting of 40% NaOH, and employing a d.c.c.d. of 3.33 amp/dcm$^2$, and a temp. of 35°, the max. current yield is obtained with an a.c.c.d. of 5.00 amp. dcm$^2$. Under these conditions the increase in current yield over that obtained with the d.c. alone is 160%. In order to obtain concd. ferrate solns. it is necessary to prevent cathodic reduction by means of a diaphragm. The temp. must not be allowed to rise above 50°, otherwise evolution of O occurs. Under suitable conditions undecompd. concd. ferrate solutions and the cryst. salt have been obtained.

CA 14, 2841-7

Evaporating with Condensed Steam
K. Schreber
Chem. Ztg. 44, 469-70 (1920)

Theoretical considerations prove that soda solns. can be evapd. to their greatest density by using condensed steam, and it becomes purely a question of costs as to whether it is better to employ that method or direct heating.

CA 14, 2973-7

Sodium Hydroxide
Schweizerische Sodafabrik
Brit., 144,266, May 17, 1920

NaOH is obtained by emulsifying a soda soln. with CaO by means of a "turbomixer" having at least one turbine-wheel or centrifugally acting blade-wheel. The reaction is effected in the cold, for instance, in about 15 min.

CA 14, 3183-9

Behavior of Alkali Chlorides in Concentrated Solutions upon Long-Continued Evaporation in the Presence of Alkali Hydroxides
Ch. Chorower
Z. Angew. Chem. 33, 201-3 (1920)

Data are given for the soly. of alkali chlorides at various temps. when alone, with each other, and with alkali hydroxides. Mass action and the phase rule are applied in explaining the heterogeneous equilibria observed in the six expts. conducted by C., and the necessity for more extended investigation is recognized.

CA 14, 3300-5

Sodium Hydroxide
S. S. Sadtler
U. S., 1,351,693, August 31

$Na_2HPO_4$, 284 parts is reacted upon by $Ca(OH)_2$ 148-222 parts in a boiling aq. mixt. in order to form NaOH.

CA 14, 3510-9

The Progress of the Melting Process in Shallow Glass Pots
J. Baldermann
Sprechsaal 53, 205-6 (1920)

In glass plants it is quite common for the workman to lay the blame for failure to accomplish proper melting upon the lack of bottom heat. A wide experience has shown that top heat is a greater importance and is more economical in the proper melting of the batch and in the fining operations. The progress of the typical melting operation is described. When the first fill is put in, there is a layer of molten cullet in the bottom of the pot. The raw batch sinks to the bottom and molten glass, rich in alkali, is formed on top. Gradually the batch reacts and becomes dissolved and in about $3\frac{1}{2}$ hrs. there is a small flat cone of raw batch only. By the 4th hour boil has started and the remaining small amount of raw batch has risen to the surface. The second fill is put on at the end of $4\frac{1}{2}$ hrs. and it floats and melts. After seven hrs. the second fill is about gone and in about $7\frac{1}{2}$ hrs. violent boil sets in. The boiling continues from $1\frac{1}{2}$ to $2\frac{1}{2}$ hrs., so that in about 10 hrs. the metal is plain. In 11-12 hrs. the fining is finished. The typical pot used in the illustrations is 42" in dia. with a bottom 6" thick and 17" from working hole to the inside of the bottom.

CA 14, 3553-2

The Vapor Pressures of Concentrated Solutions
G. R. Paranjpe
J. Indian Inst. Sci. 2, 59-72 (1918)

Measurements were made between 0° and 40° of the vapor pressure of solns. of (1) KOH for concns. between 18.81 and 138.2 g. of the anhydrous hydroxide in 100 g. of water; (2) NaOH for concns. between 14.62 and 113.1 g. in 100 g. of water; (3) $CaCl_2$ for concns. between 14.81 and 119.5 g. of the anhydrous salt in 100 g. of water. The results obtained for KOH are not in very close agreement with those obtained by Dieterici (cf. Ann. Phys. Chem. 42, 513-36; 62, 616-43 (1897); 67, 859-70 (1899).

CA 14, 3599-7

Electrolysis of Alkali Chlorides
John B. C. Kershaw
Chem. Trade J. 67, 3-5 (1920)

The "Basle" type of diaphragm cell, characterized by a "propulsive cathode" (Brit. pat. 11,872, 1913; (CA 8, 3537)) is now employed extensively in France, Italy and Switzerland. An Fe cathode is placed within a narrow chamber of permeable material such as asbestos fabric. This is contracted at the top so that the froth of $H_2$ bubbles rises in it and flows over into a suitable receiver. Here $H_2$ gas is sepd. out, leaving caustic liquor of 11-13% NaOH or 15-17% KOH. The upward flow brings in fresh electrolyte and especially prevents migration of the OH ions which usually causes loss. The p.d. is 3.5 - 4.5 v. per cell. The C anodes and asbestos bags containing them last about 3 years, though the latter must be removed for cleaning twice a year. High quality $H_2$ and $Cl_2$ are produced.

CA 15, 33-1

Electrolysis of Sodium Chloride Solutions
A. Luib and E. Steinbuch
U. S., 1,354,498, October 5

In electrolysis of NaCl to form NaOH and Cl or in the electrolysis of other liquids to produce a solute and evolve a gas, the solute is expelled from the electrolytic cell by the buoyancy of the evolved gas. An app. is described.

CA 15, 788-8

The Solubility of Copper Hydroxide in Strong Sodium Hydroxide Solutions
E. Muller
Z. Angew. Chem. 33, I, 303-5 (1920)

Copper hydroxide dissolved in concd. NaOH soln. (12 N) giving a violet soln. This gives a brown ppt. on standing that redissolves on the addition of more NaOH, giving a brown soln. M. discards the colloidal explanation and, after describing considerable exptl. work, arrives at the conclusion that the phenomenon is one of complex formation, thus: $Cu(OH)_2 + 2OH = CuO_2'' + 2 H_2O$. Hence: $K = (C^2_{OH'}/C_{CuO_2''})$ or, since the concn. of Cu is proportional to $CuO_2$ and that of NaOH to OH, he writes: $K = C^2_{NaOH}/C_{Cu}$. He determines these concns., and finds K is approx. const. between concns. of 6.09 and 15.50 mols. NaOH/liter.

CA 15, 973-8

Measurements of Vapor Pressures of Certain Potassium Compounds
D. D. Jackson and J. J. Morgan
J. Ind. Eng. Chem. 13, 110-8 (1921)

The following vapor pressures of the K compds. in mm. of Hg are reported: KOH at 795° 8, KCl at 801° 1.54, at 948° 8.33, at 1044° 34.1, $K_2O$ in $K_2CO_3$ at 970° 1.68, at 1130° 5.0; $K_2SO_4$ at 1130° 0.4; natural silicates, glauconite, orthoclase, and leucite up to 1335° nil ----. Article contains a detailed drawing of a high temp. Mo wound electric furnace and a full discussion of the vapor pressure method. The authors have shown that the order of volatility of the compds. important in the recovery of potash by volatilization is: KOH, KCl, $K_2O$ from $K_2CO_3$, $K_2SO_4$, natural silicates.

CA 15, 1468-8

The Causticization of Sodium Sulfate
B. Neumann and E. Karwat, Breslau
Z. Elektrochem. 27, 114-24 (1921)

Measurements have been made on the soly. of CaO in aq. solns. of NaOH and of $CaSO_4$ in aq. solns. of $Na_2SO_4$ and the reaction $Na_2SO_4 + Ca(OH)_2 = CaSO_4 + 2NaOH$ has been studied at several temps. The equil. has been attained from both sides. The equil. const., K, detd. from soly. data for CaO and $CaSO_4$, has at 18° a value $(OH)^2/(SO_4) = 0.388$. It has been ascertained that the displacement of the equil. with temp. is in accordance with the van't Hoff equation of the reaction isochore. At 40° K = 0.317, i.e., the OH concn. decreases with increase in temp. The calcd. values for the equil. const. agree fairly well with those detd. by expt., the deviations being due to dissociation behavior and not to the formation of double salts. The yield of NaOH decrease with

increase in both the concn. of the starting materials and the temp. At ordinary temp. the max. conversion amounts to 60% and at 100° to 27%, the resulting NaOH being very dil. (7-2.7 g. per l.). With concd. solns. of the starting materials the conversion drops to but 10%. On evapg. the dil. solns. of NaOH a retrograde conversion sets in. In view of the above it is not likely that the process will be of any technical importance.

CA 15, 1669-4

The Electrometric Estimation of Carbonic Acid and its Salts
I. M. Kolthoff
Z. anorg. allgem. Chem. 112, 155-64 (1920)

Solns. of $H_2CO_3$ from 0.0015 to 0.02 mol. in strength can be titrated electrometrically with alkali. The cond. straight-line curve becomes steeper after the formation of the $H_2CO_3$, and again steeper after the formation of the normal carbonate. The breaks in the curve, however, are not sharp, especially in very dil. solutions, in which owing to the considerable hydrolysis of the carbonate, the straight-line portions become rounded into a continuous curve. The sharpness of the titration can be greatly increased by having present an excess of Ca salt ($CaCl_2$) to ppt. the carbonate as it is formed. Time must be allowed during the titration for the pptn. of the $CaCO_3$. $H_2CO_3$ cannot be titrated with carbonate to the hydrogen carbonate electrometrically, because the angle between the two portions of the curve is too obtuse. On the other hand, carbonate can be titrated with acid. According to the dilution, the cond. may fall (in dil. soln.) or rise (in stronger solns. above 0.1 N) up to the hydrogen carbonate point. From this point, which is not sharp, to the neutral point, the cond. increases gradually, and at the neutral point there is a sharp rise. The neutral point is very sharp in extremely dil. solns. Free alkali hydroxide can be estd. in presence of carbonate by titration with acid if not present in too small an amt. The amt. of hydrogen carbonate can be detd. by titration with alkali or acid, but its amt. must not be too small, or the direction of the corresponding portion of the curve cannot be detd. with sufficient accuracy. A very weak acid, such as boric acid, can be titrated in presence of $Na_2CO_3$ with alkali hydroxide with satisfactory results.

CA 15, 2376-9

Vapor Pressures of Some Salts
H. V. Wartenberg and Ph. Albrecht
Z. Elektrochem. 27, 162-7 (1921)

Measurements have been made of the vapor pressures of NaCl, NaI, KCl, KBr, KI, NaBr, NaOH and KOH at a number of temps. between the b.p. of the salts and 200-300° below the b.p. From the data obtained vapor pressure formulas have been adduced.

CA 15, 3949-2

Electrolyzing Salt Solutions
A. H. Hooker
U. S., 1,388,466, August 23

In the electrolysis of salt soln. to produce NaOH in diaphragm cells, an aq. electrolyte carrying solid salt is supplied to the electrolytic cell, in order to maintain the electrolyte approx. satd. at working temp.

CA 16, 393-3

Preparation of Carbonate-Free Alkali
I. M. Kolthoff
Pharm. Weekblad. 58, 1413-7 (1921)

Prep. a soln. approx. 1.1 N from com. NaOH. Add 50 cc. milk of lime per $\ell$. Allow to settle overnight and siphon off the supernatant liquid, titrate a portion and dil. with $CO_2$-free $H_2O$ to 0.1 N. The Ca content does not exceed 1-2 mg/$\ell$., which is not objectionable for practically all analytical purposes.

CA 16, 468-4

HCl and NaOH
R. Volart y Jubany
Brit., 164,742, June 13, 1921

Fused NaCl and superheated steam $\xrightarrow[\text{pumice stone}]{\text{cat. such as}}$ HCl and NaOH. Reaction chamber and melting receptable are made of volcanic lava to avoid corrosion by acid and alkali.

CA 16, 468-5

Nitric Acid; Caustic Soda
R. Volart y Jubany
Brit., 166,557, July 13, 1921

$NaNO_3$ is decompd. by superheated steam under the action of a catalyst to produce $HNO_3$ and NaOH. The nitrate is dried in a pan and fed to melting pots and thence to the reaction vessel.

CA 16, 468-6

Caustic Soda
C. Cramer
U. S., 1,392,814, Oct. 4

In the production of NaOH, a soln. of $Na_2CO_3$ is emulsified in the cold with milk of lime in a "turbomixer" comprizing one or more turbine wheels, in order to prevent incrustation of the particles with $CaCO_3$.

CA 16, 694-4

Preparation of NaOH Free from $CO_2$
J. Cornog
J. Am. Chem. Soc. 43, 2573-4 (1921)

To boiled and cooled water $Et_2O$ is added to make a 3-4 cm. layer and Na added in pieces < 1 cm. diam. They fall no further than the $Et_2O$ layer and the slowly formed NaOH passes readily to the water layer. There is no danger of explosion or fire if the $Et_2O$ layer is kept 3-4 times the diam. of the largest piece of Na added. Most of the $Et_2O$ can be pipetted off, and the remainder removed by boiling.

CA 16, 878-5

Electrolysis
K. Heinemann and Hoesch and Co.
Brit., 171,751, Aug. 14, 1920

Pure H, O, and caustic alkalies are obtained from impure lyes by electrolysis with a Hg cathode and subsequent action of $H_2O$ on the amalgam formed. A Pt, Ni or Ag anode may be used.

CA 16, 1191-8

Some Properties of Fused NaOH
T. Wallace, A. Fleck
J. Chem. Soc. 119, 1839-60 (1921)

(1) The water content, (2) Action upon Fe, Ni, and Cu in air, and (3) Action upon Fe, Ni, and Cu of fused NaOH contg. 5% $Na_2O_2$ were studied. By fusion in a vacuum and absorbing the moisture with $P_2O_5$, the av. $H_2O$ content was found to be 1.1%.

From these expts. in vacuo it was observed that presence of O is necessary before fused NaOH can become colored in its usual manner, as in the absence of air the Fe of the contg. vessel is able to act as a reducing agent upon the impurities of the molten hydroxide. The action upon Fe, Ni, and Cu was studied between 350° and 600°. In no case was

the amt. of metal dissolved very high, the max. being 0.73% in the case of Cu. Fe is less vigorously attacked than Cu, but more than Ni. In the study of the action of NaOH upon metals, and especially when 5% $Na_2O_2$ was added, the formation of cryst. substances was noted between 500° and 700°, which though sol. at higher temps. crystd. out on cooling. The yellow crystals obtained from Fe corrosion upon analysis showed a compn. approx. $Na_3Fe_5O_9$. The reaction between NaOH, $Na_2O_2$, and Fe or Ni is almost certain to have a parallel with similar metals such as Co, Cr, or Mn, and it is extremely probable that further research on lines indicated would reveal new cryst. substances similar to those described.

CA 16, 1838-5

Sodium Hydroxide, Carbonate and Thiosulfate
E. E. Naef
Brit., 174,653, Nov. 10, 1920

Hydrated $Na_2S$, reduced to powder, reacts with air or O at ordinary temps., in the presence of finely divided active charcoal, to give a product contg. chiefly NaOH and $Na_2S_2O_3$.

CA 16, 2064-9

Molecular Refraction of Some Molten Salts
G. Meyer and A. Heck
Z. physik. Chem. 100, 316-33 (1922)

The indices of refraction of molten $NaNO_3$, $KNO_3$, NaOH and KOH have been measured at a no. of temps. between 320 and 440° by a modification of the autocollimator-method. The indices of refraction of the salts are dependent linearly on the temp. New detns. have been made of the d. of molten NaOH and KOH: NaOH. $d_{34} = 1.89$, $d_{44} = 1.84$; KOH, $d_{38} = 1.87$; $d_{44} = 1.81$. The mol. refractivities have been used to determine the degree of dissoc. of the molten salts.

CA 16, 3041-5

Reactions of Caustic Soda with Al Salts
Edward Grobet
J. Chim. Phys. 19, 331-5 (1922)

In an unpublished thesis of 1916, Korsakoff has investigated the behavior of Al compds. on addn. of NaOH by observing the conductance of the solns. during the progress of the reaction.

CA 17, 186-7

NaOH
R. O. Jones, Courtaulds, Ltd.
Brit., 182,411, June 11, 1921

$Na_2CO_3$ is removed from solns. of NaOH such as solns. produced by the two-stage caustifying process described in 182,661 (CA 16, 4303) by adding excess of $CaCO_3$ and, if desired, seeding with $CaCO_3$-$Na_2CO_3$. A ppt. of $CaCO_3$-$Na_2CO_3$ is produced, from which the $Na_2CO_3$ may be recovered by treatment with $H_2O$. The remaining $Na_2CO_3$ may be removed by concentrating the soln. to a strength of 30-35% and cooling to 10-20° when small crystals of $Na_2CO_3$ sep., or by treating with the necessary quantity of $SrO_2$ and $BaO_2$. The soln. thus further purified contains less than 1% $Na_2CO_3$.

CA 17, 935-5

Electrolytic Production of Caustic Alkali
H. H. Dow, T. Griswold, E. O. Barstow
U. S., 1,441,408

Production from aq. soln. of NaCl or similar halide.

CA 17, 1112-6

Caustic Alkalies
C. Deguide
U. S., 1,440,211, December 26

A Ba polybasic silicate, e.g., bi- or tri-barytic silicate is decomposed by $H_2O$ and $Na_2SO_4$ or $K_2SO_4$ at a temp. of about 80° in order to form NaOH or KOH. The polybasic silicate is regenerated by heating the solid reaction residue with C at 1400°. Cf. CA 16, 2391.

CA 17, 1602-9

Application of Scheele's Reaction to Preparation of KOH
W. Dominik
Przemysl Chem. 6, 25-36 (1922)

The reaction $2KCl + 4\ PbO + H_2O \rightleftharpoons PbCl_2 + 3\ PbO + 2\ KOH$ was studied by using mixts. contg. not more than 20 g. of PbO per 100 cc. of KCl soln., filtering when the reaction was complete, adding a further quantity of PbO to the filtered liquid, and repeating these operations until equil. was attained. It was found that to obtain 1g. of KOH about 16 g. of PbO is necessary. At the ordinary temp. the equil. between KOH and KCl may be expressed by the equation: $K = KOH/KCl = \{1/(0.422 + 0.074\ [OH])\} - 1$, and the max. concn. attainable is 112 g. KOH per 1.

CA 17, 2086-8

Pure Caustic Alkalies from Impure Solns.
K. Heinemann
U. S., 1,453,132

Impure caustic alkali solns. are electrolyzed using Hg cathodes, and the resulting alkali amalgam is decompd. by $H_2O$.

CA 17, 2393-5

The Electrolytic Production of Acid and Alkali from Sodium Sulfate Soln.
H. V. Atwell and Tyler Fuwa
Ind. Eng. Chem. 15, 617-20 (1923)

A summary of results on the electrolysis of waste $Na_2SO_4$ solns. aiming at the commercial production for local consumption of NaOH and $H_2SO_4$. Production cost of NaOH compares favorably with that from NaCl and there is saving of the cost of raw material. The value of the anode products, $H_2SO_4$ and O, is, however, less than that of Cl from the salt process.

CA 17, 2837-6

Production of Sulfuric Acid and Caustic Soda by Electrolysis of Sodium Sulfate
E. R. Watson
J. Soc. Chem. Ind. 42, 251-2 T (1923)

S and pyrites are not available in India, while $Na_2SO_4$ is available in reh salts. Electrolysis of a 40% $Na_2SO_4$ soln. with Pt, Fe, or Cu cathode and Pt, Pb, or C anode results in the formation of NaOH and $H_2SO_4$ with current and energy efficiencies of 90% and 50%, resp., provided electrolysis is not carried beyond an av. conversion of 25%. $Na_2SO_4$ crystallizes out of the alk. liquor, leaving nearly pure NaOH. $NaHSO_4$ is formed similarly from acid liquor. $H_2SO_4$ is best obtained from the bisulfate.

CA 17, 2939-5

Barium Hydroxide from Barium Carbonate
R. W. Shafor
U. S., 1,460,180, June 26

A $BaCO_3$ residue is treated with HCl to form $BaCl_2$, and an excess of NaOH is added to ppt. $Ba(OH)_2$ and form a NaCl soln. contg. a small amt. of Ba salts. The mixt. is cooled and the sepd. $Ba(OH)_2$ ppt. is removed. NaOH is added to the NaCl soln. to keep impurities in soln. and it is concd. to produce a mother liquor contg. NaCl crystals in suspension, NaOH and a small amt. of dissolved NaCl and Ba salts.

The NaCl crystals are sepd. and the remaining liquor is used in the $Ba(OH)_2$ pptn. The NaCl is dissolved and electrolyzed to form NaOH and Cl and H and the latter are combined to form HCl for continuing the process.

CA 17, 2983-6

Diminishing the Attack of Alkali Solns. on Al by Addn. of Water Glass
Rohrig
Chem. Ztg. 47, 528-9 (1923)

Al on which a layer of Al silicate was formed was not attacked by solns. contg. 0.5 g NaOH and 0.5 g waterglass per l. even when boiled with it for 15 days.

Coating is stable up to 1.5 g NaOH per l.

CA 17, 3235-9

Barium Hydroxide
J. Michael and Co.
Brit., 192,415, Jan. 29, 1923

BaS is dissolved in hot $H_2O$ and cooled to obtain hydrated crystals. The crystals are sepd. and heated to 20-100°, dissolved in hot $H_2O$, and the soln. is cooled to obtain crystals of $Ba(OH)_2$, while $Ba(SH)_2$ remains in soln.

CA 17, 3456-9

The Anode Effect
Kurt Arndt and Hans Probst
Z. Elektrochem. 29, 323-34 (1923)

The anode effect, or disturbance which takes place at the anode during the electrolysis of molten salts, has been studied with $CaCl_2$, $SrCl_2$, $BaCl_2$, $PbCl_2$, NaCl, KCl, NaF, $Na_3AlF_6$, NaOH and KOH. Graphite and two kinds of C electrodes were used. With each of the salts the crit. c.d. (i.e., the c.d. at which the phenomenon is manifested) was detd. The values obtained for the crit. c.d. varied between 20 (with KOH and NaOH) and 1 amp./sq. cm. (with $BaCl_2$). The presence of impurities raises the crit. c.d. With some of the salts the crit. c.d. increased with the porosity of the electrodes employed; with others it decreased, while with NaCl it appeared independent of the porosity of the electrodes.

CA 17, 3730-7

Concentrating Liquids
W. Vozelbusch
Brit., 196,935, April 28, 1923

In evapg. liquids, such as NaOH soln., the liquid, passing downwards through a series of heating elements, is passed between each heating element on to shelves in the evapg. chamber. A suitable construction is specified.

CA 17, 3755-5

NaOH
R. O. Jones, Courtaulds, Ltd.
Brit., 197,198, May 16, 1922

Solns. of NaOH obtained by causticizing strong solns. of $Na_2CO_3$ with CaO and filtering are concd. by cooling to between 0° and -15° to remove the $Na_2CO_3$ as decahydrate. In this way solns. contg. 15-25% NaOH and not more than 1% $Na_2CO_3$ may be obtained.

CA 18, 616-3

The Anomalies of Cr and its Behavior in Electrolysis
N. Isgarishev, A. Obrutsheva
Z. Elektrochem. 29, 428-34 (1923)

Soly. of Cr as electrode in KOH and KCl was detn. A.c. increased soly. compd. to d.c. apparently breaking down colloidal skin. Cr dissolved as $Cr^{III}$ and $Cr^{VI}$. Evidence favored view that passivity is due to colloidal skin.

CA 18, 638-1

Solubility of Titanic Acid in Alkalies and Alkali Carbonates
Crystallized Titanium Oxychloride
V. Auger
Compt. rend. 177, 1302-4 (1923)

Soly. measurements were made in hydroxides, carbonates and bicarbonates of Na and K with gels of $TiO_2 \times H_2O$, cold acid-sol., $TiCl_4$ poured into excess of alkali soln., and alk. fusion extd. with successive small portions of water. The data show that $TiO_2$ is only slightly sol. in the hydroxides, the soly. increasing with concn. of the base, greater in KOH than in NaOH and varying from 2 mg. per 100 cc. in 10% NaOH to 120 mg. in 40% KOH. It is insol. in satd. $Na_2CO_3$ soln. From alk. fusions water exts. considerable $TiO_2$, in a metastable state from which within 24 hrs. it ppts. completely from $Na_2CO_3$ but from $K_2CO_3$ only after

diln. and boiling. Bicarbonates appear to form a double carbonate very readily hydrolyzed. In analysis loss of $TiO_2$ is best avoided by using $Na_2CO_3$ solns., the data show that the sepn. of Ti from Fe by soln. of the former in alkalies proposed by Coffignier (CA 17, 2232) is impossible. This is based on an old statement that $Na_2TiO_3 \cdot 4H_2O$ and $K_2TiO_3 \cdot 4H_2O$ can be crystd. from alk. soln. A.'s soly. detns. show this is untrue. By evapn. over $H_2SO_4$ of a $TiCl_4$ soln. cold-satd. with HCl, colorless rhombic crystals were obtained: analysis indicated $TiO_2 \cdot HCl \cdot 3H_2O$ or $Cl\text{-}Ti \equiv (OH)_3 \cdot 2H_2O$. Attempts to prep. an oxychloride with two or three atoms of Cl were unsuccessful.

CA 18, 1603-1

The Dissociation Constant of Lithium Hydroxide
I. M. Kolthoff
Rec. trav. chim. 42, 969-72 (1923)

In detg. the salt error of Li compounds it was found that the error had the opposite sign to that of all of the other salts investigated. This indicates that the Li ion binds OH ions and that LiOH is a weaker base than KOH and NaOH. Further study of these results showed that the dissociation constant for LiOH is about 0.5. Kohlrausch (Ann. Phys. (Wied.) 6, I, 145 (1879)) and Calvert (Z. physik. Chem. 38, 513 (1901)) obtained about the same value by other methods.

CA 18, 2060-2

Barium Hydroxide
C. Deguide
U. S., 1,490,769, April 15

Tri-barytic silicate is decomposed by $H_2O$ in order to form $Ba(OH)_2$ and monobarytic silicate. The latter is then heated to 1300-1500° with $BaCO_3$ to regenerate tri-barytic silicate.

CA 18, 2409-6

Causticizing Sodium Carbonate by Ferric Oxide
I. G. Matsui and Y. Yasuda
Chem. Ind. (Japan) 26, 827-42 (1923)

Na ferrite, prepd. by heating a mixt. of 1 part of $Na_2CO_3$ and 1.2-2.0 parts of $Fe_2O_3$ at 680-860°, was decomposed into NaOH and $Fe_2O_3$ by boiling with hot water, and the unchanged $Na_2CO_3$ and the NaOH produced were detd.; from the results the amt. of ferrite formed was calcd. When the amt. of $Fe_2O_3$ was 1.8 parts or more and the reaction temp. was about 75°, the yield was 96-97%; the less the amt. of the oxide, the lower the yield. The ferrite is formed rapidly at 680-720°, and slowly at higher temps. The color of the ignited products changes from yellowish brown to blackish green according to the degree of

change and the time of heating. The product would decompose owing to the action of $CO_2$ on exposure in the open air for a long time. The ferrite is almost stable to water below 35°, but decomposes rapidly at 40-60°, and completely at 70°. The unchanged $Na_2CO_3$ in the product was extd. to the extent of 50-60% at 35°, and completely at 50°. The $Na_2CO_3$ could be removed from NaOH by repeated lixiviation at various temps. The degree of decompn. of the ferrite decreased inversely as the concn. of the caustic lye used for the lixiviation, e.g., by 2.5 N soln., 95%; 5 N soln., 90%; 7 N soln., 80%; and by 10 N soln., 45%. The color of the lixiviated soln. was sometimes purple-red while hot and changed to green when cooling, probably owing to the presence of Fe.

CA 18, 2452-4

The Viscosity of Aqueous Mixtures of Chromic Anhydride and Alkalies. The Viscosity of Chromates and Sulfates in Relation to their Isomorphism.
L. J. Simon
Compt. rend. 178, 1606-9 (1924)

The viscosities for $Na_2CrO_4$, $K_2CrO_4$, $Na_2Cr_2O_7$, $K_2Cr_2O_7$, $Na_2SO_4$, $K_2SO_4$, mixts. of $K_2CrO_4$ and KOH, mixts. of $Na_2CrO_4$ and NaOH, and mixts. of NaOH and $CrO_3$, are given. $K_2Cr_2O_7$, between the temp. limits 10° and 25°, does not modify appreciably the viscosity of $H_2O$ in which it is dissolved. The viscosities of solns. of chromates and neutral sulfates are practically identical. Mols. of isomorphous substances modify the viscosity of water to the same extent, at the same temp. and within certain concn. limits.

CA 18, 2650-1

Concentrations of Alkali in Cathode Liquors of Diaphragm Cells
Giulio Consiglio
Atti congresso naz. chim. pura applicata 1923, 273-8

A discussion with detailed data of the soly. of NaCl in NaOH soln. and its relation to the evapn. and recovery of NaOH from solns. contg. NaCl.

CA 18, 2677-5

Effect of pH on the Submerged Corrosion of Steel
W. G. Whitman, R. P. Russell, V. J. Altieri
Ind. Eng. Chem. 16, 665-70 (1924)

The main factors in the corrosion of steel submerged in natural waters, dil. alkalies, and dil. acids are the protectiveness of films of corrosion products and the rate of O diffusion. In alkalies (above pH 9.5) increased pH makes the liquid next to the metal more alk. and

causes the formation of a protective film. In the natural water field (pH 9.5-4.5) the film protection, and, therefore, the corrosion rate are const., since the liquid next to the metal is maintained at a pH of 9.5 by the soly. of $Fe(OH)_2$. In acids (pH less than 4.5) corrosion may proceed both by H gas evolution and by the action of dissolved O.

CA 18, 2790-7

Caustic Soda
R. O. Jones
U. S., 1,500,993, July 8

A soln. contg. about 20% $Na_2CO_3$ is causticized as completely as possible with lime, the soln. is filtered off and there is then dissolved in it a further 10% of $Na_2CO_3$ which is further causticized as completely as possible. On cooling a liquor is obtained which contains at least 18% NaOH and some $Na_2CO_3$. U. S., 1,500,994 relates to reducing the amt. of $Na_2CO_3$ in a NaOH soln. by treating the soln. with $CaCO_3$, which forms a pptd. double compd. with the $Na_2CO_3$. U. S., 1,500,995 specifies cooling a soln. contg. both NaOH and $Na_2CO_3$ to a temp. below 0° to effect sepn. of $Na_2CO_3$.

CA 18, 3104-1

The Electrolytic Caustic Soda and Solvay Processes
P. Parrish
Chem. Age. (London) 10, 666-8 (1924)

A review of comparative efficiencies of the two processes. Few electrolytic cells are commercially successful. The Hg cell involves heavy cost. Diaphragm cells are closed as those: (a) with submerged diaphragms and cathodes, (b) in which the electrolyte is brought in contact with one face of an unsubmerged diaphragm. The latter class is subdivided into: permeable and impermeable. The Allen-Moore cell has a permeable diaphragm. Its construction and characteristics are illustrated. Comparative cell information is tabulated and the Solvay process described. NaOH may be produced more cheaply by the electrolytic method, provided a suitable outlet is afforded for the secondary products resulting from the utilization of the H and Cl. To displace the Solvay process it will be necessary to develop by research additional uses and markets for secondary products involving the use of Cl.

CA 18, 3133-8

Electrical Conductivity of Molten NaOH
K. Arndt, G. Ploetz
Z. Physik. Chem. 110, 237-42 (1924)

The app. consisted of a Ag crucible with a Ag disk as inner electrode and a high-frequency machine served as a source of current. All the

samples contained NaCl, $Na_2CO_3$, or both salts, the quantity being detd. By adding further amounts of the salts, the influence of each on the cond. was found and the values were extrapolated to that for pure NaOH. At the four temps., 320°, 350°, 400°, and 450°, the sp. conds. are 2.12, 2.38, 2.82 and 3.27 resp., a linear increase with a temp. coeff. of 0.00412.

CA 18, 3357-5

Liberation of Hydrogen from Carbon Compounds I. The Interaction of Acetylene, Methanol and Formaldehyde with Fused Caustic Alkalies
H. Shipley Fry, Elsa L. Schulze and Helen Weitkamp
J. Am. Chem. Soc. 46, 2268-75 (1924)

Certain compds. in the vapor state interact with fused caustic alkalies according to an apparently general type reaction (M = Na of K): $RH_n + nMOH \longrightarrow R(OM)_n + nH_2$. This reaction involves the acidic dissociation of the alkalies, oxidation of the C compds. to carbonates through the replacement of H atoms by $OM^-$ radicals and the liberation of H. $C_2H_2$, MeOH and HCHO are, resp., oxidized to the orthocarbonate or carbonate stage according to the following reactions: $C_2H_2 + 2MOH = M_4CO_4 + H_2 + CH_4$; $MeOH + 2MOH = M_2CO_3 + 3H_2$; $CH_2O + 2MOH = M_2CO_3 + 2H_2$. Quant. data indicate that the amt. of H evolved and of carbonates formed in the last 2 reactions closely approx. resp., the theoretical ratios $3\ H_2:CO_2$ and $2H_2:CO_2$.

CA 18, 3554-7

Purification and Electrolysis of Sodium Chloride
E. G. R. Angel
Swed., 57,296, Sept. 3, 1924

A soln. of raw salt in amts. corresponding to the NaOH and pure NaCl intended to be produced is electrolyzed between solid metal electrodes. The soln. is purified partly by sepn. of org. impurities, partly by decompn. of such substances by the Cl. The soln. of NaOH obtained is evapd. till NaCl is pptd. The salt is obtained in a coarse-grained form either by slow evapn. of the lye after it has reached a sp. gr. of 1.25-30 or by introducing the fine-grained salt in a soln. of pure NaCl which is accordingly evapd. very slowly. The coarse-grained salt is freed from the mother liquor by centrifuging or filtering and is then washed with pure water, dried and removed from the process.

CA 19, 382-9

Nitrogen Oxides and Caustic Alkali
D. B. Bradner
U. S., 1,516,588, November 25

A charge of $NaNO_3$ and $Fe_2O_3$ is heated in a furnace by combustion gases which provide sufficient heat for the entire heating. The charge is agitated and maintained in continuous movement from the intake to the outlet of the furnace and evolved N oxides are removed by the combustion gases moving in an opposite direction to that of the charge. The residue is treated with $H_2O$ to produce NaOH and regenerate $Fe_2O_3$.

CA 19, 442-6

Canadian Salt Company's Process for the Manuf. of Alkali-Chlorine Products
D. A. Pritchard and G. E. Gollop
Can. Chem. Met. 8, 210-4 (1924)

CA 19, 593-7

Rate of Absorption and Equilibrium of Carbon Dioxide in Alkaline Solutions
R. V. Williamson and H. Mathews
Ind. Eng. Chem. 16, 1157-61 (1924)

The rate of absorption of $CO_2$ from $CO_2$-air mixt. by KOH and $K_2CO_3$ solns. was measured under various conditions of liquid flow, gas flow, KOH concn., $K_2CO_3$ concn., temp., and $CO_2$ conc. Three types of counter-current absorption towers were used: (1) a baffled tower; (2) a tower packed with pebbles; and (3) a specially constructed absorption box in which the surface of the absorbent liquid was nearly level as possible and without movement in any particular direction, although the liquid beneath the surface was flowing at a rate of 10 cm. per sec. There is a substantial increase in the rate of absorption when the rate of liquid flow is increased, even when there is no disturbance of the surface. The greatest increase, however, is produced under conditions of greatest liquid turbulence. Doubling the rate of gas flow increases the rate of absorption by 40% but the amt. of $CO_2$ escaping unabsorbed is about 60% of the increased flow. The rate of absorption is very greatly increased by increasing the concn. of KOH, but approaches a max. of about 2 N KOH. The data are in accord with Whitman and Keat's 2-film theory of absorption (cf. CA 16, 1354). The rate of absorption in $K_2CO_3$ soln. is independent of the $K_2CO_3$ concn. The rate of absorption in $K_2CO_3$ solns. increases as the temp. is raised, reaching a max. at about 70° for all cases studied. From the rate of absorption in water for a given app. it is possible to represent the rate for any soln. in that app. by the formula, Rate = $(K' \times C_{OH}) - (K' \times C_H) + R$, where R is the rate for water, K' and K''

are consts. and $C_H$, $C_{OH}$ are the concns. of the H and hydroxyl ions, resp. The variation of equil. ratios, $C_{K_2CO_3}/C_{(KHCO_3)}$, with the temp. is given for the range 5-85° and partial pressures of $CO_2$ of 36, 160, and 300 mm. of Hg.

CA 19, 794-8

Analysis of Alkali and Carbonate Mixes with H Electrode
E. Little and E. Durand
J. Am. Leather Chem. Assoc. 20, 19-31 (1925)

Std. HCl added to solns. of NaOH, $NaHCO_3$ and pH values detd. Thymol blue and bromphenol blue preferred to the usual phenolphthalein and methyl orange.

CA 19, 1617-6

Alkalies
E. Heinze
U. S., 1,532,489

An amalgam of an alkali-metal is treated with $H_2O$ in presence of an alloy of Fe and Cr to accelerate the reaction. Alloy may also contain Ni.

CA 19, 2156-3

The Activities of Strong Electrolytes. II. A Revision of the Activity Coefficients of K, Na, Li Chlorides and KOH
Geo. Scatchard
J. Am. Chem. Soc. 47, 648-61 (1925)

The mean activity coeffs. of the ions of KCl, NaCl, LiCl and KOH have been revised by calcn. from the available data on the e.m.f., f.p. and v.p. of solns. of these electrolytes. The equation used in the calcn. has the form: $-\log \gamma = 0.5 \sqrt{M} - Bm$, where $\gamma$ = the mean activity coeffs. of the ions, m is the molality and B is a const., depending on the medium, the temp., the valence type of the salt, and the mean diam. of the ions. The relation of the equation to the Debye theory and Huckel theory is discussed.

CA 19, 2591-8

Studies on Reaction in the Solid State
V. D. Balareff
Z. anorg. allgem. Chem. 145, 117-21 (1925)

$Ca(OH)_2$ dissociates at 450°, $Sr(OH)_2$ at 700°, and $Ba(OH)_2$ at 900°.

CA 19, 2729-8

Barium and Strontium Hydroxides
B. C. Stuer and Rhenania Verein Chemischer Fabriken Akt.-Ges.
Brit., 227,666, March 10, 1924

A soln. of the sulfide is treated with $NH_3$, or, for more complete conversion, with $NH_3$ and caustic alkali.

CA 20, 482-8

Separating NaOH and KOH
T. Sutter
U. S., 1,562,805, November 24

A soln. contg. both NaOH and KOH is concd. until crystn. occurs at a relatively high temp. ($\sim 60°$) and KOH crystals are sepd. at this temp., and in order to sep. NaOH, the mixture is dild. so that crystn. occurs only at a lower temp., and NaOH crystals are sepd. at this lower temp.

CA 20, 695-3

Thermochemistry of Be
C. Matignon and G. Marchal
Compt. rend. 181, 859-61 (1925)

Heats of reaction: $BeSO_4$ + NaOH (111.8 g/l.) Q = 34.5 kg cal.

CA 20, 1214-5

Alloys Resistant to Alkalies
N. V. Hybinette
Brit., 236,931, July 12, 1924

Fe is alloyed with Ni 18-40 and Cr 28-40% with or without 10% Co and up to 2% Cu. C 1.5, Si 1, and Al and Mn 0.5% each may be present.

CA 20, 1956-2

Electrolytic Caustic Soda
C. Elliott
Chem. trade J. 75, 31-2; 59-61; 91-3; 123-4; 151-3; 211-2; 239-40; 327-8; 387-8; 515-6; (1925)

CA 20, 2228-9

Manufacture of Caustic Soda by the Lime Process
A. Krause
Roczniki Chem. 5, 395-402 (1925)

The elimination of sulfates from dil. NaOH by means of the addn. of $BaCl_2$ is impracticable, since the Ba is pptd. by the $Na_2CO_3$ present, resulting in serious losses in manuf. An examn. of the equil. of the system: concd. NaOH soln.—$Na_2SO_4$, shown that for the prepn. of NaOH with a min. content of sulfate the soln. should be evapd. to a conc. of 73-75%, and then cooled to 50° to cause sepn. of $Na_2SO_4$, prior to further concn.

CA 20, 2288-2

Electrolysis by the Siemens-Billiter Process for the Manuf. of Chlorine and Caustic from Salt
Theodor Nissen
Chem. App. 12, 224, 231-2 (1925)

Descriptive, with 3 cuts of cell, 1 cut of cell room and some operating data. Cf. CA 19, 1665.

CA 20, 2566-3

Stable Mixed Crystals
H. G. Grimm
Brit., 240,884, May 2, 1924

NaCl 10 and KOH 1, fused together, yield nonhygroscopic crystals.

CA 20, 2621-8

Electrolytic Preparation of Pure Potassium Hydroxide from Crude Potash
L. A. Vernitz
Trans. R. Inst. Applied Chem. (Russian) 1925, No. 4, 11-6

KOH is generally prepd. by electrolysis of KCl, a Hg cathode being used. In Russia, where $K_2CO_3$ is inexpensive, it is desirable to prep. KOH by the electrolytic decompn. of this salt. Fe cells being unsuitable for this purpose, V. prepd. a wooden electrolyzer, coated the wood with a layer of paraffin to protect it from the action of potash. In the first stage, $K_2CO_3$ soln. is decomposed and K amalgam is formed. During this operation the cathodic Hg must be continually and rapidly renewed, or otherwise the amalgam soon becomes viscous and difficult to handle. The anode consisted of a Pt wire attached to a glass rod. Particular attention must be paid to the following factors: c.d. and speed of inflow of Hg. The higher the amperage the quicker must the Hg be renewed.

Other factors of importance are: concn. of $K_2CO_3$ soln. and its temp. V. used a 21-33° Bé soln. corresponding to 18-30%; the higher concn. gives the more favorable results. The temp. of the bath was room temperature. In the second stage the K amalgam obtained is transformed into KOH by electrolysis since the methods of its transformation into KOH either by hot water or by Fe are slow and incomplete. A Ni cathode was used and the recovered Hg was used again as cathode in the electrolysis of $K_2CO_3$. The concn. in the anode compartment of KOH was allowed to increase until it reached 25-30%. Heavy metals, $SiO_2$, chlorinated or sulfated compds. were absent. Some $K_2CO_3$ was present because of the absorption of atm. $CO_2$; its amount was only a fraction of 1%. The yields in KOH were 45-46% instead of the theoretical 50%. The expense in energy was 4.3 kw. hrs. per 1 kg. of KOH, with 15 amp. and 4.6-4.7 v. The same method is applicable for NaOH.

CA 20, 3259-1

Reactions Between Ferric Sulfate and Alkalies
A. Krause
Z. anorg. allgem. Chem. 148, 265-78 (1925)

K. studied the reactions at 15° between $Fe_2(SO_4)_3$ and KOH, NaOH, $NH_3$, $K_2CO_3$, $Na_2CO_3$, $NaHCO_3$ and $C_6H_5NH_2$ solns. The compn. of the ppt. obtained from 14.5% soln. of $Fe_2(SO_4)_3$ and the various alkaline substances is not constant. Ppts. free from sulfate are obtained only by adding an excess of alkali. The compn. of the ppt. depends on the pH value of the mother liquor. A curve is given which indicates that if the pH value is greater than 5.6, basic sulfates may exist, the compn. varying from $Fe_2O_3 \cdot 3SO_3 \cdot$ aq. to $4Fe_2O_3 \cdot SO_3 \cdot$ aq. $NH_3$ functioned as a strong or as a weak base, depending on the acidity of the mother liquor.

CA 20, 3398-1

Electrolytic Decomposition of Chlorides
E. Schlumberger
U. S., 1,598,018, August 31

C or graphite anodes are used and the electrolyte, e.g., NaCl soln. for the production of Cl and NaOH, is introduced through pores of the anodes.

CA 21, 694-7

Electrical Resistance at the Contact Surface of the Electrode and Electrolyte
O. Scarpa
Chimie and Industrie Special No., 488-91 (Sept., 1926)

A method of measurement is described and numerous curves obtained under various conditions with Pt, Pd, Au, Ag, Cu, Ni, Fe, Pb, graphite and retort charcoal in NaOH and $H_2SO_4$ electrolytes are given and briefly discussed.

CA 21, 992-8

Barium Hydroxide
A. Jahl
Brit., 249,402, April 18, 1925

Ba sulfide is treated with a soln. of a polysulfide or a caustic alkali or a suspension of an alk. earth hydroxide and the mixt. is leached with hot $H_2O$ to obtain a soln. from which, on cooling, $Ba(OH)_2$ crystallizes. The mother liquor may be treated with $CO_2$ to ppt. $BaCO_3$ mixed with S. This mixt. may be heated with C and with $BaCO_3$ pptd. from sugar solns. to obtain Ba sulfide.

CA 21, 1333-1

Caustic Soda from Soda and Quick Lime
Heinrich Moliter
Asphalt. Teerind. Ztg. 26, 451-3 (1926)

The decompns. of 15-18% of $Na_2CO_3$ soln. with $Ca(OH)_2$ is carried out in Fe cylinders heated by superheated steam under 3-4 atm. The NaOH is washed out, clarified, evapd. under vacuum and purified.

CA 21, 1734-2

Electrical Conductivity and Viscosity of Pure Sodium and Potassium Hydroxides
K. Arndt and G. Ploetz
Z. Physik. Chem. 121, 439-55 (1926)

The elec. cond. of fused KOH has been detd. between 400° and 600° by a method similar to that employed for NaOH (CA 18, 3133). As with NaOH, the value for the pure substance was obtained by extrapolating data for KOH contg. varying amts. of $K_2CO_3$. Tables are given showing the effect of silica and lime on the conductivities of both Na and K hydroxides. The densities and viscosities of the fused hydroxides contg. known amts. of chloride, carbonate, silica and lime have also been detd. and used in the same way. A special app. for measuring the viscosity by the capillary flow method is described.
See also: Z. Physik. Chem. 110, 237-42 (1924)

CA 21, 1741-9

Surface Tension and Viscosity of Aqueous Solutions of Potassium, Sodium, Lithium, Thallium and Barium Hydroxides and Sodium Carbonate Solution
O. Faust
Z. anorg. allgem. Chem. 160, 373-6 (1927)

The surface tensions were measured by the drop weight method. Surface tensions and viscosities were detd. at 20°, for concns. up to 6 N.

CA 21, 1939-1

The Solubility of Chromic Hydroxide in Alkalies
R. B. Corey
J. Chem. Education 4, 532-3 (1927)

The clear supernatant liquid left by $Cr(OH)_3$ settling from its soln. in NaOH gave a negative test for Cr. This observation is in line with previously published investigations (cf. CA 16, 3418; 17, 659), which indicate that the soly. of $Cr(OH)_3$ in an excess of alkali is due to the formation of a colloidal soln. and not of a chromite.

CA 21, 2362-5

Caustic Soda
C. Sundstrom and C. S. Lykes
Can., 268,951, March 8, 1927

NaOH is purified by concg. a crude caustic liquor by evapn., agitating the concd. NaOH soln., and then removing the ppt. impurities while a suitable temp. is maintained for the effective sepn. of the impurities from the clear purified soln.

CA 21, 2590-3

The Conductance of Dilute Aqueous Solutions of the Alkali Hydroxides at 25°
Merle Randall and C. C. Scalione
J. Am. Chem. Soc. 49, 1486-92 (1927)

The cond. of dil. solns. of the 5 alkali hydroxides were detd. at 25° in a cell designed to avoid the formation of carbonate. The limiting cond. was calcd. by assuming the cond. ratios for the alkali hydroxides are the same as that of HCl. The various values of the equiv. cond. were divided by the cond. ratios of HCl and the quotients plotted against the sq. root of the concn. The validity of this assumption was evidenced by the fact that no trend to the results appeared. The limiting conductivities obtained were: LiOH, 234.7; NaOH, 243.9; KOH, 266.8; RbOH, 270.4; CsOH, 269.5.

CA 21, 3428-2

Barium Oxide and Hydroxide
B. P. Hill and Blaydon Manure and Alkali Co. (1877), Ltd.
Brit., 259,395, October 30, 1925

$BaCO_3$ is distributed in finely divided form in highly heated gaseous material such as combustion gases or flame from coal, crude oil or gas. The semi-fused residual product, which may contain some $Ba(OH)_2$ together

with BaO and fuel ash, is collected and may be extd. with $H_2O$ for producing cryst. $Ba(OH)_2$.

CA 21, 3835-1

Pure Caustic Potash from Technical Potash by Electrolysis Using the Mercury Cathode
L. A. Vernitz
Trans. Russian Inst. for Appl. Chem. No. 4, 10-16 (1925)

V. describes (1) an appl. for the electrolysis of a potash soln. (from wood and plant ashes) and the production of a Hg amalgam and (2) an electrolyzer for the decompn. of the amalgam into KOH and Hg. Drawings of the app. are given.

CA 21, 4029-5

A New Method for the Evaporation of Electrolytic Caustic
W. L. Badger
Trans. Am. Inst. Chem. Eng. 18, 231-48 (1927)

An evaporator of the vertical tube type was designed with forced circulation by an external pump. The velocities were 5-10 ft. per sec. at the bottom of the tubes. The result was a very high coeff. of heat transfer, and the heating surface for a commercial machine became so small that it could be made of Ni tubes. No trouble was experienced from salting. The coeffs. were so high that small working temp. drops could be used, and this made possible concn. from cell liquor to 40% NaOH in triple effect with steam at 25 lbs. gage. A diagram giving the boiling points of NaOH solns. at diff. pressures is given, but it is in error at high concns. In the discussion, caustic embrittlement of steel is covered at length.

CA 21, 4030-6

Production of Soda Products from Sodium Sulfate
P. A. Chekin
J. Chem. Ind. (Russia) 2, 664-5; Chem. Zentr. 1926, II, 1169-70

Soda can be prepared from $Na_2SO_4$ by the Leblanc or the Penjakow process. The latter process is based on the reactions $4Al_2O_3 + 4Na_2SO_4 + 2C \longrightarrow 8NaAlO_2 + 4SO_2 + 2CO_2$ and $2\ NaAlO_2 + CO_2 \longrightarrow Al_2O_3 + Na_2CO_3$. The first reaction proceeds at a bright red heat, the second reaction in water at room temp. Though the Penjakow process has advantages over the Leblanc process, it cannot compete with the Solvay process. It can, however, be utilized for the manuf. of NaOH. The $NaAlO_2$ is dissolved in water and agitated with freshly pptd. $Al(OH)_3$. After 24-36 hrs. about 80% of the Al settles out as $Al(OH)_3$ in a form which is readily sepd. The remainder of the Al is pptd. according to the reaction: $2NaAlO_2 + Ca(OH)_2 \longrightarrow 2NaOH + Ca(AlO_2)_2$. The alkali liquor is concd.

in the usual way and worked up, the ppt, is decompd. by boiling $Na_2CO_3$ soln. under pressure, the $NaAlO_2$ which is formed in soln. is decompd. by $CO_2$ and the $Al(OH)_3$ returned to the process.

CA 22, 11-8

Prepn. of Standard Alkali for Buffer Solns.
Edgar Newberry
Ind. Chemist 3, 462 (1927)

For $CO_2$-free NaOH: weigh approx. 32 g. each of $Ba(OH)_2 \cdot 8H_2O$ and $Na_2SO_4 \cdot 10H_2O$, dissolve separately in 200 cc. boiling $H_2O$, mix while boiling and transfer to stoppered liter flask, making up to 1 liter at once. When the ppt. has settled, the soln. may be tested for excess Ba or $SO_4$ and titrated to det. exact alk. strength. The soln. should be decanted into paraffin-lined bottles with good rubber stoppers.

CA 22, 53-7

Practical Problems of Corrosion I. A Critical Examination of the Use of Inhibitive Chemicals
U. R. Evans
J. Soc. Chem. Ind. 46, 347-55T (1927)

Six inhibitors, NaOH, $Na_2CO_3$, $Na_3PO_4$, $K_2Cr_2O_7$, $Ca(OH)_2$ and Na silicate, have been studied to det. the pitting effect when chlorides are present in soln. Partially immersed steel specimens were used to study the water line effect. With progressive addn. of inhibitor the corrosion changed from general to localized (largely at the water line) to complete immunity. Inhibitors may cause serious pitting at breaks in the scale. The quantity of inhibitor to give immunity is greater for rusted metal than for bare. Motion of the soln. reduces the amt. of inhibitor needed. Conclusion: Alk. inhibitors should be added only in sufficient amts. to neutralize any acidity, but not enough to cause pitting.

CA 22, 524-2

The Absorption Velocity of Carbon Dioxide by the Still Surface of Caustic Soda Solution
S. Mitsukuri and Y. Sakamoto
J. Chem. Soc. Japan 48, 495-500 (1927)

The authors measured the absorption velocity of $CO_2$ by the change of partial pressure of $CO_2$. From 1 N to 3 N, the absorption velocity of $CO_2$ by the soln. surface is proportional to the partial pressure of the gas. That is, $-\Delta m/\Delta t = kp$, where $-\Delta m$ is the quantity of $CO_2$ which is absorbed on the soln. surface for $\Delta t$ time, p is partial pressure of the gas, k is a const. variable only with the concn. of

NaOH soln. From 4 N to 8 N, the absorption velocity first increases and reaches max. value and then decreases rapidly. The authors explained this phenomenon by the autocatalytic action of $CO_2$ already present in soln.

CA 22, 717-8

Heat of Solution of Dilute Solutions
S. M. Naude
Z. Elektrochem. angew. physik. Chem. 33, 532-4 (1927)

In support of Nernst (CA 22, 342) Naude has found that the heats of soln. (W) detd. for (0.333-0.04 mol/l.) solns. of NaCl. KCl, $NaNO_3$ and $KNO_3$ agree very well with those calcd. from the equation $W = -U(1-\alpha) + B\alpha\sqrt{\alpha c}$. B = 320 (18°), and decreases 8 units per degree decrease; U = heat of dissociation per mol.; $\alpha$ = degree of dissociation; $B\sqrt{c}$ = heat of interionic forces according to the Debye-Huckel theory . The concn. at which W is reversed in sign is well defined.

CA 22, 846-6

Determining the Heat Consumption for Caustic Dehydration
G. Angel
Chem. Met. Eng. 34, 683-5 (1927)

The detailed calcns. of the heat necessary to conc. NaOH solns. of definite concns. are given. The reduction in the heat necessary for such concn. in vacuum kettles is only 4% of that necessary for other processes. This is due to the fact that neither the heat of diln. nor the superheat is appreciably changed and that the reductions in caustic and satd. steam heat are both small. In elec. heated app., the only decided advantage gained by vacuum operation is the longer life of the pots due to the lower temps., although where coal firing or other direct combustion means are used, the temp. reduction causes such a decrease in stack and radiation losses, that the improvement may be as high as 20%. Where elec. heating cannot be used, vacuum kettles are advised, but where power is cheap, fuel-heated kettles are a poor investment.

CA 22, 905-5

Specific Heat of Electrolytes
K. Bennewitz
Z. Elektrochem. angew. physik. Chem. 33, 540-2 (1927)

Starting with the expression, $E_k = (3/2)\ pv - (1/2)\Sigma\phi\ (r),r$ (derived from the theorem of the virial), and $\phi\ (r) = \pm ar^n$ (law of force), B. derives the formula $C = [(n+3)/(n+1)] \cdot (3/2)\ R$, for the sp. heat of

a system which is composed of monoat. particles, and in which the outer virial is negligible. C is positive except for values of n = -1 to -3. Over this range the sp. heats of such systems are negative. In the formula $C_1 = 1-(P/100M_s)(M_s + x)$, for monoat. ions, x = 3R = 6. Values of x for the chlorides, bromides and hydroxides of Li, Na, K, Rb, Cs and H range from 12 to 35, indicating that hydration of ions occurs with all these electrolytes.

CA 22, 1658-4

Producing Caustic Soda or Similar Compounds by Reaction of a Fluoride with an Alkaline Earth Hydroxide
M. Buchner
Brit., 271,440, May 19, 1926

Details are given for prepg. $Ca(OH)_2$ for use in the process.

CA 22, 1830-2

The Manufacture of Caustic Soda
H. Molitor
Notiz. chim.-ind. 2, 435-7, 498-502, 556-8, 694-7 (1927)
3, 75-77 (1928); cf. CA 21, 1333.

A detailed description, with quant. data and explanation of all chem. reactions and technic involved, of the earliest methods of prepn. of NaOH, the Leblanc process, present day electrolytic and purely chem. methods of prepn. with special reference to the process of Berl, Defris and Boltenstern (CA 16, 1490), the utilization of by-products, the properties and uses of NaOH, detailed procedures for analysis of the raw materials, intermediate products and com. grades of NaOH, including detns. of total alkali, residue insol. in water, total alky., BaCl, Fe, $CaCO_3$, NaOH, CaO, $CaSO_4$, $CaCl_2$, and the analysis of by-products of the processes.

CA 22, 2247-1

Concentrating or Purifying Caustic Soda, etc.
C. F. Hammond
U. S., 1,668,504, May 1

Material such as NaOH is conducted over the surface of a hot liquid mass, e.g., molten Pb, heated directly by the flame or gases of a submerged flame burner and the products of combustion are withdrawn at a portion of the surface which is not covered by the material under treatment. App. described.

CA 22, 3099-1

Electric Furnace for Fusing Caustic Soda
J. S. Keenan
Elec. News (Toronto) 36, 48-9 (1927); Science Abstrs. 31B, 129.

Describes a 500-kw. elec-heated furnace for fusing caustic soda. The Ni-Cr resistors are hung from fire-brick walls and heat the cast-iron pot by radiation. The temp. is controlled by thermocouples . . . .

CA 22, 3124-9

Studies on the Resistivity of Chromium-Plated Metals to the Action of Chemical Reagents
Toru Murakami
J. Soc. Chem. Ind. Japan 31, 132-6 (1928)

Metallic Cr is generally in two states, passive and active. Commercial Cr is ordinarily passive and is highly resistant to acids and alkalies, excepting HCl. But the new surface obtained by breaking commercial Cr is not resistant to acids. Moreover, passive Cr which is in contact with Zn, Fe or some other metals in acids becomes active and is no longer resistant to acids. Electroplated Cr generally has pin holes and thus the base metal beneath is exposed through them. The fresh Cr film is not resistant to acids, but after a time it becomes passive. The Cr film prepd. by Y. Kato and M. (CA 22, 2329) is resistant to many reagents and gases. Tables showing the exptl. results for the action of many acids, alkalies, salts and the atmosphere on Cr-plated metals are given. Length of time after plating, and pin holes in the Cr film are the two important factors in testing the resistivity of Cr-plated metals.

CA 22, 3497-7

Barium Hydroxide
Soc. Francaise Sucrateries (Brevets et Procedes Deguide)
Fr., 633,368, April 26, 1927

$Ba(OH)_2$ is formed by attacking at about 1500° natural $BaSO_4$ with silica and grinding the product in the presence of $H_2O$. As by-products HCl and caustic alkalies and carbonates are prepared.

CA 22, 3586-8

The Electrolysis of Fused Sodium Hydroxide and of its Mixtures with other Metallic Oxides
Mazza Luigi
Atti congresso naz. chim. pura applicata 2, 719-47 (1926)

In the electrolysis of NaOH the electrode material is of prime importance. The three principal electrodes studied were Fe, Ni and Ag. Fe and Ni show extremely small change in wt. with diff.-current densities. The Fe electrode is easily polarized in comparison with that of Ni. The author's expts. with fused NaOH to some extent agree with the results obtained by Leblanc and Brode, but differ with respect to the polarization values of the two electrodes as compared with the decompn. range. The expts. with mixts. of soda and SnO were more complicated than with NaOH alone. For the cathodic polarization there is an abrupt change at 0.80 v. which corresponds to that of H on Ni. The anodic charge rapidly drops to zero. The decompn. tension shows three points of deflection at 1.10 v., 1.50 v. and 1.95 v. The first and last are due to H and Na and the second is due to Sn. With fused NaOH contg. 5% lead oxide there is a sepn. of lead at the cathode. The cathodic decompn. tension shows a deflection at 1.10 v. and another more accentuated at 1.60 v. The results obtained with Cr are more complicated than with the preceding electrodes.

CA 22, 3611-9

Cast Iron Resistant to Acids and Alkalies
H. G. Haase
Stahl U. Ersen 47, 2112-7 (1927)

.....The cast iron most resistant to alkali contains 3.3-3.5% C, 1.2-1.4% Si, 0.3-0.4% Mn, not more than 0.3% P, not more than 0.08% S and 0.3-0.5% Ni. Increases in P reduces the resistance to attack by alkali hydroxides, as also does increase of Si to a max. of 7% Si. Metal with the casting skin intact is more resistant than metal from which this skin has been removed.

CA 22, 3744-9

Alkali Metal Hydroxides
Leo P. Curtin
U. S., 1,678,767, July 31

An aq. suspension of PbO is agitated while adding an alkali metal sulfide such as that of Na and the supply of sulfide is regulated to avoid any substantial accumulation of sulfide ions in the soln.

CA 22, 4033-5

Viscosity Measurements and the Nature of the Solutions of a Few Hydroxides in Potassium and Ammonium Hydroxide
K. Mohanlal and N. R. Dhar, Allahabad Univ., India
Z. anorg. allgem. Chem. 174, 1-10 (1928); cf. CA 20, 1158, 2141

This is a study of the solns. of the hydroxides of Al, Cr, Sn, Zn, Pb, Be, Cu, Cd and Ag in KOH and $NH_4OH$, with the object of detg. whether they are true solns. or contain the hydroxides in colloidal form. To this end, viscosity measurements are made in N and 0.5 N KOH and in N, 2N and 5N $NH_4OH$ solns. at 30°. The viscosity of N KOH is 0.008954 and 0.5 N KOH is 0.008462, while for the solns. of the metallic hydroxides the following results are obtained: In N KOH: M/40 $Al_2O_3$, 0.009055; M/9 ZnO, 0.009243; M/18 ZnO, 0.009153; M/42 $Cr_2O_3$, 0.009265; M/19 BeO, 0.009022; M/11 BeO, 0.009093; M/11.5 $SnO_2$ 0.009000; M/7 $SnO_2$, 0.009124; M/13.1 PbO, 0.009008; in 0.5 N KOH; M/100 $Al_2O_3$, 0.008534; M/84 $Cr_2O_3$, 0.008943; M/38 BeO, 0.008509; M/13 $SnO_2$, 0.008502; M/19.7 PbO, 0.00853. The viscosity of N $NH_4OH$ is 0.008211, 2N is 0.008360 and 5N is 0.008694, while the viscosity of the hydroxide solns. is as follows: In 2 N $NH_4OH$: 0.22 g. CuO/100 cc., 0.008582; 0.1344 g. CdO/100 cc., 0.008421: 0.221 g. ZnO, 0.008495; 1.717 g. $Ag_2O$, 0.008631. The elec. cond. of similar solns. is also measured, the soln. of the metallic hydroxide showing decreased cond. Thus when 2.2 g $SnO_2$ is dissolved in 100 cc. N KOH, cond. is diminished 13% and when 0.448 g. ZnO is dissolved in 100 cc. N KOH, cond. is reduced 7%. To obtain comparative values with acids which form true solutions, viscosity and cond. are measured on addn. of HCl, boric and benzoic acids to KOH. Thus on adding M/3.6 boric acid to N KOH; viscosity is 0.009495 and sp. cond. is 0.1577; on adding M/18.5 benzoic acid to N KOH, viscosity is 0.009037 and sp. cond. is 0.2002; on adding 2.34 g. HCl to 100 cc. N KOH, viscosity is 0.008694. Conclusion: The hydroxides of Be, Al, Cr, Zn, Sn, and Pb in KOH and the hydroxides of Cu, Cd, Zn and Ag in $NH_4OH$ are partly present in a colloidal condition. The decrease in elec. cond. is explained as due to the absorption of alkali by the hydroxide for its peptization and the replacement of OH ions by aluminate, chromite, stannate and similar ions.

CA 22, 4448-8

Investigations of the Action of Alkalies and Various Salts on Iron
K. Taussig
Arch. Warmewirt, 8, 337-40 (1927)

A critical resume of the work of Berl, Staudinger and Plagge (Ver. deut. Ing. Forschung-sarbeiten 295 (1927)) on the action of solns. of Fe at high temp. and pressures.

CA 22, 4728-8

The Blattner Process for the Manuf. of Caustic Soda from Sodium Carbonate
Hirchberg
Chem. Ztg. 51, 765 (1927)

The process described is a modification of the Loewig process (Ger. pat. 203,271 (1923). A part of the crude $Na_2CO_3$ is heated with $Fe_2O_3$. $CO_2$ is evolved and the residue is leached with $H_2O$ to give a NaOH soln.

CA 23, 365-1

Suitable Protection Against Acids and Alkalies
E. Staemmler
Korrosion Metallschutz 4, 204-5 (1928)

A discussion of the factors detg. the applicability of certain materials as containers for alkalies and acids.

CA 23, 746-9

Dilatometric Measurement of the Thermal Expansion of Unstable Crystalline Salts
W. Klemm, W. Tilk and S. V. Mullenheim
Z. anorg. allgem. Chem. 176, 1-22 (1928)

The thermal coeff. of cubic expansion ($\alpha$) is detd. by a dilatometric method

$\alpha \times 10^6$ =

LiOH (20-120°) = $\sim$ 80
NaOH (20-120°) = $\sim$ 80
KOH (30-130°) = $\sim$ 190

density $d_4^{25}$

| | |
|---|---|
| LiOH | 1.43 |
| NaOH | 2.02 |
| KOH | 2.12 |

anion vols. are calcd. from mol. vol. extrapolated to -273°

| | | |
|---|---|---|
| LiOH | = | 10.4 |
| NaOH | = | 8.0 |
| KOH | = | 3.6 |

CA 23, 747-5

Dilatometric Measurement of the Thermal Expansion of Unstable Crystalline Salts
W. Klemm, W. Tilk and S. V. Mullenheim
Z. anorg. allgem. Chem. 176, 1-22 (1928)

$d_4^{25}$ $MgF_2$ 3.13, $ZnF_2$ 4.95, LiOH 1.43, NaOH 2.02, KOH 2.12

Anion vols. $MgF_2$ 6.4, $ZnF_2$ 5.8, LiOH 10.4, NaOH 8.0, KOH 3.6

CA 23, 1225-3

Baryta
Rhenania Kunheim Verein Chemischer Fabriken A.-G
Fr., 641,551, August 3, 1927

Crystals of $Ba(OH)_2 \cdot 8\ H_2O$ are obtained by treating silicates of Ba with water under pressure above 100° or with a soln. of baryta.

CA 23, 1354-9

Electrolysis of Sodium Sulfide Solutions
W. R. Fetzer
J. Phys. Chem. 32, 1787-1807 (1928)

A cell of the Castner-Kellner type for prepg. carbonate-free NaOH is described. Methods are developed for detg. the constituents of a $Na_2S$ soln. after electrolysis. When electrolysis is carried out at low current d. the only product is Na polysulfide; at higher current d. sulfate and dithionate are formed. When NaSH is electrolyzed, the products are $1Na_2S_2:2H_2S$. The limiting current (l.c.), or the current necessary to liberate S from a soln. of $Na_2S$ or $Na_2S_2$, increases at first with the conc. of polysulfide, passes through a max. and decreases toward zero. The l.c. for polysulfide solns. remains unchanged when rotation is increased from 220 r.p.m. to 700 r.p.m.; with $Na_2S$ this change doubles the l.c. Increase in temp. increases the l.c.

CA 23, 2253-2

A New Caustic Soda and Soda-Ash Process
Wilhelm Siegel
Chem.-Ztg. 53, 145-7 (1929)

The basis of the new process is: $CaF_2 + SiF_4 + 2NaCl$ (+ acid) = $Na_2SiF_6 + CaCl_2$; $Na_2SiF_6$ (at 700°) = $2NaF + SiF_4$; $2\ NaF + Ca(OH)_2$ = $2\ NaOH + CaF_2$. No difficulties are found with the last reaction;

the real problem is in converting the pptd. $CaF_2$ into NaF simply and cheaply. Various patents for this are considered. It is improbable that this process will compete with NaCl electrolysis or the Solvay process.

CA 23, 2350-5

Further Studies on the Thermochemical Behavior of NaOH Solns.
T. W. Richards and L. P. Hall
J. Am. Chem. Soc. 51, 731-6 (1929)

The heat of diln. of NaOH • 100 $H_2O$ was measured at 16° and 20°. All this labs heat cap. and heat of diln. data on NaOH were recalcd. The heat of neutralization of HCl and NaOH at infinite diln., at 20° was calcd. to be 13,650 cal.

CA 23, 2411-5

Resistance of a Few Steels to Chemical Action in Relation to Carbon, Nickel and Chromium Contents
Fritz Schmitz
Z. Metallkunde 21, 64-5 (1929)

The types of metal examd. were unalloyed steel with increasing C content (0.06-0.92%), steel with Cr content between 8 and 18% and Ni content increasing from 0.5 to 62%, and steel with high Cr content (15-18%) and relatively low Ni content, but with very high C content (1.33-1.84%). The reagents studied were cond. $H_2O$, sea water, $HNO_3$ (dil. and concd.), $H_2SO_3$, $H_2SO_4$ (dil. and concd.), HCl (dil. and concd.), 80% acetic acid, citric acid (1:2), concd. $NH_4OH$, KOH (1:2), and aqua regia, results are expressed in terms of % wt. loss after 180 hrs. treatment. In unalloyed steel the effect of increasing C content is increased protective action against sea water, cond. water, $H_2SO_3$, dil. or concd. HCl and oxidizing gases, but action by dil. $H_2SO_4$ is more severe with high C content. The influence of increased Ni content in a Cr-Ni steel is at first an increase in attack with dil. $H_2SO_4$, followed by reduction in attack. In cond. and sea water, dil. $HNO_3$, citric acid, $NH_4OH$ and KOH, increase in Ni content has very little effect. In $HNO_3$ and KOH, these Ni-Cr steels can be regarded as completely passive. The results show that in oxidizing agents the protective action is due solely to Cr, while in dil. $H_2SO_4$, and dil. and concd. HCl, the Ni is the constituent which exerts a protective action. Thus an alloy with 0.42% Ni and 14.5% Cr shows 38.5% loss in dil. $H_2SO_4$, while an alloy contg. 54.4% Ni and 12.4% Cr shows only 0.193% loss in the same reagent.

CA 23, 2538-4

Osmotic Purification of Caustic Soda
Leonardo Cerini
Fr., 33,608, May 31, 1927. Addn. to 616,821

The arrangement of diaphragms is given.

CA 23, 2623-4

The Vapor Pressures of Binary Systems; The Aqueous Solutions of Orthophosphoric Acid, Sodium Hydroxide and Potassium Hydroxide
Ukitiro Nakaya
Trans. Faraday Soc. 24, 543-5 (1928)

Empirical equations are constructed for vapor pressures of $H_3PO_4$, NaOH and KOH from Tammann's data in Landolt-Bornstein for a temp. of 100°. The mol. fractions at any concn. are represented by $\mu_1$ for water and $\mu_2$ for the solute. The $H_3PO_4$ curve shows an inflection at $\mu_1 = \mu_2 = 0.5$, indicating a loose compd. of $H_3PO_4 \cdot H_2O$ in soln. For NaOH and KOH the curves indicate that beyond $\mu_2 = 0.5$ all water mols. combine with the solute and show no sensible vapor pressure.

CA 23, 2644-4

Specific Heats of NaOH and KOH Solns.
T. W. Richards and L. P. Hall
J. Am. Chem. Soc. 51, 707-12 (1929)

| | Sp. heats at 18° |
|---|---|
| $NaOH \cdot 25H_2O$ | 0.9127 |
| $NaOH \cdot 50H_2O$ | 0.946 |
| $NaOH \cdot 100H_2O$ | 0.9690 |
| $KOH \cdot 100H_2O$ | 0.9567 |

CA 23, 2791-7

Caustic Soda
Giuseppe Donagemma
Fr., 648,584, February 9, 1928

NaOH formed as a residue in chem. treatments, particularly in the artificial silk industry, is purified from org. material by osmosis through diaphragms formed of volcanic stone or conglomerates of volcanic stone.

CA 23, 2926-2

Alloys
The International Nickel Company, Inc. and E. J. Bothwell
Fr., 649,574, February 22, 1928

A Cu-Ni alloy which has special phys. properties and is resistant to acid and alk. corrosion and not affected by superheated steam contains Si 0.5-5%. Suitable compns. are Ni 55-80, Si 0.5-5, Fe 0.5-5, C 0.0-0.5, Mn up to 3% and the remainder Cu. The properties are improved by sudden cooling from about 1038°, followed by drawing at 482-870°.

CA 23, 3329-4

Absorbing Liquids for Technical Gas Investigations
Otto Wolf and Artur Krause
Arch. Warmewirt. 10, 19-21 (1929)

The rate of absorption of $CO_2$ by KOH solns. rises rapidly up to 4% by wt., then more slowly with a max. at 28%. The rate for NaOH is nearly the same as KOH up to 4% then falls slowly . . . . .

CA 23, 3544-5

The Manufacture of Caustic Soda
H. Morin
Russa 4, 525-31 (1929)

Description of the manuf. of NaOH by chem. and electrolytic processes (electrolysis of NaCl solns., and of fused NaCl), and of the concn. of NaOH solns.

CA 23, 3547-5

Purifying Caustic Soda
D. A. Pritchard and United Alkali Company, Ltd.
Brit., 299,995, October 21, 1927

Dil. caustic liquor such as the effluent from electrolytic cells may be purified from NaCl by evapn. and subsequent addn. of $Na_2SO_4$ (or other suitable salt of $H_2SO_4$) or of $H_2SO_4$ itself. Various details are given.

CA 23, 3550-9

The Action of Glass Towards Sodium Hydroxide at High Temperatures
Fritz Friedrichs
Sprechsaal 61, 967-9, 980-6 (1928)

The loss of wt. and alkali loss or gain in 1 N NaOH soln. was detd. for 14 glasses of different compns. in the temp. range of 100-300°. The alkali loss in 1 N NaOH decreases with increased $B_2O_3$ content. Porcelain shows no alkali loss; instead, even at low temps., it takes alkali from the soln. On investigating the influence of time on the action of 1 N NaOH toward 3 characteristic glasses, it was found that at temps. above 170° the loss of wt. becomes independent of the time of action. An equil. results between the glass and soln. This equil. is not obtained at temps. below 170°. The effect of NaOH concn. from 5 N to infinite diln. was obtained for 3 glasses. For strongly acid glasses the loss of wt. for a definite time as well as for a definite concn. of N NaOH becomes const.

CA 23, 3780-6

Barium Hydrate
Rhenania-Kunheim Verein Chemischer Fabriken A.-G.
Fr., 653,346, April 23, 1928

$Ba(OH)_2$ is prepd. by the hydrolysis of silicates of Ba, which have been wetground to a fine degree. The grinding may be continued during the heating for hydrolysis.

CA 23, 3829-9

New Apparatus Materials for Chemical Industries
A. Kufferath
Chem.-tech. Rundschau 44, 12, 49 (1929)

Krupp introduced, in 1912, 2 types of non-rusting steels; the VM group contg. 13-15% Cr and a little Ni; the VA group contg. 18-25% Cr and more Ni than VM. The alloy V2A has a high resistance to acids, which is further increased by cooling rapidly from 1170°; m. 1400°; sp. gr. 7.86; heat cond. 0.04 or approx. 1/3 that of Fe. This alloy can be cold pressed, rolled, drawn and welded. VA steel is not attacked by $HNO_3$ (sp. gr. 1.04-1.40) at ordinary or boiling temp. or by fuming $HNO_3$ (sp. gr. 1.52) below 20°, but is attacked at higher temps.; it is not attacked by a 1:1 mixt. of concd. $HNO_3$ and concd. $H_2SO_4$, by concd. $H_2SO_4$ (sp. gr. 1.84) at ordinary temps.; by fuming $H_2SO_4$ (free $SO_3$ = 60%) at 70°, by $H_3PO_4$ below 45% or by 80% $H_3PO_4$ at 60°. It resists the action of most org. acids as well, but is attacked by some at higher temp. It is resistant to the action of alkalies, of many dissolved and molten salts, i.e., solns. Al acetate, $Al_2(SO_4)_3$,

$NH_4NO_3$, Pb acetate, $KNO_3$, $KClO_3$, $Cu(NO_3)_2$, $MnCl_3$, $Na_2SO_3$, $ZnSO_4$, $Na_2SO_4$, of molten $KNO_3$ and $AgNO_3$, and of concd. $H_2O_2$. For distn. of solns. of the latter in vacuo VA steel is better than Al app. On account of this notable resistance to reagents, this steel is particularly suited for use in chem. app. and in containers. The properties and use of Monel metal and Haveg are also described.

CA 23, 3858-4

Electrolysis of Alkali Chlorides
A. Levasseur
Bull. Soc. Franc. Elec. 8, 798-804 (1928); Science Abstracts 31B, 636

Many difficulties are encountered in the process, such as diffusion within the bath, which tend to lower the efficiency. Various methods of overcoming these difficulties are examd: the use of diaphragms, of circulation, of circulation and diaphragms, the use of a Hg cathode. The theory is given of the formation of chlorates and perchlorates. The use of a Hg cathode, while involving a heavy capital outlay, has notable advantages in that it enables a concd. soln. of NaOH to be obtained directly, which soln., contg. no chlorides, is of special value for the prepn. of artificial silk.

CA 23, 4183-3

Iron and Steel Castings
W. Klepsch
Brit., 302,254, August 10, 1927

For rendering iron or steel castings resistant to fire, acids, and alkalies, they are cast in molds the sand of which is mixed with sufficient decarbonizing material to produce a superficial layer 0.3-40.0 mm. thick contg. not more than 2.6% (and preferable over 1.4%) C. The iron may contain Al, B, Cr, Co, Cu, Mg, Mn, Mo, Ni, Si, Ti, V or W.

CA 23, 4302-1

Caustic Soda
Wilhelm Kolb
Metallborse 18, 2581-2, 2638-40, 2693-4, 2750-1, 2806-7, 2861-4 (1928)

Although KOH is made from KCl by electrolysis in Germany, NaOH is prepd. chiefly by causticizing $Na_2CO_3$ obtained by the Solvay process.

CA 23, 4783-3

Separation of Sodium and Potassium Hydroxides
Soc. Anon. pour L'Ind. Chim.-A. Bale
Ger., 477,952, April 25, 1925

KOH and NaOH in lye mixts. are sepd. by concg. at 40-100°, when the KOH crystals sep., and then diluting and cooling when the NaOH separates out. Thus, a lye mixt. is evapd. at 60° in a crystn. drum until the deposit of crystals ceases. These are practically pure KOH. They are sepd. and the liquor is diluted and cooled. NaOH crystals then deposited contain 8-10% KOH. These can be redissolved and the process repeated.

CA 23, 4868-9

The Solubility of Na and K Hydroxides in Methanol and Ethyl Alcohol
A. G. Murray
J. Assoc. Official Agr. Chem. 12, 309 (1929)

NaOH and KOH in excess were placed in bottles of EtOH and MeOH and allowed to stand with occasional shaking at room temp. (about 28°) for about 3 weeks. Ordinary lab. reagents were used. The soly. in g. per 100 ml. and the d. of the satd. soln. were found, resp., 29.0 and 1.04 for KOH in EtOH, 40.3 and 1.14 for KOH in MeOH, 13.6 and 0.93 for NaOH in EtOH, 23.9 and 1.01 for NaOH in MeOH.

CA 23, 5279-9

Concentrating Caustic Alkalies
I. G. Farbenind. A.-G.
Brit., 306,935, February 29, 1928

In order to produce fused KOH or NaOH a concd. soln. is evapd. in an inclined rotary tube, the entire inner surface of which is covered with the soln. or melt. The tube may be elec. heated and lined with Ag.

CA 23, 5554-7

Fused Quartz as a Material for Construction in the Chemical Industry
Z. von Hirschberg
Korrosion 4, 25 (1929)

A table gives the resistance of quartz to $NH_4OH$, NaOH, KOH, $Na_2CO_3$, $Ba(OH)_2$ and $Na_2HPO_4$.

CA 24, 15-8

The Thermodynamic Behavior of Concentrated Solutions
R. Fricke
Z. Elektrochem. 35, 631-40 (1929)

A continuation of previous work on the heat and work of diln. (cf. CA 22, 717). Exptl. data are given for the vapor pressures of solns. of $Th(NO_3)_4$, $NH_4NO_3$, NaOH, urea and glycerol at different concns. Heats of diln. for solns. of $ZnCl_2$, $MgCl_2$, $Th(NO_3)_4$, NaOH, NaOAc and glycerol were detd. calorimetrically. The calorimeter is described. From these data the differential heats of diln. are calcd. by Kirchoff's equation. The work of diln. is also computed. F.'s previous statement that for solns. with strong pos. heats of diln. the heat is greater than the work at high concns. and less than the work at low concns. is confirmed except for $MgCl_2$ and glycerol. Conclusion: The Kirchoff equation gives the best results for solns., with high diln. heats.

CA 24, 472-1

Dehydrating Caustic Alkali
Justin F. Wait
U. S., 1,734,699, November 5

Caustic alkali contg. over 10% of moisture is introduced into a closed vessel until the vessel is filled to about 40% of its capacity and is heated at a pressure below 12 lbs. abs., weak caustic liquor is introduced into the vessel while maintaining the temp. of the liquor in the vessel at 200-300°, and after the supply of this weak liquor is discontinued the temp. is raised to above 400° while maintaining a pressure of about 2 lbs. abs.

CA 24, 472-2

Purifying Caustic Soda
Albert H. Hooker and W. J. Marsh
U. S., 1,733,879, October 29

A soln. contg. about 40-46% NaOH and substantially satd. with NaCl at about atm. temp. is dild. with water and cooled below the point at which it becomes satd. with $NaOH \cdot 3\frac{1}{2} H_2O$, in order to effect sepn. from soln.

CA 24, 472-4

Regenerating Alkali Solutions
I. G. Farbenind A.-G.
Brit., 309,237, January 11, 1928

Solns. contaminated with org. matter, such as spent lye contg. cellulosic substances from viscose manuf. or mercerization of cotton, are heated under pressure with O or with gases contg. O to above 100°. $Na_2CO_3$ formed is decomposed to form NaOH by adding BaO, SrO, $Ba(OH)_2$ or $Sr(OH)_2$ or by subsequent treatment with lime.

CA 24, 692-3

Causticization of Sodium Carbonate by Ferric Oxide. XII. The Mathematical Solutions of the Dissociation Pressure Expressions of Sodium Carbonate in the Presence of Ferric Oxide
Mototaro Matsui
J. Soc. Chem. Ind. Japan 31, 706-10 (1928);
Suppl. Binding 31, 166-9B (1928); cf. CA 21, 1524, 2534-5

In previous papers, the dissocn. pressure of $Na_2CO_3$ in the presence of $Fe_2O_3$ was reported, and numerical consts. were given for each of 20 kinds of empirical equations. In the present paper, 8 equations are selected and the temp. at which the dissocn. pressure is 760 mm. is calcd. by applying Newton's method of approximation. The temp. is 849.1°. Eight expressions for reaction heat ($\triangle H$) and as many free energy ($\triangle F$) equations are derived. $\triangle H_p$ = 760 mm. = 29.702 cal, $\triangle H_t$ = 298.1 = 34,479 cal., $\triangle S_p$ = 760 mm. = 25.57-27.47 cal. and $\triangle S_t$ = 298.1° = 27.49-55.39 cal. The same temp. calcd. from former measurements by means of Lagrange's formula of interpolation, is 848.32°.

CA 24, 763-5

The Absorption Velocity of Gases by Liquids. II. Absorption of Carbon Dioxide by Sodium Hydroxide Solution
Sirozi Hatta
J. Soc. Chem. Ind. Japan 32, 809-14 (1929); cf. CA 23, 5083

By the same app. used in the former expt., the velocity of absorption of a mixt. of $CO_2$ and air in NaOH soln. (1.0, 2.14, 3.16 and 4.15 N) at 20 and 30° and sometimes under 1.53 atm. pressure was studied. Under the same conditions, absorption is always slower in NaOH than in KOH. The curve representing the relation between velocity of absorption and concn. of the residual free alkali has quite different characteristics for NaOH and for KOH. For NaOH the velocity decreases continuously along a curve as the free alkali decreases; there

is no range of const. velocity and also no range of inclined straight line, all of which occur in KOH. This is attributed to the remarkable difference in the chem. reaction between $CO_2$ and NaOH or KOH, the velocity for NaOH being much smaller. Though the method used is not accurate enough, the calcn. seems to show that the reaction velocity is proportional, though not linearly, to the nth power of $CO_2$ pressure, where n is a decimal.

CA 24, 1046-3

Solubility of CaO in NaOH and $CaCl_2$
A. M. Wright and H. O. Askew
Trans. Proc. New Zealand Inst. 60, 267-70 (1929)

The soly. of CaO in solns. of NaOH at 13° and $CaCl_2$ at 16-20° is shown to pass through a min. value in about 1.4% (0.35 N) and 1.0% (0.19 N) soln. resp.

CA 24, 1599-9

Determination of Sodium Hydroxide in the Presence of Sodium Carbonate
W. Poethke and P. Manicke
Z. Anal. Chem. 79, 241-55 (1929)

On the basis of some 109 expts. the following procedure is recommended for the analysis of dil. NaOH solns. contg. carbonate. Dil. the soln. to 100 cc. with $CO_2$-free water. In an aliquot part det. total alky. by titration with HCl, methyl orange being used as indicator. Add another portion from a pipet to 25 cc. of soln. contg. sufficient $BaCl_2$ to ppt. all of the $CO_3^{--}$ present and leave the soln. about 0.1 N in excess Ba. Mix, add a little phenolphthalein and titrate the $OH^-$ with HCl in the presence of the $BaCO_3$ ppt.

CA 24, 1708-7

Alkali Hydroxide
A. F. Meyerhofer
Swiss, 134,358, May 3, 1927

Alkali hydroxides are prepd. by the action of alkali fluoride on alk. earth hydroxides in the presence of liquid. Thus, KF is heated with $Ca(OH)_2$ to 80-120° in water.

CA 24, 1941-9

Caustic Alkalies
I. G. Farbenind A.-G.
Fr., 670,335, February 26, 1929

Molten caustic alkalies are prepd. by evapn. of concd. lyes in a rotating inclined tube, the external surface of which is heated.

CA 24, 2248-6

Dehydrating Molten Alkaline Materials such as Caustic Alkali
J. F. Wait
U. S., 1,749,455, March 4

The material is passed between electrodes supplied with sufficient current to evap. moisture and the evolved vapors are removed by a current of inert gas.

CA 24, 2838-2

Manuf. of Caustic Soda from Sodium Sulfate
V. I. Kurikov
J. Chem. Ind. (Russia) 6, 119-20 (1929)

In view of the scarcity of NaOH in U.S.S.R. $Na_2SO_4$ may be used for the manuf. of NaOH, e.g., wood charcoal 0.8 and $BaSO_4$ 3 are pulverized, intimately mixed and calcined at 1000-1200° about 5-6 hrs. The BaS obtained is treated by direct steam at temps. above 100°, giving $Ba(OH)_2$ soln. into which a soln. of hydrated $Na_2SO_4$ 4 in water 8 is poured slowly while boiling. The pptd. $BaSO_4$ can be used in the next operation. Hydrated $Na_2SO_4$ 4 and charcoal 0.8 give NaOH 1.

CA 24, 3608-9

Evaporation of Caustic Soda to High Concentrations by Means of Diphenyl Vapor
W. L. Badger, C. C. Monrad and H. W. Diamond
Am. Inst. Chem. Eng. (Detroit meeting) 1930, 22 pp. (preprint)

The possibilities of app. in which evapn. could be carried out with high-temp. vapors as a heating medium are discussed. $Ph_2$ was selected for the heat transfer material. Various phys. and thermal properties of $Ph_2$ are shown. A $Ph_2$ boiler is described and details are given of the exptl. evaporator. Mech. difficulties are discussed as well as method of operation. The detn. of the heat transfer coeffs. involved, as well as all of the operating data on the $Ph_2$ evaporator are given. An app. has been devised in which NaOH has been concd. to 98+% with $Ph_2$ as a heating medium. A large no. of detns. are given for film coeff. of heat transfer between boiling NaOH solns. and a metal wall. The app. was evolved with no precedent or previous experience, nevertheless NaOH was almost completely dehydrated. A properly designed com. app. would be entirely practical. Also in Ind. Eng. Chem. 22, 700-7 (1930).

CA 24, 3862-7

Double Decompn. of Ammonium Carbonate and Alcoholic KCl Solns.
Alfred Stern
Z. angew. chem. 43, 425-7 (1930)

The Solvey-process reaction is $NaCl + NH_4HCO_3 \rightleftharpoons NaHCO_3 + NH_4Cl$. The best temp. is 30°. A change of 10° reduces the $NaHCO_3$ yield considerably. In aq. soln. $KCl + NH_4HCO_3 \rightleftharpoons KHCO_3 + NH_4Cl$ and $2KCl + (NH_4)_2CO_3 \rightleftharpoons K_2CO_3 + 2NH_4Cl$ proceed from right to left giving practically no $KHCO_3$ or $K_2CO_3$. $NH_4HCO_3$ is decomposed rapidly by EtOH but $(NH_4)_2CO_3$ only slowly. With EtOH as solvent the max. yield of $K_2CO_3$ is at +5° and 85% alc. Exptl. errors are about 3%, due to decompn. of $(NH_4)_2CO_3$ by EtOH. The pptd. salt mixt. contains $K_2CO_3$ and KCl. If the mixt. is causticized and evapd., KOH is obtained and KCl recovered. The temp. must be controlled closely.

CA 24, 3953-2

Electrolytic Chlorine and Caustic Soda Industry in Japan
Tsutomu Shoji
J. Soc. Chem. Ind., Japan 33, Suppl. binding 187-9 (1930)

CA 24, 4593-1

Caustic Alkalies
Bozel-Maletra
Fr., 683,603, January 26, 1929

Caustic alkalies are prepd. by heating $Cr_2O_3$ or substances or ores contg. it in the presence of alkali carbonates or bicarbonates in a non-oxidizing or reducing atm. and decomposing with water.

CA 24, 4905-2

Producing Other Compds. from Barium and Strontium Sulfates
Fritz Rothe and Hans Brenek (to Rhenania Verein Chemisches Fabriken A.-G)
U. S., 1,772,269, August 5

Ba and Sr sulfates are mixed with $SiO_2$ in such proportion that silicates of a type between $Me_2SiO_4$ and $Me_3SiO_5$ are formed and the mixt. is heated in an oxidizing atm. in the presence of steam to 1100° or higher. Water forms $Ba(OH)_2$ in good yield from the product.

CA 24, 5115-9

Barium Hydroxide
Kali-Chemie, A.-G. (Friedrich Rusberg and Gustav Clauss, inventors)
Ger., 503,496, June 23, 1927

$Ba(OH)_2$ is prepd. by hydrolyzing Ba silicates in finely divided form, the size of the particles ranging from colloidal fineness up to 0.1 mm. The process may be effected by wet grinding the silicates with heating.

CA 24, 5444-4

Phosphorous and Potash
Edward Urbain
Fr., 684,927, February 15, 1929

P and KOH are prepd. by treating in a shaft furnace a mixt. of an Al K silicate such as feldspars, $Ca_3(PO_4)_2$ and charcoal.

CA 24, 5654-5

Metallic Oxides and NaOH
J. d'Ans. and J. Loffler
Ber. 63 B, 1446-55 (1930)

A metallic oxide and NaOH are allowed to interact. The resulting compds. are water, which is titrated, a mixed oxide and an excess of one of the reactants, which are sepd. by soly. differences in suitable acids. The existence of the following compds. has been detected: $Na_4SiO_4$; $Na_2ZrO_3$; $Na_4TiO_4$; $Na_8Ti_5O_{14}$; $Na_2Ti_5O_{11}$; $Na_2CeO_3$; $Na_2Al_2O_4$; $Na_2Fe_2O_4$; $Na_2FeO_4$; $Na_2Cr_2O_4$; $Na_2CrO_4$; $Na_2Cr_2O_7$. No definite compds. were obtained in the systems $Na_2O$-$ThO_2$; $Na_2O$-ZnO and $Na_2O$-MgO. This method is applicable to ternary systems, as demonstrated by the formation of $Na_2ZrSiO_5$.

CA 25, 174-9

Evaporating Caustic Alkali Solutions
R. M. Winter and Imperial Chem. Ind. Ltd.
Brit., 332,250, Jan. 16, 1929

Concn. is effected by evapg. in vessels formed of, or lined with, an alloy of Ni with Cu or Cr substantially free from Fe.

CA 25, 385-5

Alkali Metal Hydroxides
Ernst Heinze
U. S., 1,784,066, December 9

An amalgam of alkali-forming metal is agitated with water by use of a stirrer composed of C material such as graphite or coke.

CA 25, 386-3

Barium Hydroxide
Kali-Chemie A.-G. (Fritz Rothe and Friedrick Rusberg, inventors)
Ger., 506,275, August 10, 1926

$Ba(OH)_2$ is prepd. by decompg. Ba silicates with $H_2O$ under pressure at a temp. above 100°. A large excess of water need not be used, so that solns. suitable for direct crystn. are obtained. Dil. solns. of $Ba(OH)_2$ may be used for the decompn. Examples are given. Cf. CA 24, 5115.

CA 25, 781-1

Barium Hydroxide
Paul Kircheisen
Ger., 509,261, April 26, 1928

In the manuf. of $Ba(OH)_2$ by hydrolysis of BaS, the latter is preliminarily mixed in the solid state with finely divided S and a little water.

CA 25, 883-5

Electrolytic Production of Salts and Alkalies such as Ferrous Chloride and Sodium Hydroxide
Peter Fireman (to Magnetic Pigment Co.)
U. S., 1,788,512, January 13

A soln. of an alkali metal salt such as NaCl is electrolyzed in the presence of a cathode and a sol. anode such as Fe; the bodies of the salt soln. in contact with the anode and cathode are sepd. by an independent body such as an electrolyte in an intermediate compartment which is constantly renewed without contacting the anode or cathode; the salt soln. is separately supplied to the soln. bodies in contact with the anode and cathode. App. is described.

CA 25, 1340-6

Sodium Hydroxide and Ammonia
Alfred Mentzel
Fr., 690,680, February 26, 1930

$NaHCO_3$ is converted into NaCN by adding C and reacting on the mixt. with N at a high temp., and this is converted to NaOH and $NH_3$ by steam at 400-500°.

CA 25, 1644-4

Potash and Alumina
F. Jourdan
Fr., 693,074, March 31, 1930

KOH and $Al_2O_3$ are obtained from leucite by heating limestone with leucite and a suitable flux to the m.p., cooling, grinding and leaching with a soln. of $K_2CO_3$ to neutralize the CaO and ppt. it as $CaCO_3$.

CA 25, 1752-9

The Action of Bases on Non-Metals
A. L. Curl
J. Chem. Education 8, 490-7 (1931)

Most of the non-metallic elements with the exception of N and the rare gases react with the alkali hydroxides. In general, the reactions take place in accordance with the type $Cl_2 + 2NaOH \longrightarrow NaCl + NaClO + H_2O$. The exact mechanism of this type of reaction is not known or discussed. Similar reactions are obtained with the alkali amides which are analogous to the hydroxides in the $NH_3$ system of compds. In $NH_3$ the polysulfides, polyphosphides, etc., are more stable than in water, but the ammono salts are less stable than the corresponding aqua salts.

CA 25, 1951-6

Purification of Caustic Soda Obtained by the Lime Process
Alfons Krause and Waclaw Kluka
Przemysl Chem. 15, 6-12 (1931)

Caustic soda obtained by the CaO process contains $Na_2CO_3$, NaCl, $Na_2SO_4$, $Na_2SiO_3$ and traces of $Al_2O_3$ and $Fe_2O_3$ as impurities derived from the raw materials. Their removal can be accomplished by concn. and cooling. The NaOH concn. should be increased up to 72-5%, higher if possible. Cooling decreases the soly. of all impurities.

To remove $Na_2SO_4$ cooling to about 50° is necessary. It is well to conc. the NaOH with a def. amt. of $CaCO_3$, which removes the $Na_2CO_3$ and $Na_2SO_4$.

CA 25, 2350-3

Vapor Pressure and Heat of Dilution. VII. V. P. of Aqueous Solutions of NaOH and of Alcoholic Solutions of Calcium Chloride
A. M. Hayward and E. P. Perman
Trans. Faraday Soc. 27, 59-69 (1931)

The v.p. of NaOH solns. in Ag tubes was detd. by the dynamic method at 30°, 40°, 60°, 70°, and 80°. The same method was used for the $CaCl_2$-EtOH solns. from dil. to nearly satd. at 20°, 30°, 40°, 50° and 60°. The heat of diln. and the osmotic pressure were calcd., the former agreeing well with exptl. data.

CA 25, 2530-3

Caustic Soda; Ammonium Chloride
Alfred Mentzel
Ger., 510,093, March 27, 1929

$NaHCO_3$ prepd. by the ammonia-soda process is mixed with C and treated with N at a high temp. The NaCN so obtained is treated with steam, NaOH and $NH_3$ being obtained. The latter is returned to the ammonia-soda process and ultimately recovered as $NH_4Cl$.

CA 25, 2605-2

Apparatus for Evaporating Corrosive Solns. as Caustic Soda
R. M. Winter
Brit., 339,657, June 14, 1929

The liquid to be evapd. is passed as a film over a surface heated directly or indirectly by radiation from one or more incandescent plates arranged parallel to the surface. The plates may be formed as described in Brit., 25,808 of 1909 or consist of a metal plate supporting an alundum plate carrying granules of magnesia or the like.

CA 25, 2628-7

Chemical Reactivity of Fused Bases. I. The Action of the Alkali Amides upon Electropositive Metals
W. C. Fernelius and F. W. Bergstrom
J. Phys. Chem. 35, 740-55 (1931)

An app. is described for the study of reactions of pure fused alkali amides which avoids contamination of the melt and permits viewing the reaction, controlling the temp., altering the fusion atms., quant. collection of gases and extn. of the melt with liquid $NH_3$. Mg reacts with $NaNH_2$ or $KNH_2$ in an $NH_3$ atm. to liberate the alkali metal: $Mg + 2KNH_2 \rightleftharpoons Mg(NH_2)_2 + 2K$, the equil. point being far to the right. Subsequent reactions are: $Mg(NH_2)_2 + 2KNH_2 \longrightarrow Mg(NHK)_2 \cdot 2NH_3 + 2K \longrightarrow 2KNH_2 + H_2$. Ca and Al also liberate K; Ca forms $CaNK \cdot 2NH_3$ and Zn forms $Zn(NHK)_2 \cdot 2NH_3$, while Al forms $AlN \cdot NH_3$ + absorbed $KNH_2$. Be forms $BeNNa \cdot 2NH_3$ with $NaNH_2$. Ce, Th and Mn are slightly attacked by fused $KNH_2$ while Hg, Cu, Cd, Tl, Ti, Zr, Ta, Cr, Ni, Pt and Ir are not noticeably attacked. Na gives with fused NaOH a blue color; Mg gives a similar color suggesting the reactions: $Mg + 2\ NaOH \rightleftharpoons Mg(OH)_2 + 2Na$; $Mg(OH)_2 + 2\ NaOH \longrightarrow Mg(OH)_2 + 2\ H_2O$; $2Na + 2\ H_2O \longrightarrow 2\ NaOH + H_2$. Ca and Na appear to give some hydride upon reaction with NaOH.

CA 25, 3134-7

Barium Hydroxide
Friedrich Rusberg and Gustav Clauss
U. S., 1,799,989, April 7

Ba silicate is subjected to fine grinding in the presence of water to cause hydrolyzing of the finely ground material. Cf. CA 24, 5115.

CA 25, 3300-6

Investigation on Corrosion and Factors Governing the Selection of Alloys in the Construction of Equipment for Manuf. of Caustic Soda and Potash
M. V. Pershke and L. Popova
Chimie and Industrie Special No., 232-6, March, 1930

After a brief review of the literature on corrosion of Fe by alkalies, results of corrosion expts. by NaOH and KOH (950 g/l. and 12 g. $Na_2CO_3$ and NaCl) for 6 hrs. at 160-400° are given, showing that, with gray cast Fe the main factor in resistance to corrosion is homogeneity of structure, and compn. is of secondary importance. Addn. of Ni reduces the corrosion, which is completely stopped with 12% or more of Ni. Addn. of Cr is less effective, particularly against action of KOH. Addn. of 6% Ni and 5% Cr is equiv. to 12% Ni. On the whole,

corrosion by KOH is 2.5-3 times as great as that by NaOH. Cu is satisfactory for the piping and fittings, as far as resistance to corrosion is concerned, but is too soft; the most satisfactory alloy was found to be obtained by addn. of 21% Ni to Cu. (Also in J. Chem. Ind. (Moscow) 7, 16-20 (1930)).

CA 25, 3552-3

Heat Content Values for Aqueous Solutions of the Chlorides, Nitrates and Hydroxides of Hydrogen, Lithium and Potassium at 18°
Frederick D. Rossini
Bur. Standards J. Research 6, 791-806 (1931); cf. CA 24, 5209

The existing data on the heats of diln. of HCl, LiCl, NaCl, KCl, $HNO_3$, $LiNO_3$, $KNO_3$, LiOH, NaOH, and KOH are converted to 18°, and a series of values for the concn. range from infinite diln. to about 2 molal are obtained. The extrapolation to infinite diln. is made with the aid of the Debye-Huckel theory of strong electrolytes. The data give values for $\Phi_h - \Phi_h^0$, the relative apparent heat content of the solute, $\bar{H}_2 - \bar{H}_2^0$ the relative partial molal heat content of the solute, the $\bar{H}_1 - \bar{H}_1^0$, the relative partial molal heat content of the $H_2O$. The procedure employed in calcg. the above quantities is given in detail.

CA 25, 3780-6

Removing Sodium Chloride from Concd. NaOH
I. G. Farbenind, A.-G.
Ger., 522,676, November 14, 1928

The concd. NaOH is cooled, cleared and reheated. $Na_2SO_4$ is then added, and the resulting sulfate-chloride mixt. is allowed to settle before removal.

CA 25, 3946-4

Resistance of Chromium Steel Against Alkali Solutions
Albert Kruger
Chem. Ztg. 55, 335 (1931)

Preliminary tests indicate the suitability of vessels, crucibles, etc., made of Cr steel as a substitute for Pt vessels for the analytical detn. of Fe, Al, and Ni, if they are pptd. as hydroxides. Glass or porcelain vessels introduce serious errors under these conditions. Cr steel is also resistant against $H_2O_2$ and $Na_2S$ in alk. solns.

CA 25, 4509-5

Acid-Resisting Metals - A Few Comparative Tests
J. W. McMyn and V. Edge
Chemistry and Industry 50, 474 (1931)

Corrosion rates, as detd. in test tubes, are given for "Staybrite" steel, "Monel" metal, "Batterium" metal and Cu in AcOH, $H_2SO_4$, HCl, NaCl, $Na_2CO_3$, NaOH, NaOCl and $Na_2S$ solns.

CA 25, 4667-2

Caustic Alkalies
J. G. Farbenind A.-G.
Brit., 344,545, December 15, 1928

Concd. caustic alkali solns. contg. at least 200g. caustic alkali per l. are formed by complete causticization of an alkali carbonate such as $Na_2CO_3$ with a suspension of $Sr(OH)_2$ or $Ba(OH)_2$ (the alk. earth carbonate formed is sepd. by a continuous filter, washed with a continuous washing app. and calcined, and the wash liquors and oxide thus obtained are used in continuing the process.) The alkali metal carbonate may be added in solid form to the suspension of the causticizing agent.

CA 25, 4670-1

Barium Hydroxide
Hans Schraube
Ger., 527,033, December 23, 1930

A soln. of BaS is heated with $Al(OH)_3$ while leading an indifferent gas and (or) steam through the mixt. The addn. of a little $Sr(OH)_2$ accelerates the process.

CA 25, 4981-6

Barium Hydroxide
I. G. Farbenind A.-G.
Ger., 526,796, February 9, 1930, Addn. to 519,891 (CA 25, 3446)

The method of 519,891 for producing $Ba(OH)_2$ by oxidizing a BaS soln. at temps. above 50° by air is modified by carrying the oxidation at temps. below 50°, in the presence of polysulfide or dissolved S.

CA 25, 4981-7

Barium Hydroxide and Strontium Hydroxide
Bernhard C. Stuer
U. S., 1,812,250, June 30

A substantially sulfide-free $Ba(OH)_2$ is obtained by treating a 9% hot soln. of BaS with about 20% of $NH_3$, cooling the soln. to effect pptn. of $Ba(OH)_2$ crystals and repeatedly washing the crystals with aqueous $NH_3$ soln. $Sr(OH)_2$ may be similarly obtained. Cf. CA 25, 3134.

CA 25, 5521-2

Alkali Hydroxides or Carbonates and Free Acids from Alkali Metal Salts
A. F. Meyerhofer
Ger., 531,205, October 2, 1923

An alkali-metal salt is treated with $H_2SiF_6$ yielding an alkali fluosilicate and the acid corresponding to the salt. The fluosilicate is decompd. by heat, yielding an alkali fluoride and $SiF_4$. The alkali fluoride is caused to react with an alk. earth hydroxide or carbonate, yielding an alkali hydroxide or carbonate and an alk. earth fluoride. The $SiF_4$ and the alk. earth fluoride react with $H_2SO_4$ to yield $H_2SiF_6$, which is used again.

CA 25, 5611-1

Thermodynamic Study of Sodium Hydroxide
Ei-Ichi Shibata
J. Chem. Soc. Japan 50, 523-32 (1929) cf. CA 22, 2101

The following values were obtained by the use of an elec. cell constructed from $NaOH \cdot H_2O$ and the estn. of vapor pressure: $Na + \frac{1}{2} H_2 + \frac{1}{2} O_2 = NaOH$; $\Delta H_{298} = -100{,}900$ cal. $Na + \frac{1}{2} H_2 + \frac{1}{2} O_2 = NaOH$; $\Delta F_{298} = -90{,}762$ cal. The entropy of NaOH at 25° $S_{298}$ (NaOH) = 17.5 entropy units.

CA 26, 263-1

Fused Caustic Alkali
J. G. Farbenind A.-G.
Ger., 531,799, March 1, 1928

In the continuous prepn. of fused KOH or NaOH, rotary tubes of Ag are used.

CA 26, 645-7

Thermodynamic Study of Potassium Hydroxide
Ei-ichi Shibata, Saburo Oda and Shizuto Furukawa
J. Chem. Soc. Japan 51, 278-88 (1930)

E.m.f. was measured from cells made of crystals of $KOH \cdot nH_2O$ and its satd. soln., K amalgam and HgO/Hg. Cryst. $KOH \cdot 1\frac{1}{2} H_2O$ was formed between 27.3 and 33.4°. 27.3° is a transition point from $KOH \cdot 2 H_2O$ to $KOH \cdot 1\frac{1}{2} H_2O$ and 33.4° from $KOH \cdot 1\frac{1}{2} H_2O$ to $KOH \cdot H_2O$. The vapor pressures of these crystals were also estd.

CA 26, 1169-5

State of Molten Salts
P. Walden
Z. physik. Chem. A157, 389-421 (1931)

. . . .At the m.p. $\lambda \eta\sqrt{M}$, where $\eta$ is the viscosity and $\lambda$ is the equiv. cond., has the value 10.5 for molten $KNO_3$, $NaNO_3$, NaCl, KCl and NaOH, and the picrates in aq. and non-aq. soln. at infinite diln. give the same figure. It is therefore deduced that the molten salts are completely dissocd. . . . .

CA 26, 1401-6

Pure Caustic Soda
Leonardo Cerini
Ger., 537,933, February 10, 1926

Pure NaOH soln. is obtained from colloidal material contg. NaOH waste lye, such as the waste lye from the dialysis process for working up viscose, by dialyzing the lye by using a vegetable fiber membrane which may be previously treated with alkali. NaOH of 90-95% purity is obtained by this process.

CA 26, 1720-4

Modified $NH_3$-soda Process
A Mentzel
Brit., 347,426 (1929)

$NaHCO_3$ converted to NaCN by reaction with C and N and material hydrolyzed with steam to produce NaOH and $NH_3$. Various details of procedure described.

CA 26, 1725-7

Caustic Potash
Bozel-Maletra
Fr., 714,276, July 7, 1930

Pure crystd. KOH · $H_2O$ practically free from NaOH, KCl and KOH · 2 $H_2O$ is obtained by first prepg. KOH · 2 $H_2O$ by cooling filtered potash lyes and transforming the KOH · 2 $H_2O$ to KOH · $H_2O$ by heating to 35° or higher.

CA 26, 1726-6

NaOH and $NH_3$
A. Mentzel
Fr., 38,940 (1930) Addn. to 690,680

Solid $NaHCO_3$ mixed with C, treated with N at high temperature to form NaCN. This treated with steam 400 - 500°C giving NaOH and $NH_3$.

CA 26, 1869-6

The Hydrates of the Oxides and Peroxides of the Alkaline Earths
C. Nogareda
Rev. acad. cienc. Madrid 26, 315-96 (1931)

. . . .The following d.'s were detd: $CaO_2 \cdot 8H_2O$ 1.700, CaO 2.620, $Ca(OH)_2$ 2.237, $Ca(OH)_2 \cdot H_2O$ 1.90, $SrO_2 \cdot 8H_2O$ 1.951, SrO 4.078, $Sr(OH)_2$ 3.305, $Sr(OH)_2 \cdot H_2O$ 2.862, $Sr(OH)_2 \cdot 8H_2O$ 1.860, $BaO_2 \cdot 8H_2O$ 2.291, BaO 5.685, $Ba(OH)_2$ 4.463, $Ba(OH)_2 \cdot H_2O$ 3.743, $Ba(OH)_2 \cdot 8H_2O$ 2.164.

CA 26, 2831-6

Caustic Soda
I. G. Farbenind A.-G.
Fr., 718,046, June 2, 1931

NaOH is obtained as a solid hydrate poor in NaCl by cooling a 50% lye, obtained by evapn. and satd. in NaCl, to 18°, removing the solid NaCl and then continuing to cool to about 10°, when the NaOH seps. and the rest of the NaCl remains in soln.

CA 26, 2917-6

A Thermodynamic Study of Potassium Hydroxide
F. L. Eiichi Shibata, Saburo Oda and Shizuto Furukawa
J. Sci. Hiroshima Univ. 2A, 85-102 (1932)

See CA 26, 645.

CA 26, 2918-2

A Study of the Heat Capacity and Related Thermodynamic Properties of Aqueous Solutions of Lithium Chloride, Hydrochloric Acid and Potassium Hydroxide at 25°
Frank T. Gucker, Jr., and Karl H. Schminke
J. Am. Chem. Soc. 54, 1358-73 (1932)

The adiabatic twin calorimeter method of detg. sp. heats of aq. solns. was improved (CA 22, 1891). The heat capacities of aq. solns. of LiCl, HCl and KOH were detd. at 25° and from 0.01 to 2.5M. The results are correct to about 0.01%. The linear relation between the apparent molal heat capacity of the solute and the square root of the molality is confirmed but there is some doubt as to the validity of extrapolation to infinite diln. (CA 21, 3814; 23, 1562). Partial molal heat capacities of the solute and solvent were also evaluated.

CA 26, 2935-1

Carbonate Content of Volumetric NaOH Solns.
J. E. S. Han and T. Y. Chao
Ind. Eng. Chem., Anal. Ed. 4, 229-32 (1932)

Numerous methods for prepg. NaOH solns. free from $Na_2CO_3$ were tested. Treatment with $Ba(OH)_2$ or Ba salt was found most satisfactory, but Sorensen's method of preparing a 1:1 soln. of NaOH, boiling and allowing to cool slowly results in the pptn. of practically all $Na_2CO_3$ so that by siphoning off the liquid and dilg., very good NaOH soln. can be obtained.

CA 26, 3078-1

Alkali Metal Hydroxides
Max Buchner
U. S., 1,851,418, March 29

Reaction is effected between an alkali metal fluoride and an alkali earth metal hydroxide at a temp. above 80° until the concn. of the soln. retards the reaction and the soln. is sepd. before reaction is completed.

CA 26, 3168-9

Thermodynamic Study of Sodium Hydroxide
F. L. Eiichi Shibata
J. Sci. Hiroshima Univ. Ser. A. 1, 215-28 (1931); cf. CA 26, 645

Cells involving $NaOH \cdot H_2O$ were studied, and vapor pressures detd. For the cell: Na amalgam (0.207%)/satd. $NaOH \cdot H_2O$, HgO/Hg with crystals, $E = 1.58505 - 0.0007202(t-25) + 0.0000205(t-25)^2$; without crystals $E = 1.58350 + 0.0001127(t-25) + 0.00000037(t-25)^2$. $P_v$ for $NaOH \cdot H_2O$ satd. at 25° is 1.72 mm. $NaOH + H_2O = NaOH \cdot H_2O$; $\Delta F_{298} = -2835$ cal., $\Delta H_{298} = -2.9$ kg. cal. $H_2O + nNaOH \cdot H_2O$ = satd. soln.; n = 0.9496, $\Delta F_{298} = -1556$ cal., $\Delta H_{298} = +633$ cal. The last heat of soln. of $NaOH \cdot H_2O$ $\Lambda_s = 2939$ cal. The free energy of formation of NaOH from the elements, $\Delta F_{298} = -90,762$ cal. The heat of formation, $\Delta H_{298} = -102,401$ cal. Entropy, $S(NaOH)_{298} = 12.43$.

CA 26, 3338-1

Caustic Soda
I. G. Farbenind A.-G.
Fr., 719,289, June 20, 1931

Fused anhyd. NaOH is obtained by evapn. under reduced pressure of a com. lye, the pressure being varied continuously or discontinuously during the evapn. in such a manner that the b.p. of the fusion bath (b.p. corresponding to that pressure in each case) approaches the temp. of the commencement of crystn. for the concn. of NaOH in each case but does not fall below that temp.

CA 26, 3338-3

Bases of Carbonates and Acids, by Decomposing Salts with HF
Max Buckner
Ger., 542,614, July 31, 1927

Metal fluorides are heated with water or steam and the resulting HF is caused to react with a salt of the metal whose hydroxide is desired. The acid is removed and the resulting metal fluoride is decompd. by the metal hydroxide formed in the first stage, giving the desired hydroxide which can be converted to carbonate by $CO_2$. Thus, $BaF_2$ is heated with steam to give $Ba(OH)_2$ and HF. The HF is caused to react with NaCl to give NaF and HCl. The HCl is removed and the NaF is caused to react with the $Ba(OH)_2$ to produce $BaF_2$ and NaOH. The NaOH is sepd. and used as such or converted into $Na_2CO_3$, while the $BaF_2$ is used to repeat the process.

CA 26, 3449-8

Reduction of NaOH
P. Villard
Compt. rend. 193, 681-5 (1931)

NaOH and Mn in a current of N or H at 600° (rapidly at 700°) yields Na (KOH behaves similarly); at the same time NaH is volatilized and deposited farther along the tube. Ferromanganese, Cr (at 800°) and W act similarly, as also does Fe in N at 750°. With a little H added to the N Fe yields only NaH; with more, fumes of Na are still produced, but there is no deposit. This is due to water from decompn. of the $Fe_2O_3$ first formed, and explains the bad yield of Gay Lussac and Thenard's process, which would be improved by substituting H by N, when a lower temp. would suffice. Co and Ni at 600-750° cause evolution of Na vapor, but no metal is deposited, and the Co and Ni are not oxidized. Zn has no action. Co and Ni reduce ZnO at 700° and 750°, resp.

CA 26, 3731-8

The Utilization of Natural Glauber Salt II
N. D. Zelinskii, et. al.
J. Chem. Ind. (Moscow)(1932), No. 1, 21-3

By placing a 1.5-2 cm. layer of solid $Na_2SO_4 \cdot 10\ H_2O$ over the Hg electrode in the electrolytic prepn. of NaOH and $H_2SO_4$, higher current efficiencies are attained, since Na is formed instead of $H_2$. Increased temp. also has a favorable effect on the efficiency.

CA 26, 3765-6

Metals that Resist Alkali Corrosion
J. L. Everhart
Chem. Met. Eng. 39, 88 (1932)

General corrosion data are given for 10 metals tested in mixed alkali liquors. Ni and Ni-rich alloys resist NaOH liquors, though cast Fe is usable because of the low cost. Cast Fe and cast steel resist $Na_2CO_3$ liquors. Ni-Cr-Mo alloy is resistant to $NH_4Cl$ liquors. Cast Fe and 18% Cr - 8% Ni alloy resist NaCl-$NH_4OH$ mixtures. Monel metal shows excellent resistance to $CaCl_2$ liquor.

CA 26, 4138-3

Alkali Metal Compounds
A. Mentzel
Fr., 721,875, August 22, 1931

A mixt. of $K_2SO_4$, C and CaO is transformed to KCN by the action of N at a high temp., the KCN being afterward sapond. to produce $K_2CO_3$ or KOH and $NH_3$. The S in the $K_2SO_4$ is transformed to $H_2SO_4$ in known manner and this is combined with the $NH_3$.
Fr., 721,876. NaOH or $Na_2CO_3$ is prepd. in the same way from $Na_2SO_4$.

CA 26, 4139-9

Barium Hydroxide or Hydrate
Serge Wittouck (to International Industrial and Chemical Co., Ltd.)
U. S., 1,861,892

A mixt. contg. C, $BaCO_3$ and silicic acid or Ba silicate is calcined, and the smelt is hydrolyzed. Cf. CA 26, 1723.

CA 26, 4235-1

The Entropies of Inorganic Substances
K. K. Kelley
Bur. Mines, Bull. 350, 63 pp. (1932)

CA 26, 4419-2

The Manufacture of NaOH by the Kiflu Process
A. Wagner
Chem. Fabrik 1932, 173-7

This process is based on the following reactions:

(1) $CaF_2 + 2\ NaCl + SiF_4 + \text{acid} = Na_2SiF_6 + CaCl_2 + \text{acid}$

(2) $Na_2SiF_6 + \text{heat} = 2\ NaF + SiF_4$

(3) $2\ NaF + Ca(OH)_2 = 2\ NaOH + CaF_2$

The $SiF_4$ from (2) and the $CaF_2$ from (3) are returned to reaction (1). The development of the process is outlined and the successive steps are described briefly. A flow-sheet, 3 cuts of app., raw materials and patent references are given.

CA 26, 4577-1

The Resistance of Metals to Corrosion by Acids and Alkalies
W. Kollrepp
J. Inst. Metals 47, 144-5

An account of expts. is given and the mechanism of the resistance is considered.

CA 26, 4577-4

Corrosion of Alloys
Johan Gorrisen
Kgl. Norske Videnskab. Selskab. Forh. 4, 169-71 (1931)

The corrodibility of various Cd-Zn alloys by N NaOH was investigated. As long as the Zn is present as a eutectic, the Cd protects well. If Zn is increased until primary Zn crystals are present, the Cd accelerates corrosion. The O concn. was found of great importance. Investigations made on the corrosion of Cd-Mg alloys in 0.01 N HCl seem to bear out the correctness of Tamman's theory of the resistance limits. Three distinct types of corrosion were shown, corresponding to alloys with more than 50 at.% Cd, to alloys with 20-50 at.% Cd and to alloys with less than 20 at.% Cd.

CA 26, 4918-6

Alkali Hydroxides
A. Mentzel
Fr., 726,211, November 13, 1931

A mixt. of alkali carbonate or bicarbonate and charcoal with the addn. of an alk. earth or Mg compd. is treated with N at a high temperature (about 1000°) and the reaction mass is sapond. at a lower temp. and lixiviated.

CA 26, 4921-3

Potash
Alfred Mentzel
Fr., 724,908, October 21, 1931

KOH or $K_2CO_3$ is obtained by cyaniding the double salt $MgCO_3 \cdot KHCO_3 \cdot 4H_2O$ (obtained by Engel process) and sapong. the product obtained with recovery of $NH_3$.

CA 26, 4921-5

Caustic Soda
Paul Krassa
Fr., 725,549, November 3, 1931

NaOH is obtained by heating to a high temp. a mixture of $Fe_2O_3$ and $NaNO_3$ contg. amorphous $SiO_2$ of high surface development.

CA 26, 4995-7

Soly. of $Na_2CO_3$ and $Na_2SO_4$ in Presence of NaOH at Various Temps.
G. V. Prikhodko
J. Applied Chem. (U.S.S.R.) 5, 31-3 (1932)

Soly. data are given for concns. of NaOH from 5 to 60% and for temps. from 50° to 140°.

CA 26, 4998-6

Chemical Thermodynamics. XII. Activities of Potassium and Sodium in Their Amalgams
Francisco L. E. Shibata
J. Chem. Soc. Japan 52, 352-65 (1931), Cf. CA 26, 645

E.m.fs. of the cells, K-amalgam (concn. = $N_2'$)/concd. KOH soln./K amalgam (concn. = $N_2$), are estd. by varying $N_2'$ from 0.001 to 0.025 mol. at 20, 22.5, 27.5 and 30°. Activities of K and Hg are calcd. at each concn. and temp. The data for Na amalgam obtained by Richards and Conant (cf. CA 16, 1356) are applied to K-amalgam. The temps. at which solns. of K, Na and Ta, resp., become ideal are estd. XIII. Changes of free energies and heat contents in the formation of sodium and potassium amalgams. Ibid. 365-70. From the values of activities of K, Na and Hg and their heat coeffs. the free energy of the reaction and change in heat content accompanied by the differential soln. of K, Na and Hg into amalgam are estd. XIV. Differential dilution of aqueous solutions of sodium hydroxide. Francisco L. E. Shibata and Fusaichi Murata. Ibid 393-403. Cells are constructed from $H_2$(Pt)/ NaOH(0.521-27.63 mol.), HgO/Hg, and the e.m.fs. at each concn. are estd. at 20-30° at 2.5° intervals. From these values, the following consts. (at 25°) are estd.: change of free energy and the heat content resulting from the differential diln. at different concns. $Hg + \frac{1}{2} O_2 = HgO$; $\Delta F_{298} = -13850$ cal., $\Delta H_{298} = -21625$ cal. The entropy of $O_2$ at 25° is discussed and $S\ (\frac{1}{2} O_2)_{298} = 24.55$ is given from the av. of 24.58 obtained in this expt., 24.44 from XV, 24.58 from the estn. of sp. heat and 24.6 from the estn. by Bronsted. XV. Differential dilution of the aqueous solutions of sodium hydroxide. Francisco L. E. Shibata, Yozo Kobayaski and Shizuto Furukawa. Ibid. 404-9. The app. and method are the same as those of preceding expts. except that

NaOH is replaced by KOH. Results are: HgO + $H_2$ = $H_2O$ + Hg; $\Delta F_{298}$ = -42714(-42710) cal., $\Delta H_{298}$ = -46690 (-46645) cal. Hg + $\frac{1}{2}$ $O_2$ = HgO; $\Delta F_{298}$ = -13846 (-13850) cal., $\Delta H_{298}$ = -21580 (-21625) cal. (The values in parentheses are the results obtained from the preceding expt.). By using the entropy value of Hg and HgO in the preceding expt., $\Delta S$ of HgO = -25.94; therefore, S($\frac{1}{2}$ $O_2$) = 16.3 - 17.8 - (-25.94) = 24.44. XVII. Differential solution of sodium hydroxide in its aqueous solutions. F. L. E. Shibata, F. Murata and Y. Toyoda. Ibid. 627-34. Cells were made of Na (amalgam)/NaOH (soln.) HgO/Hg. The concn. of NaOH in the cell varied from dil. soln. to satd. soln. at 25°. From the estn. of e.m.fs. of the cells at different temps., change of free energy on differential soln. of NaOH in water and heat content are estd. The same estns. were made also by the diln. of NaOH of known concns. XVIII. Differential solution of potassium hydroxide in its aqueous solutions. XIX. Differential solution of sodium sulfate in its aqueous solutions. Ibid. 635-9, 639-44. XX. Activity coefficients of potassium hydroxide, sodium hydroxide and sodium sulfate in their concentrated solutions. F. L. E. Shibata and F. Murata. Ibid. 645-50. From the detns. of e.m.f. in cells of the preceding expts. (XVII, XVIII and XIX) and the other data detd., activity coeffs. of concd. solns. of NaOH, KOH and $Na_2SO_4$, resp., are calcd.

CA 26, 4998-8

Thermodynamic Studies of Lithium Hydroxide and Lithium Chloride
Yuji Ueta
J. Chem. Soc. Japan 52, 740-55 (1931)

The e.m.fs. of the reversible cells Li-amalgam/LiOH · $H_2O$, satd. soln., $H_2O$/Hg contg. different amts. of amalgam were detd. at 20°, 25° and 30°. The vapor pressures of the systems satd. solns.-LiOH · $H_2O$ and LiOH · $H_2O$-LiOH at 20-40° were detd. The e.m.fs. of the cells Li-amalgam/LiCl · $H_2O$, satd. soln., HgO/Hg were detd. at different concns. of amalgam at 25°. The vapor pressures of the systems satd. soln.—LiCl · $H_2O$ and LiCl · $H_2O$-LiCl at 15-35° were detd. and the transition point of LiCl · $H_2O$ $\rightleftharpoons$ LiCl · $2H_2O$ was located at 19.10°. Estns. of the heat of soln. of LiOH and LiOH · $H_2O$ in 400 mols. $H_2O$ and the dil. soln. of LiOH · $mH_2O$ were made. From the above data Li + $\frac{1}{2}$ $O_2$ + $\frac{1}{2}$ $H_2$ = LiOH; $\Delta F_{298.1}$ = -105128 cal., $\Delta H$ = -115253 cal. Li + $\frac{1}{2}$ $Cl_2$ = LiCl; $\Delta F_{298.1}$ = -91612 cal. $S_{LiCl}$ = 14.8 cal/deg.

CA 26, 5016-9

The Electrochemical Oxidation of Mo in KOH solns.
M. de Kay Thompson and Albert L. Kaye
Trans. Electrochem. Soc. 62 (11 pp) (1932)

The current efficiencies and electrode potentials were detd. at 25° for the simultaneous electrolytic oxidation of Mo to sol. molybdate and to insol. oxide at c. ds. between 0.005 and 0.4 amp/sq. cm. in KOH solns.

ranging between 0.2 N and 5 N. The c.d.-electrode potential relation for the formation of molybdate and of oxide is shown by curves. At high c.d. and low concns. of KOH, the oxide product consists of a mixt. of greenish $Mo(OH)_4$ and the colloidal blue $Mo_3O_8$. The average valence of the Mo in this mixture was 5.3. The two Mo compds. could not be satisfactorily sepd. for analysis. The current efficiency for molybdate formation, which takes place according to the reaction: $Mo + 8\ OH^-$ (+ 6 Faradays) $= MoO_4^{--} + 4\ H_2O$, increases with increasing concn. and decreasing c.d. The curves showing the relation between electrode potentials at given c.d. and the concn. of KOH are similar to those found for ferromanganese anodes. On the other hand, no min. was found in the curves of current efficiency plotted against concn. of electrolyte, as appears for both ferromanganese and ferrochromium anodes. Results indicate that with increase in c.d. the polarization in the anodic oxidation of Mo to molybdate is greater than the polarization in the oxidation to oxide.

CA 26, 5388-6

The Process for Obtaining Caustic Soda Containing Traces of Sodium Chloride
B. G. Gribanovskii and A. K. Kats
J. Chem. Ind. (Moscow) (1932), No. 5, 20-3

On filtering a NaOH soln. through a layer of $Na_2SO_4$ at 140°, and cooling the filtrate to room temp., NaCl ppts. About 0.12 - 0.25% of the salt remains in soln. The concn. of $Na_2CO_3$ is also reduced.

CA 27, 14-3

Redetermination of Thermal Dissociation Equilibria of Inorganic Compounds. III. Determination of Dissociation Equilibrium of Calcium Hydroxide by Means of High-Temperature Vacuum Balance
S. Tamaru and K. Siomi
Z. Physik. Chem. A161, 421-6 (1932), cf. CA 26, 3171

The dissocn. pressure was detd. at 405-500°.

CA 27, 170-1

"Ammonia - Soda Process for Producing NaOH and $NH_3$"
F. Bartling
U. S., 1,877,489, September 13

$CO_2$ is introduced into a soln. contg. NaCl and $NH_3$, whereby $NaHCO_3$ is pptd. and $NH_4Cl$ is obtained in soln; the pptd. $NaHCO_3$ is treated in presence of C with N at an elevated temp. by which NaCN is produced, and the NaCN is caused to react with steam at an elevated temp. to form $NH_3$ and NaOH; the evolved $NH_3$ is returned and the $NH_4Cl$ soln., whereby the $NH_4Cl$ is obtained in solid form. An arrangement of app. is described.

CA 27, 378-2

Alkali Hydroxides
Mentzel
Ger., 555,929, March 3, 1931. Addn. to 555,168 (CA 26, 5181)

$BaCO_3$ is used as the added causticizing agent in the process of Ger., 555,168. The soln. obtained by extg. the reaction product with water may be treated with alkali carbonate in an amt. equiv. to its $Ba(OH)_2$ content. An example is given.

CA 27, 476-5

The Use of KOH as a Fusion Agent
P. F. Thompson
Soc. Chem. Ind. Victoria, Proc. 32, 699-704 (1932)

Fusion with KOH in Ni crucible has been found advantageous for detg. S and As in pyritic ores and mats, analyzing W ores, Sn concentrates and chromite.

CA 27, 570-4

Alkali Hydroxides
Ring Gesellschaft Chemische Unternehmungen M. B. H.
Ger., 557,661, February 10, 1927

Alkali hydroxides are prepd. by treating alkali fluorides with KOH in stages, the liquid being sepd. from the solid material at each stage before the reaction reaches a condition of equil. Excess of alkali fluoride is used.

CA 27, 570-4

Alkali Hydroxides
Curtin
Ger., 557,660, March 22, 1928

An aq. soln. of an alkali sulfide is added to an aq. suspension of PbO and the mixture stirred vigorously till no sol. sulfide remains.

CA 27, 573-3

Calcined or Caustic Soda and Ammonium Chloride from Coal and Common Salt
Mentzel
Ger., 557,620, May 20, 1930

The above products are obtained by the following processes: (1) coal (or lignite) is distd. and partly hydrogenated. (2) The $CO_2$ from (1)

and NaCl are subjected to the ammonia - soda process to give $NaHCO_3$. (3) The $NaHCO_3$ is cyanided by N and the C residue from (1). The cyanide from (3) is treated with steam to give calcined soda or NaOH and $NH_3$. (5) The $NH_3$ from (4) is treated with the lye from (2) to give $NH_4Cl$. Cf. CA 26, 3338.

CA 27, 573-3

"NaOH, $NH_4Cl$, $NaNO_3$, and HCl from NaCl"
Mentzel
Ger., 557,619, August 16, 1930

The above obtained by following processes: (1) solid $NaHCO_3$ obtained during the $NH_3$-soda process is heated with C and N $\longrightarrow$ NaCN. (2) NaCN + $\longrightarrow$ water vapor, low heat $\longrightarrow$ $NH_3$ + NaOH. (3) $NH_3$(2) $\longrightarrow$ $NH_4Cl$. (4) Also, $NH_3$(2) oxidized $\longrightarrow$ N oxides $\longrightarrow$ $HNO_3$ + NaCl $\longrightarrow$ $NaNO_3$ + HCl.

CA 27, 813-6

Caustic Potash
Soc. D'Etudes pour la Fabrication et L'Emploi des Engrais Chim.
(Hackspill and Rollet, inventors)
Ger., 562,005, February 13, 1930

KCl and $H_3BO_3$ are reacted in such proportions as to give $K_2O \cdot 5\ B_2O_3$ and HCl. The reaction may be effected under dry or wet conditions, in the latter case in the presence of $NH_3$. The $K_2O \cdot 5\ B_2O_3$ is then treated in aq. soln. or suspension with $Ca(OH)_2$, giving KOH and a ppt. of $CaB_2O_4$. This reaction may be effected in stages, with intermediate filtration and diln. The pptd. $CaB_2O_4$ may be treated with $NH_4Cl$ to give $H_3BO_3$, $NH_3$ and $CaCl_2$.

CA 27, 815-6

Concentrating Caustic Solutions such as Sodium Hydroxide
Wilson (to Standard Oil Co. of Ind.)
U. S., 1,883,211, October 18

The soln. is heated to about 400° in a closed conduit and then introduced into a separator chamber and treated with an inert gas such as N for further removal of water. App. is described.

CA 27, 815-8

Potassium Hydroxide and Ammonia
Mentzel
Ger., 558,236, October 25, 1930

To recover KOH from $MgCO_3 \cdot KHCO_3 \cdot 4\ H_2O$, the latter is mixed with C and heated in N, and the resulting cyanides are decompd. with steam to give the corresponding hydroxides and $NH_3$.

CA 27, 885-9

"The Solubility of $Ba(OH)_2$ in Dilute Solutions of NaOH"
Neale and Stringfellow
Trans. Faraday Soc. 28, 765-6 (1932)

Solid $Ba(OH)_2$ and solns. of NaOH were agitated over night at 25° ± 0.05. The concn. of $Ba(OH)_2$ was calcd. from the change in alky. In the following results the concn. of NaOH in equivs./l. is given first and the soly. of $Ba(OH)_2$ in equivs./l. follows: 0, 0.546; 0.4417, 0.3052; 0.6135, 0.2445; 0.9177, 0.1727; 1.230, 0.1211; 1.837, 0.084.

CA 27, 886-8

Vapor Tension Over Aqueous Solutions of KOH
Yozo Kobayashi
J. Sci. Hiroshima Univ., Ser. A, 2, 269-74 (1932)

The vapor pressure of KOH solns. was calcd. as a function of molality by using the data obtained in e.m.f. studies. Cf. CA 26, 4998.

CA 27, 1101-8

Caustic Alkalies
Ring Ges. Chemischer Unternehmungen M. B. H.
Ger., 561,623, July 6, 1927

Caustic alkalies are prepd. by treating alkali fluorides obtained by the thermic decompn. of complex alkali fluorides with $Ca(OH)_2$. The decompn. of the complex fluoride takes place in the complete absence of water or water vapor and in vacuo, to give vaporous alkali fluoride. If water is unavoidably present, CaO or dry $Ca(OH)_2$ is used. In the example, $Na_2SiF_6$ is decomposed, giving pure NaF, which with $Ca(OH)_2$ gives NaOH.

CA 27, 1102-3

Alkali Metal Hydroxides
Ring Ges. Chemischer Unternehmungen M. G. H.
Ger., 561,622, May 20, 1926

Water-sol. hydroxides of the alkali metals are prepd. by treating solid hydroxides of metals forming insol. fluorides, with alkali fluorides in the presence of water. Thus NaF, KF, etc., are treated with solid hydroxides of Ca, Sr, Ba or Mg in the presence of water to give NaOH, KOH, etc. Cf. CA 27, 570.

CA 27, 1102-4

Alkali Hydroxides
Mentzel
Ger., 561,624, January 17, 1931

A cyanide mass obtained by heating an alkali-coal mixt. in the presence of N is treated with steam. The cyanide mass is spread out in thin layers to facilitate the action of the steam and the $CO_2$ formed is rapidly removed to avoid formation of alkali carbonate. Examples are given. Cf. CA 27, 378.

CA 27, 1457-5

Drying Alkali Hydroxides by Treatment with Alkali Oxides
Deutsche Gold-und Silber-Scheideanstalt Vorm. Roessler
Ger., 567,445, August 22, 1930

CA 27, 1460-3

Caustic Soda
Pritchard
U. S., 1,888,886, November 22

For producing NaOH solns. and solid NaOH therefrom of a high degree of purity, concd. NaOH liquors or solns. are treated with $Na_2SO_4$ or a reagent such as $H_2SO_4$ which will increase the amount of $Na_2SO_4$ in the liquors or solns. to such an extent that the major portion of the NaCl originally present is pptd.

CA 27, 1721-6

Barium Hydroxide and Polysulfides
I. G. Farbenindustrie A.-G.
Brit., 365,198, October 21, 1929

The partial oxidation of Ba sulfide liquors with production of $Ba(OH)_2$ and Ba polysulfides is effected by air or other O-contg. gas at temps. exceeding 50°, e.g., 90-95°. The hydroxide seps. out on cooling, and the mother liquors may be returned to the process, e.g., they may be used to dissolve crude BaS and oxidation may be then effected at 60°.

CA 27, 1721-7

Barium Hydroxide and Polysulfides
I. G. Farbenindustrie A.-G.
Brit., 365,651, October 25, 1930. Addn. to 365,198.

In a modification of the process of 365,198, a soln. of BaS is subjected to oxidation by air or gases rich in O in the presence of polysulfides or dissolved S at temps. not exceeding 50°. Increased pressure may be used. In examples $BaS_3$ or the filtrate from a prior operation is added to the soln. prior to oxidation with air or O.

CA 27, 1996-9

Alkali Hydroxides and Carbonates
Ring Ges. Chem. Unternehmungen M. B. H.
Ger., 568,207, April 9, 1926

An alkali fluosilicate is treated with $NH_3$ in known manner to produce an alkali fluoride, $NH_4F$ and $SiO_2$. The mixed fluorides are treated with an alk. earth hydroxide or carbonate, giving an alkali hydroxide or carbonate, an alk. earth fluoride, and $NH_3$ for use in the process. The alk. earth fluoride and $SiO_2$ are used to make alk. fluosilicate. Other complex alk. fluorides may replace the fluosilicate. Cf. CA 27, 1102.

CA 27, 1998-4

Barium Hydroxide
International Industrial and Chem. Co., Ltd.
Brit., 366,169, February 17, 1930. See U. S., 1,861,892 (CA 26, 4139)

CA 27, 1999-3

Caustic Soda
I. G. Farbenind A.-G.
Brit., 366,404, June 15, 1931. See Fr., 718,046 (CA 26, 2831)

CA 27, 2078-7

Preparation and Crystal Structure of Lithium Hydroxide
Theodor Ernst
Z. Physik. Chem. B20, 65-88 (1933). See CA 26, 3711

CA 27, 2087-9

The Heat Capacity and Related Thermodynamic Properties of Aqueous Solutions. II. Lithium and Sodium Hydroxides at 25°
F. T. Gucker and K. H. Schminke
J. Am. Chem. Soc. 55, 1013-19 (1933) Cf. CA 26, 2918

The previous method was used to obtain the sp. heats of aq. solns. of LiOH and NaOH at 25° from 0.04 M to over 2 M. Apparent molal heat capacity of the solute was calcd. Equations are given for the apparent and partial molal heat capacity of the solute as well as the relative partial molal heat capacity of the solvent. It is possible to calc. the heat capacity of these solns. with great precision at any concn. in the range studied by means of these equations.

CA 27, 2257-7

Caustic Soda
I. G. Farbenind A.-G.
Brit., 369,124, November 4, 1930

Anhyd. NaOH is produced from lyes of tech. concn. by evapn. under reduced pressure, the vacuum being so varied during evapn. that the b.p. of the melt approaches but does not fall below the temp. of incipient crystn.

CA 27, 2384-9

Removal of Salt from Caustic Soda Produced by Diaphragm Cells
J. H. Hubel and L. E. Sweetland
Can. Chem. Met. 17, 52, (1933)

A new process is based on the formation of a triple salt contg. NaCl, $Na_2SO_4$ and NaOH, when $Na_2SO_4$ in the required quantity is added to 106° Tw. caustic liquors from the vacuum effects. Approx. 50 g. of salt cake per l. of this liquor is added, the mixture agitated and settled in a Dorr-type thickener or sepd. on an Oliver-type filter. The NaCl content may be reduced to 0.2% on the fused basis. The mol. formula of the triple salt appears to be $4\ NaOH \cdot 4\ NaCl \cdot 5\ Na_2SO_4$. This process of producing low-chloride NaOH from diaphragm-cell caustic soda is believed cheaper than any method so far devised.

CA 27, 2768-5

Caustic Soda
I. G. Farbenind A.-G. (Karl Staib)
Ger., 567,897, November 5, 1930

CA 27, 2906-6

Prepn. of NaOH Solns. of Low Carbonate Content by Centrifugation
N. Allen and G. W. Low, Jr.
Ind. Eng. Chem., Anal. Ed. 5, 192 (1933)

The use of the centrifuge tube in connection with the "oily alkali" method of Sorensen serves to give an unusually low carbonate content with a saving of time. "Samples of the oily alkali were prepared by dissolving 50 grams of pellet NaOH in 50 ml. of $CO_2$-free $H_2O$. After cooling, each lot was transferred to a Pyrex centrifuge tube, made from a 125-ml. Erlenmeyer flask by rounding out the base and blowing out an opening to fit a No. 2 rubber stopper. The neck of the flask was drawn off and a tube 5 cm. long and 0.8 cm. i.d. sealed on. Centrifuging for 30 min. at 2200-2300 r.p.m. gave absolutely clear solns. with the undissolved carbonate and alkali tightly packed in the bottom."

CA 27, 3041-5

Alkali Hydroxides
I. G. Farbenind A.-G.
Ger., 573,430, December 16, 1928

Concd. alkali hydroxide solns. are manufd. by treating alkali carbonates with SrO in the presence of an amount of water insufficient to dissolve all the SrO as $Sr(OH)_2$.

CA 27, 3041-7

Dehydrating Caustic Alkali Solutions
C. E. Miller (to Champion Fibre Co.)
U. S., 1,899,627, February 28

Evapn. is effected by direct contact exposure to burning H.

CA 27, 3298-7

Soda and Potassium Hydroxide
Thorssell
U. S., 1,903,073, March 28

In producing soda and KOH while simultaneously obtaining $NH_4Cl$ from sylvinitic crude K salts, $NH_3$ and $CO_2$, an alk. earth sulfate such as $SrSO_4$ is cyclically used in a process including the successive steps: (1) a soln. contg. $NH_4Cl$ and $NH_4HCO_3$ obtained in carrying out the process is stirred up with alk. earth sulfate also obtained during the process and the alk. earth carbonate formed is sepd.; (2) the mother liquor from (1) is stirred up with crude sylvinitic K salt

and $NH_3$ is added, whereupon the resulting ppt. consisting of glaserite and KCl is sepd. and decompd. with cold water to $K_2SO_4$; (3) the mother liquors from (2) are combined and the free $NH_3$ is removed, whereupon the mother liquors are cooled to sep. part of their $NH_4Cl$ content; (4) the removing mother liquor is worked up into $NaHCO_3$ and soda according to the ammonia-soda process, whereby the soln. contg. the $NH_4Cl$ and $NH_4HCO_3$ employed in 1 is obtained; (5) the alk. earth carbonate obtained from 1 is converted into oxide and hydroxide and decompd. in water with the $K_2SO_4$ from 2, whereby a soln. of KOH and alk. earth sulfate is obtained, and finally the sepd. alk. earth sulfate is treated, as in 1, and KOH is obtained from the soln. by evapn.

CA 27, 3565-1

Dehydrating Alkali Hydroxides
Deutsche Gold-und-Silber - Scheideanstalt Vorm. Roessler
Brit., 373,511, May 26, 1932. See Fr., 723,031 (CA 26, 4138)

CA 27, 3787-2

Anhydrous Caustic Soda
Lynn and Miller (to Pittsburgh Plate Glass Co.)
U. S., 1,907,988, May 9

For sepg. anhydrous NaOH from an aq. soln., water is evapd. and crystn. simultaneously effected under a vacuum of over 16 in. of Hg and the crystals formed are sepd. from mother liquor.

CA 27, 3787-2

Soda Ash
Lynn (to Pittsburgh Plate Glass Co.)
U. S., 1,907,987, May 9

For prepg. dense soda ash suitable for use in glass manuf. there is first formed a slurry of $Na_2CO_3 \cdot H_2O$ crystals in satd. soln. and the temp. of the slurry is raised above the transition temp. between $Na_2CO_3 \cdot H_2O$ and anhyd. $Na_2CO_3$ under the pressure necessary at such temps., and the deposited anhyd. product is sepd.

CA 27, 3870-9

Electrical Conductivity of Aqueous Solutions of Sodium and Potassium Hydroxides and the Limiting Mobility of the Hydroxide Ion at 25°
G. H. Jeffery and A. I. Vogel
Phil. Mag. 15, 395-408 (1933)

The conductivities of aq. solns. of NaOH and KOH were detd. at 25° in pyrex cells. A correction for the solvent cond. was applied. The

limiting cond. for NaOH is 261.5, for KOH, 285.5. The limiting mobility of the OH ion is 211.9.

CA 27, 4354-1

Caustic Alkali
Elektro-Chemische Fabriken G. M. b. H.
Ger., 573,795, April 6, 1933

The alkalies are prepd. by following stages: (a) Complex alkali fluorides thermally decompd. with exclusion of $H_2O$, preferably in vacuo to give fluoride (b) the alkali fluoride (a) is treated with dry $Ca(OH)_2$ in presence of water under raised temp., to give caustic alkali and $CaF_2$; (c) the volatilized fluorides from (a) are led into soln. at stage (b) while still hot, a small amt. of acid being present as contact agent.

CA 27, 4358-7

Caustic Soda
Elektrochemische Fabriken G. M. B. H.
Ger., 572,895, Mar. 24, 1933

A continuous process for obtaining NaOH: (a) HCl + mixt. of $CaF_2$, $SiO_2$ and NaF, the $CaF_2$ obtained from (d), and $SiO_2$ and NaF from (b); (b) $Na_2SiF_6$ from stage (a) is treated with $NH_4OH$ from stage (e); (c) the $NH_4F$ from stage (b) is treated with NaCl to give NaF and $NH_4Cl$; (d) the NaF from (c) is causticized with $Ca(OH)_2$ to give NaOH and $CaF_2$; (e) the $NH_4Cl$ of (c) is also treated with $Ca(OH)_2$ to give $NH_4OH$ for use in stage (b).

CA 27, 5158-4

Caustic Soda
Paul Krassa
U. S., 1,922,591, Aug. 15; Brit., 391,462, April 28, 1933

See Fr., 725,549 (CA 26, 4921)

CA 27, 5486-4

The Preparation of NaOH from Sodium Sulfate by a Cyclic Process with Barium Hydroxide
Losev and Nosenko
J. Chem. Ind. (Moscow) 1933 No. 4, 51-3

BaS hydrolyses best when a 0.05 N soln. is boiled. About 50% hydrolysis occurs, and the percentage decreases as the BaS concn. is increased.

If 3% excess solid $Ba(OH)_2$ is added to a boiling 30% $Na_2SO_4$ soln. with stirring, 75% yields of NaOH result.

CA 27, 5487-6

Chemicals Used for Cleaning Metals
Standards Committee of the Electrodepositors' Tech. Soc.
J. Electrodepositors' Tech. Soc. 8, Preprint 3, 10-12 (1933)

Since exact specifications are not required for chemicals used for cleaning metals, general specifications for the following compds. are given: NaOH, soda ash, Na silicate, Na phosphate, KOH, $K_2CO_3$, $CCl_4$ and $C_2HCl_3$.

CA 27, 5627-7

Thermodynamic Studies of Lithium Hydroxide and Lithium Chloride
Yuji Ueda
Science Repts. Tohoku Imp. Univ., First Ser. 22, 448-74 (1933)
(in English) - See CA 26, 4998

CA 27, 5905-4

Caustic Soda
Elktrochemische Fabriken G. M. B. H.
Ger. 576,963, May 19, 1933

NaOH is produced from HCl, $Ca(OH)_2$ and NaCl by the following processes:

(a) $HCl + CaF_2 + SiO_2 + NaCl \longrightarrow H_2O + Na_2SiF_6 + CaCl_2$

(b) $Na_2SiF_6 \xrightarrow{\text{heat}} SiF_4 + NaF$

(c) $SiF_4$(b)$+NH_4Cl \longrightarrow HCl + SiO_2 + (NH_4)_2SiF_6$

(d) $(NH_4)_2SiF_6 + SiO_2 + HCl + NH_4OH \longrightarrow SiO_2 + NH_4F + NH_4Cl$

(e) $NH_4F$ (d) $+ NaCl + NH_4Cl \longrightarrow NaF + NH_4Cl$

(f) $NH_4Cl + Ca(OH)_2 \longrightarrow NH_4OH + CaCl_2$

and NaF (b, and e) $+ Ca(OH)_2 \longrightarrow NaOH + CaF_2$

Cf. CA 27, 4354

CA 28, 38-5

The Thermal Expansion of Certain Crystals with Layer Lattices
Helen D. Megaw
Proc. Roy. Soc. (London) A142, 198-214 (1933)

The expansion perpendicular to the cleavage plane of mica (phlogopite) has been detd., and complete detns. have been made of the thermal expansion of brucite, hydrargillite and $Ca(OH)_2$, by measuring with x-rays the change in lattice spacings between 0° and 100°. The hydroxides show marked anisotropy, the expansion coeff. perpendicular to the layer being greater than those in the layer.

CA 28, 421-2

Alkali Lye
Akt.-Ges. fur Zellstoff-und Papierfabrikation and Erich Bayer.
Ger. 577,607, June 2, 1933

Foreign metals removed from alkali lye by treatment with alkali amalgam. The lye may be electrolyzed for this purpose with Hg or amalgam as the cathode.

CA 28, 588-1

Purifying NaOH Solutions
Harold M. Broadhurst and Imperial Chem. Ind., Ltd.
British 396,456

Aq. NaOH solns. are freed from their sulfate content by treatment with $CO_2$ or salt(s) of $H_2CO_3$ and sepn. of the ppt., contg. sulfate and carbonate, from the clear liquor. Thus, the soln. may be passed slowly through a filter bed comprising $Na_2CO_3$ and (or) $CaCO_3$.

CA 28, 862-9

Alkali Hydroxides
No Author
Societa Italiana Potassa
(Fr. 751,693, September 7, 1933)

Silicates such as leucite treated with steam at high temp. to form alkali hydroxides, steam being condensed and re-evapd. to sep. the hydroxides and is used again.

CA 28, 865-1

Potash
Alfred Mentzel
Ger. 582,504, August 16, 1933

$K_2CO_3$ or KOH prepd. by heating $K_2SO_4$ with C and treating the heated mixt. with steam and $CO_2$. The product is heated with N to give KCN. This is then treated with steam to give $NH_3$, KOH, and $K_2CO_3$, the latter compds. being leached out of the reaction mass.

CA 28, 865-4

Caustic Soda
Walter Zisch, inventor
Elektrochemische Fabriken G. M. B. H.
Ger. 578,792, June 17, 1933, Addn. to 572,895

In preparing NaOH by the continuous process described in 572,895, the $Na_2SiF_6$ is replaced by $BaSiF_6$. Process is as follows: (a) $CaF_2$, $SiO_2$, and BaF allowed to react to give $BaSiF_6$, $CaCl_2$ and water; (b) $BaSiF_6$ treated with $NH_4OH$ to give $NH_4F$, $BaF_2$, $SiO_2$, and water; (c) NaCl treated with $NH_4F$ to give NaF and $NH_4Cl$; (d) NaF treated with $Ca(OH)_2$ to give NaOH and $CaF_2$; (e) $NH_4Cl$ treated with $Ca(OH)_2$ to give $NH_4OH$ and $CaCl_2$.

CA 28, 1145-6

Caustic Lyes
I. G. Farbenind A.-G
Fr. 751,312, August 31, 1933

Alk. caustic lyes are made by decomposing amalgams by a counter current of water, e.g., in a tower filled with coke, charcoal, Fe, Fe-Ni or Cr in small pieces.

CA 28, 1149-9

Soda and Ammonia
Alfred Mentzel
Ger. 583,396, September 2, 1933

Addn. to 582,504 (CA 28, 865-1). The process of 582,504 for producing $K_2CC_3$ and $NH_3$ from $K_2SO_4$ is applied to $Na_2SO_4$. Thus $Na_2SO_4$ is heated with C, steam and N to give NaCN. This is then treated with steam to give $Na_2CO_3$, $NH_3$, and NaOH.

CA 28, 1481-3

Caustic Soda
Paul Krassa
Ger. 586,972, October 28, 1933

NaOH prepd. by action of $Fe_2O_3$ on $NaNO_3$ at high temps. in presence of air and water vapor and amorphous $SiO_2$. Yields 80-90% are given.

CA 28, 1893-9

A Ni Vessel for Storing Standard Caustic Alkali Solutions
Edwin C. Richellato
Analyst 59, 104 (1934)

Tenth-normal NaOH kept in a Ni bottle remains clear and with unchanged concn.

CA 28, 2135-3

Purifying Caustic Soda Solution
Harry Bender
U. S. 1,944,630, January 23

A salt of the compn. $NaOH \cdot NaCl \cdot Na_2SO_4$ is crystalized from a solution containing NaOH and NaCl by adding $Na_2SO_4$.

CA 28, 2250-9

Rate of Absorption of Gases by Liquids
R. C. Brimley
Chemistry and Industry 1933, 472-3

The rate of soln. of $CO_2$ in $H_2O$ or aq. NaOH controlled by low rate of diffusion of $CO_2$ through the surface layer of the liquid and varies with age of surface.

CA 28, 2474-2

Obtaining Alkalies from Silicates
Filix Jourdan
Brit. 401,567, November 16, 1933

In treatment of silicates, e.g., leucite, with wet steam at high temp. to obtain alkali hydroxides, the silicate, which may be mixed with substances facilitating the reaction, e.g., $Ca(OH)_2$ is charged into the upper portion of an autoclave the lower portion of which contains $H_2O$, the steam produced being condensed after attacking the silicate and the $H_2O$ then evapd. and used again, the cycle being repeated until all the alkali has been extd. or the condensed liquid satd.

CA 28, 2477-6

Friable Caustic Soda
John W. Koenders (to Dow Chem. Co.)
U. S. 1,946,863, February 13

Solid NaOH having a fibrous cryst. structure, the crystals of which exhibit a preferred orientation and possess a definite fiber axis as shown by an x-ray diffraction pattern, and which is softer and more easily crushed than the ordinary product, is prepd. by filling molten NaOH into a container such as a sheet iron drum to which a small amount of an oil such as paraffin oil or a heavy motor oil is added prior to introducing the molten NaOH.

CA 28, 2856-3

Alkali and Ammonium Compounds
Friedrich Bartling
U. S. 1,947,671, February 20

An alkali sulfate such as $Na_2SO_4$ is heated with lime and carbon in an atm. of N; the resulting product is treated with steam to produce an alkali compd. such as NaOH, a S compd. and $NH_3$; the S compd. is converted. $H_2SO_4$ and the $NH_3$ is absorbed in the $H_2SO_4$ to produce $NH_4$ sulfate.

CA 28, 2858-1

Caustic Soda
I. G. Farbenind A.-G (Walter Schmid)
Ger. 535,951, January 10, 1934 (Cl. 121.15)

See Fr. 718,046 (CA 26, 2831)

CA 28, 2976-1

Conductivities of NaOH and KOH Solutions at Elevated Temperatures
P. M. Korotkov and N. K. Sokolov
J. Gen. Chem. (USSR) 3, 670-8 (1933)

Sp. conduct. (in $ohms^{-1}$) of KOH and NaOH solutions carefully prepared from metallic K and Na are as follows: NaOH at 54.8, 63.7, and 77.0°; resp.: 14.2N, 0.517, - , 0.883; 9.9N, 0.635, - , 0.985; 9.0N, - , 0.792, 1.000; 7.9N, 0.706, - , 1.021; 7.0N, 0.723, 0.837, 1.019; 6.2N, 0.727, 0.824, 1.010; 4.4N, 0.695, 0.785, 0.928; KOH at same temperatures: 10.6N, 0.928, 1.058, 1.264; 9.2N, 0.950, 1.108, 1.312; 8.8N, 1.006, 1.127, 1.324; 7.4N, 1.016, 1.137, 1.331; 6.9N, 1.014, 1.130, 1.320; 6.1N, 1.004, 1.115, 1.291; 3.8N, 0.853, 0.937, 1.078. Expts. show that concns. of NaOH and KOH correspond to maximum cond. vary with temp. The concns. (in % by wt.) and max. conduct. at 18°, 50°, 55°, 64°, 77°, and 100° are, resp: NaOH: 13.8, 4.762; 19.7, 1.476; 20.5, 1.370; 21.5, 1.190; 23.0, 0.980; 27.5, 0.708; KOH: 27.2, 1.84; - , - ,; 31.5, 0.98; 32.0, 0.875; 33.0, 0.75; - , - .

CA 28, 3193-5

Converting Alkali Sulfates to Hydroxides or Carbonates
Gyula Zorkoczy and Vilmos Weisz
Hung., 108,039, Jan. 15, 1934

Sulfates are reduced to sulfides and these decompd. by superheated steam or a mixt. of superheated steam and $CO_2$.

CA 28, 3194-3

Caustic Potash and Oxalic Acid
Rudolph Koe[illegible]p and Co. Chemische Fabrik A.-G.
Fr., 759,216, Jan. 31, 1934

$K_2SO_4$ is treated with an alk. earth formate to form HCOOK which is converted to K oxalate by heating and this changed to KOH and alk. earth oxalate. The KOH lye is sepd. and the oxalate treated with $H_2SO_4$ to obtain oxalic acid.

CA 28, 3700-7

Exp. in Manufacture of Alkali Resistant Cast-Iron Kettles
E. P. Babich
Khimicheskoe Mashinostroenie 1933 No. 7, 9-15

Admixts. which displace C in iron, such as Si, P and Ni harm its alkali resistivity. On the contrary, elements such as Mn, Cr, S, W and Mo which assist in retaining the C in a combined state, are beneficial when used in a definite quantity.

CA 28, 3970-5

Thermodynamics of Aqueous NaOH Solns. from EMF Measurements
Herbert S. Harned and John C. Hecker
J. Am. Chem. Soc. 55, 4838-49 (1933)

With measurements of e.m.f. of the cells $H_2/NaOH(m)/Na_xHg/NaOH(0.05)/H_2$, the work of Harned (CA 19, 1365) is extended to temps. ranging from $0^\circ$ to $35^\circ$ at $5^\circ$ intervals. From these data are calcd. activity coeffs., relative partial molal heat contents and heat capacities for NaOH. Calcd. values agree well with calorimetric data. An equation is developed for extrapolation of molal heat content.

CA 28, 4188-2

Anhydrous Fused Caustic Soda
Karl Staib (to I. G. Farbenind A.-G.)
U. S., 1,956,138, April 24

A lye of "technical concn." is heated, so as to maintain it continuously in boiling condition, first under a pressure of about 70 mm. Hg until a concn. of about 80% is reached, then under an increased pressure of about 520-600 mm. Hg until a concn. of about 91% NaOH is reached, and finally under a reduced pressure of about 70 mm. Hg until all the water contained in the melt is removed.

CA 28, 4325-3

Preparation of Caustic Soda Solns. Free from Carbonate
W. Stahl
Z. anal. Chem. 97, 86-9 (1934)

An adaptation of F. W. Kuster's method of allowing water vapor to react with Na under a bell jar provides 2 distinct improvements: (1) the water in the app. is heated to 35-40° by means of an incandescent elec. lamp and (2) the NaOH soln. that forms first is discarded. 25 g. of Na can be converted into NaOH soln. in 12 hrs. The Na is placed in a perforated cone over $CO_2$-free water. $CO_2$ cannot enter the app. during the expt. because of a seal of NaOH soln. In about 2 hrs. NaOH soln. begins to trickle through the cone and after some of it has run off, a dish is pushed beneath the cone to collect the drops.

CA 28, 4844-7

Concentrating Sodium Hydroxide Solutions
Robert B. MacMullin (to Mathieson Alkali Works)
U. S., 1,961,590, June 5

$NH_3$ is added to an aq. soln. contg. over 20% NaOH and the soln. is sepd. into 2 layers, the lower of which contains a higher concn. of NaOH than the original soln., at a temp. of above 35° (suitably about 60°).

CA 28, 5719-5

Ni Vessel for Storing Std. Alkali Hydroxide Solns.
E. C. Righellato
Analyst 59, 104 (1934)

CA 28, 5938-2

Caustic Potash
Bozel-Maletra Soc. Industrielle de Produits Chimiques
Ger., 599,422, July 2, 1934 (Cl. 121.15)

See Fr., 714,276 (CA 26, 1725)

CA 28, 6359-5

The "Induced" Solubility of Ferric Hydroxide and Several Other Hydroxides in Caustic Solutions in the Presence of Chromium Hydroxide
Hedwig Knoche
Kolloid-Z. 68, 37-41 (1934)

Bivalent Co, Cu, Mn, Ni, Cd, Mg and trivalent Tl hydroxides show an induced soly. in alkali solns. in presence of Cr. Co, Ni, and Mg solns. with Cr become turbid rapidly; Fe, Tl, Cu, Cd, and Mn remain clear, showing some chromate formation. In all cases KOH has a higher dissolving power than NaOH on account of the aging effect of NaOH and NaCl. Fe and Tl hydroxides have highest solubility and are the only ones with soly. products smaller than that of $Cr(OH)_3$. Dil. $Cr(OH)_3$ sols. peptize Fe, Tl, Mn, Cu, and Cd hydroxides but not Mg, Co, or Ni hydroxides. Al and Zn hydroxides are neither dissolved nor peptized by caustic $Cr(OH)_3$ liquors.

CA 28, 7189-8

The Properties of Calcium Hydroxide I
D. G. R. Bonnell
J. Soc. Chem. Ind. 53, 279-82 T (1934)

The relation between the properties of $Ca(OH)_2$ and the method of prepn. from CaO was studied. "The results show that the phys. properties of the hydroxide depend, to a great extent, on the procedure adopted in the hydration of the oxide. The probable factors which bring about these variations in phys. properties are discussed."

CA 29, 13-3

The Enthalpy Concentration Chart - A Useful Device for Chemical Engineering Calculations
Warren Z. McCabe
Trans. Am. Inst. Chem. Engrs. Nov. 1934, (preprint) 34 pp.
Merkel (Z. Ver. Deut. Ing. 72, 109 (1928); Z. Ges. Kalte - Ind. 35 130 (1928); CA 23, 3281; Merkel and Bosnjakovic, Diagramme and Tabellen zur Berechnung Des Absorptions - Kaltemaschinen"; CA 23, 3760

Emphasized the use of a chart for binary solns. which combines in one diagram the thermal properties of a soln., simplifies the heat-balance

calcns., and insures thermodynamic consistency. Merkel and vapor pressure charts are presented for solns. of NaOH + $H_2O$ to illustrate the method.

CA 29, 26-5

Rate of Absorption of $CO_2$ Effect of Concentration and Viscosity of Caustic Solutions
Lauren B. Hitchcock
Ind. Eng. Chem., 26, 1158-67 (1934)

Exptl. data are reported on the initial (steady state) rate of absorption of $CO_2$ by solutions of NaOH up to 7 N and KOH up to 14 N in a vessel stirred at const. speed and maintained at 30°C. The viscosity of the caustic solns. at 30° was detd. and related to concn.; the deviation of absorption-rate from a straight line relation with concn. as called for by the Hatta equation was expressed as a variation with viscosity.

CA 29, 29-9

The State of Sodium Dissolved in NaOH Melts
F. Halla and H. Tompa
Z. anorg. allgem. Chem., 219, 321-31 (1934)

X-ray studies revealed that Na dissolves in fused NaOH forming $Na_2O$ + NaH. Pure NaOH in 327.6 + 0.9°. The m.p. (t) depends on the amt. of $H_2O$ (w) and of $Na_2CO_3$ ($p$) in NaOH and can be calcd. by the formula:

$$t = 327.6 - 0.196p - 0.0011p^2 - 0.30w.$$

CA 29, 302-5

Alkali Metal Hydroxides
Hermann Fricke and August Meier
U. S., 1,979,151, Oct. 30

Briquets of a sulfate such as $Na_2SO_4$ and carboniferous material such as brown coal are heated to about 900° to form sulfide and produce pores in the briquets by evolution of gases; the product is heated to 400-500° while treating it with $CO_2$ and steam to effect carbonation, then heated to 900-1000° while treating with N to effect cyanization, while maintaining the porous structure of the briquets; the product is then hydrolyzed in thin layers, at a temp. of about 400°, and alkali metal hydroxide is subsequently recovered by lixiviation.

CA 29, 559-6

Alkali Hydroxides
Norman C. Hill
Brit., 414,497, Aug. 9, 1934

In the manuf. of aq. alkali hydroxide solns. by the reaction of an alkali metal carbonate with lime in the presence of $H_2O$, a liquor free from Fe and Al is obtained by adding a purifying reagent, selected from the group consisting of the oxides, hydroxides and $H_2O$-sol. salts of Mg, Ba or Sr, to the liquor prior to the sepn. of the pptd. $CaCO_3$. The process may be effected by using a lime produced by calcining dolomitic limestone.

CA 29, 562-6

Separating NaOH and KOH
Charles J. Aydelotte, et al
U. S., 1,982,241, Nov. 27

A soln. contg. both NaOH and KOH is treated with $SO_2$ and the Na sulfite which forms is sepd. by filtration or decantation.

CA 29, 687-6

Manufacture of Caustic Soda
Pizzini Pompeo
Racca 1, 4, 13-15 (1932); Anales Asoc. Quim. Argentina 22, 181B (1934)

The electrolytic plant of the Celulosa Argentina at Rosario is described.

CA 29, 1215-3

The Preparation of NaOH from Soda Solns. by Granular Lime
V. E. Voronchikhin and G. S. Plakhotnyuk
J. Chem. Ind. (Moscow) 1934, No. 10, 33-9

When soda solutions are treated with $Ca(OH)_2$ the $CaCO_3$ formed takes too long to settle. Addition of $Fe_2O_3$ or starch to the soln. increases the rate of settling. Better results are obtained if granulated lime is added to the soda with mech. stirring. The best lime grains are prepd. by triturating slaked lime with strong soda soln. and allowing the paste to stand in a closed vessel. The mass soon becomes solid and can be easily broken up into small grains.

CA 29, 1216-6

Caustic Alkalies
I. G. Farbenind A.-G.
Brit., 417,465, October 5, 1934

Granules, etc., of caustic alkalies are obtained by causing the melted material to fall in a thin stream through an inert gas from a height appropriate to allow the solidification thereof.

CA 29, 1216-7

Alkali Metal Hydroxides; Hydrogen
I. G. Farbenind A.-G.
Brit., 415,466, August 27, 1934

Alkali metal hydroxide solns. are obtained by passing alkali metal amalgam in countercurrent to $H_2O$ over a suitable catalyst; e.g., graphite, coke, Fe, alloys of Fe with Ni and (or) Cr, at an elevated temp., e.g., 30-100°.

CA 29, 1592-9

Caustic Alkalies
Eric Dutt and Andre Helbronner
Fr., 773,473, Nov. 19, 1934

NaOH is made by the action of $MgSO_4$ on NaCl followed by treatment with $Sr(OH)_2$, the $MgCl_2$ and $SrSO_4$ being recovered and re-entering the cycle as $MgSO_4$ and $Sr(OH)_2$.

CA 29, 1947-3

Alkali Metal Hydroxides from Carbonates and Bicarbonates
Friedrich Bartling (to Alterum Kredit A.-G.)
U. S., 1,989,579, Jan. 29

An alkali metal carbonate or bicarbonate is mixed with carbon and with an alk. earth metal or Mg compd. such as a carbonate and the mixt. is heated to about 1000° in the presence of N to form alkali metal cyanide and the oxide of the alk. earth metal or Mg; the reaction mixt. is spread in a thin layer to permit ready escape of $CO_2$ during hydrolysis, and is treated with steam to hydrolyze it (the alk. earth oxide of MgO serving to causticize alkali carbinate present) and the alkali metal hydroxide is leached from the product.

CA 29, 2055-7

The Condition of Sodium Dissolved in Fused NaOH. Additional comments on an article under the same title.
F. Halla and H. Tompa
Z. anorg. allgem. Chem. 221, 18-20 (1934); cf. CA 29, 299

The work of H. and T. confirms that of Rinck (CA 27, 1806) and also gives an upper limit for the equil. const. of the reaction $K_2O + Na = Na_2O + K$ at 400°.

CA 29, 2056-3

New Determinations of the Thermal Dissociation Equilibrium of Inorganic Compounds. IV. Determination of the Dissociation Equilibria of Strontium and Barium Hydroxide by Means of High Temperature Vacuum Balance
Setsuro Tamaru and Kengo Shiomi
Z. physik. Chem. A171, 221-8 (1935) cf. CA 27, 14

The dissocn. pressure of $Sr(OH)_2$ can be expressed by the formula $\log p = -(25{,}190/4.575T) + 8.531$. The pressure of formation is independent of the compn. of the solid phase and therefore neither a compd. nor a solid soln. of $Sr(OH_2)$ and SrO formed at the temp. studied. The temp. corresponding to a dissocn. pressure of 1 atm. is 710° for $Sr(OH)_2$. The dissocn. pressure of pure $Ba(OH)_2$ can be expressed by the formula $\log p = -(25{,}100/4.575T) + 6.906$. The pressure of the BaO-$Ba(OH)_2$ mixt. depends upon the compn. and decreases as dissocn. progresses. A solid or liquid soln. is formed depending upon the amt. of hydroxide. The pressure of the $Ba(OH)_2$-BaO mixt. also depends upon the direction of the reaction. An explanation of this phenomenon is offered. V. The determination of dissociation equilibria of hydrates of strontium and barium hydroxides by means of high temperature vacuum balance. Ibid. 229-33. The equil. pressure of the thermal dissocn. of the hydrates of $Sr(OH)_2$ and $Ba(OH)_2$ was detd. from both sides of the equil. The old data on the hydrates $Sr(OH)_2 \cdot 2H_2O$, $Ba(OH)_2 \cdot 3H_2O$ and $Ba(OH)_2 \cdot 16H_2O$ cannot be confirmed. The equil. between $Sr(OH)_2 \cdot 8H_2O$ and $Sr(OH)_2 \cdot H_2O$ and also that between $Ba(OH)_2 \cdot 8H_2O$ and $Ba(OH)_2 \cdot H_2O$ are easy to det. but not that between $Sr(OH)_2 \cdot H_2O$ and $Sr(OH)_2$ or $Ba(OH)_2 \cdot H_2O$ and $Ba(OH)_2$. The reciprocal diffusion of both solid components is very slow and gives equil. values dependent upon the direction of the reaction.

CA 29, 2062-5

Catalytic Decomposition of Na-Amalgam III.
A. P. Mashovetz and P. B. Shivotinskii
Ukrain. Khem. Zhur. 8, 372-80 (1933)

A continuous process for the electrolytic prepn. of NaOH from NaCl, involving the catalytic decompn. of Hg-Na in a side chamber, is described.

CA 29, 2102-8

The Etching and Solution Phenomena on Tungsten
B. Schmidt
Dissertation, Greifswald 1924, 53 pp.; Physik. Ber. 6, 610

S. studied the action of aq. alk. solns., fused alkali and aq. acid solns. on W in the form of spheres, cylinders and irregularly shaped specimens. The velocity of soln. in the direction of the various crystallographic axes was detd. from the nature of the etched specimen. An increase in temp. or concn. of the solvent produced a better development of the etched surfaces. Etch lines which indicate traces of (110) surfaces were considered as gliding lines. The cleavage plane of W was found to be at (100).

CA 29, 2317-1

Evaporating $H_2O$ from Alkali Solution Obtained in the Electrolysis of NaCl
N. M. Solomatin and B. M. Volkov
Russ., 33,143, Nov. 30, 1933

Alkali solution that has been almost completely freed from $H_2O$ is passed through a tubular heater and into a dil. soln. of the NaOH, whereby the heat of the former is utilized for the vapn. of the $H_2O$ from the latter.

CA 29, 3209-1

Viscosity and Density of Pure Alkaline Solutions and their Mixtures
Lauren B. Hitchcock and J. S. McIlhenny
Ind. Eng. Chem., 27, 461-6 (1935)

Viscosity and d. were detd. at 20°, 30°, and 40° for aq. solns. of NaOH, $Na_2CO_3$, KOH, and $K_2CO_3$ and for mixts. of NaOH and $Na_2CO_3$ and of KOH and $K_2CO_3$, up to 8N. At a given temp. and concn. the order of decreasing viscosity is $Na_2CO_3$, NaOH, $K_2CO_3$, KOH. The order of decreasing d. is $K_2CO_3$, $Na_2CO_3$, KOH, NaOH. Viscosities of alk. mixts. deviate from a simple, additive mixt. rule in which the vol. fraction of 1 component is used, by as much as -10% at 8N concn. The Ostwald-Fenske Viscometry technique is applicable to any clear liquid, and is simple, rapid, and accurate, as compared to most other procedures.

CA 29, 3579-4

An Attempt to Determine the Limiting Equiv. Cond.
K. Gostkowski
Acta Phys. Polonica 2, 215-18 (1933)

With the aid of the simple relation between the electrokinetic potential V and the equiv. cond. $\lambda_\infty$ viz: $\lambda'_\infty/\lambda''_\infty = KV''/V'$ and from known data for KCl and HCl the limiting equiv. cond. for HCl is calcd. to be 444.

If $Pb(NO_3)_2$ is taken instead of KCl, the value $\lambda_{\infty}$ HCl is 446, while with $\lambda_{\infty}$NaOH (204.5) it equals 409°. In fact the value 204.5 for NaOH seems to be too small, since the sum of both Na and OH mobilities equals 218. The new value calcd. from the above formula is 222, which gives 444 again for HCl. The product $\lambda_{\infty}$ V is a const. of the app. (in the present expts. 408).

CA 29, 3611-8

Alkali and Alkaline Earth Metals
Ivar J. Moltkehansen
Fr., 777,001, Feb. 9, 1935

A fused alkali and alk. earth metal salt is electrolyzed in the presence of an auxiliary salt of the same metal capable of fixing chemically the anodic products and forming in exchange gaseous and inert products. Thus, NaOH is electrolyzed in the presence of $NaNH_2$ to give $NH_3$, or $NaNO_3$ in the presence of $Na_2CO_3$ to give $CO_2$.

CA 29, 3747-6

Purifying Caustic Solns.
Wilmer H. Koch
U. S., 1,997,691, April 16

Caustic liquor such as that contaminated with Fe is treated with MgO or $Mg(OH)_2$ and the ppt. thus formed is sepd.

CA 29, 3790-5

Purifying Concentrated Caustic Soda Solns. with Addition of Sodium Sulfate
Raymond E. VanderCook and Earl Sweetland
U. S., 1,998,471, April 23

After adding $Na_2SO_4$, the substantially insol. complex salt which it forms with NaCl and NaOH is removed from the soln. and is treated with a selective solvent such as $H_2O$ which dissolves NaCl and NaOH; this leaves at least a portion of the $Na_2SO_4$ undissolved, and the solids are sepd. from the soln.

CA 29, 4532-3

NaOH and $Na_2SO_4$
I. G. Farbenind A.-G.
Brit., 422,689, Jan. 16, 1935

NaOH-lye, poor in NaCl, and Glauber's salt (I) are produced by treating crude brine with $Na_2CO_3$ to ppt. Ca and Mg, electrolyzing the brine contg. $Na_2SO_4$, and concg. the resultant NaOH-lye to deposit NaCl contg. $Na_2SO_4$,

which is washed to remove the $Na_2SO_4$, the soln. thus obtained is concd. and cooled to deposit I. The washed NaCl together with the mother liquor from I is returned to the electrolysis. Part of I is caused to react with warm concd. NaOH-lye to form a triple salt contg. NaCl, $Na_2SO_4$ and NaOH which is pptd., a lye poor in chloride being left. The triple salt is dissolved in $H_2O$, and I, which can be re-used in the process is deposited by freezing, the resultant soln. being treated with (gases contg.) $CO_2$ to yield a $Na_2CO_3$ soln. for use in purifying brine.

CA 29, 4904-7

Properties in Ni and Ni Alloys in Caustic Processing Equipment
Takashi Okamoto
Japan Nickel Information Bur. Tech. Information B-19, 50 pp. (1934)

A 50% caustic soln. in a Ni evaporator usually contains about 0.00002% Ni. Steam high in $CO_2$ corrodes Ni. Potentials as high as 0.5 v. are obtained by contact between Ni and Fe with strong, hot caustic solns. Hard drawn Ni tubing has good strength and hardness for evaporator tubing. Caustic solns. of all concns. at room temp. have practically no effect upon Ni or monel metal. Ni is very resistant to fused caustic. Sample caustic evaporator tubes after 2 years' use have usually shown no visible corrosion. Caustic made by the electrolytic process is more corrosive than that made by the $NH_3$-soda process.

CA 29, 4906-2

Purifying Sodium Hydroxide Solutions
Harold M. Broadhurst (to Penn. Salt Mfg. Co.)
U. S., 2,003,734, June 4

See Brit., 396,456 (CA 28, 588-1)

CA 29, 4907-3

Potassium Hydroxide and Carbonate
Friedrich Bartling and Hermann Fricke (to Alterum Kredit A.-G.)
U. S., 2,002,684, May 28

The double salt $MgCO_3 \cdot KHCO_3 \cdot 4H_2O$ is mixed with C and the mixt. is heated to about 950° in the presence of N to produce a mixt. of contg. KCN and MgO; this mixt. is treated with steam at 350-500°, and MgO which is sepd. is caused to react with KCl to form a further quantity of the double salt.

CA 29, 4995-6

The Amphoteric Behavior of Metallic Hydroxides. IX. The Solubility of $Ba(OH)_2$ in NaOH
R. Scholder and R. Patsch
Z. anorg. allgem. Chem. 222, 135-44 (1935)

The soly. of $Ba(OH)_2$ at 20° was detd. at concns. of NaOH varying from 0 to 20N. The increase in soly. between 8 and 11.9N is explained by the formation of complex hydroxo-barium anions of the type $[Ba(OH)_{2+x}]^{x-}$, where x is the number of $OH^-$. The unknown $BaO \cdot 5H_2O$ and $BaO \cdot 2.5\ H_2O$ were obtained.

CA 29, 6849-5

Caustic Soda
Soc. Anon. Krebs and Co.
Fr., 783,164, July 9, 1935

The alk. amalgam obtained in Hg-cathode electrolysis is decomposed in a battery composed of a no. of connected compartments at 40-120° according to the concn. of lye desired.

CA 29, 7590-2

Southern Alkali Corp. Completes First Years' Operation of New Plant
W. E. Trauffer
Pit and Quarry 28, No. 3, 22-6 (1935)

Limestone and coke are burned in a vertical kiln. The $CO_2$ is forced through ammoniated salt brine to give crude $NaHCO_3$, which is calcined to yield $Na_2CO_3$. The CaO from the kiln is used to recover $NH_3$ used in the process. The soda ash is causticized to give NaOH. The mud used in the causticizing process is reburned in a rotary kiln with shell to provide make-up CaO. The plant is described.

CA 29, 7867-7

Determination of $Na_2CO_3$ in NaOH
Sokolov and Bartashevich
Zavodskaya Lab. 4, 511-15 (1935)

In the detn. of $Na_2CO_3$ in NaOH by Winkler method, the soln. obtained after pptn. of $Na_2CO_3$ with BaCl should be titrated with HCl not $H_2SO_4$ because of absorption of NaOH by $BaSO_4$. The titration with the exclusion of air by this method gave results equal to those obtained by the Fresenius method.

CA 29, 8247-5

The Reduction and Caustification of Sodium Sulfate III. Caustification of Sodium Sulfate by Means of Barium Hydroxide
Toshiro Okuno
J. Soc. Chem. Ind., Japan 38 Suppl. binding 421-5 (1935),
Cf. CA 29, 6710-7

Experimental data and thermodynamics calcns. are presented for the heterogeneous equil. of the system $BaSO_4 + 4\ CO = BaS + 4\ CO_2$, on the influence of the reaction temps. and periods upon the yield of $BaS + CuO + H_2O = Ba(OH)_2 + CuS$ and $Ba(OH)_2 + Na_2SO_4 = BaSO_4 + 2\ NaOH$.

CA 29, 8252-2

Purifying Alkali Lyes
Akt.-Ges. Fur Zellstaff and Papier Fabrikation
Ger., 615,523, July 6, 1935 (Cl 12*l*. 15)

App. for removing metals from caustic alkali lye by treatment with Hg-alkali amalgam is described.

Cf. CA 28, 421-2

CA 29, 8254-6

Barium Hydroxide
R. E. Winkecker
U. S., 2,016,530, Oct. 8

An intimate mixt. of $BaCO_3$, lime and a carbonaceous material such as coke or coal is heated to a temp. (suitably about 1480°) sufficient to convert the $BaCO_3$ to BaO, and the resulting material is subjected to an oxidizing atm. at an elevated temp. and the product is treated with water. U. S., 2,016,529 relates to a process in which a similar initial mixt. is heated in an open kiln to form a product which is then treated with water.

CA 30, 578-6

Dehydrating Caustic Alkalies
Arnold Hanchett
U. S., 2,022,037, Nov. 26

An aq. soln. of NaOH or the like in regulated quantity is brought into contact with a quantity of substantially anhyd. caustic of sufficient mass and temp. to vaporize the water from the liquid. App. is described.

CA 30, 607-3

Purifying Aqueous NaOH Solutions Containing Mercaptides, such as those used for Washing Gasoline
R. E. Burk and E. C. Hughes (to Standard Oil Co. of Ohio)
U. S., 2,020,932, Nov. 12

A mercaptide-contg. soln. of NaOH is washed with S and an org. solvent such as naphtha, which is immiscible with NaOH soln. and in which both S and the reaction product of S with the mercaptide are sol. and the org. solvent soln. is sepd. from the aq. NaOH soln.

CA 30, 825-5

Barium Hydroxide
Chemische Fabrik Coswig-Anhalt G.m.b. H. (Edward von Drathen, inventor)
Ger., 620,170, Oct. 15, 1935 (Cl. 12m.1)

$Ba_3(PO_4)_2$, obtained as a by-product in the manuf. of $H_2O_2$ from $BaO_2$ and $H_3PO_4$, is heated with C to yield $BaC_2$ and P. The $BaC_2$ is treated with water to yield $C_2H_2$ and $Ba(OH)_2$. The P may be reconverted into $H_3PO_4$.

CA 30, 826-1

Reducing Iron Contamination of Caustic Soda Solutions
Albert H. Hooker
U. S., 2,023,271, Dec. 3

For reducing the contamination by Fe in 42-54% solns. of NaOH that have been concd. by evapn. from solns. initially satd. with respect to the combined soly. of NaOH, salts from which it was originally formed and any other salts associated therewith or present as contaminants and allowed to cool, the soln. is agitated in contact with its own natural sludge not less than 24 hrs. at a temp. of 15-35° and is clarified.

CA 30, 937-5

Conductance Measurements of Dilute Solutions
M. Hlasko and A. Salitowna
Roczniki Chem. 15, 273-82 (1935)

The method used and previously described by the authors (CA 29, 6127-1) permits measurement of the conductance of very dil. solns. ($10^{-7}$N). The limiting conductance of $Ca(OH)_2$, $Sr(OH)_2$, $Ba(OH)_2$ and TlOH is detd. directly. The mol. conductance of $Mg(OH)_2$ and AgOH agrees closely with the limiting conductance. The latter is attained in solns.: $2 \times 10^{-8}$ N $Ca(OH)_2$, $5 \times 10^{-8}$ N $Sr(OH)_2$, $1 \times 10^{-7}$ N $Ba(OH)_2$, $2 \times 10^{-6}$ N TlOH, $3 \times 10^{-9}$ N AgOH, within a exptl. error of 0.2%. These agree within 0.2% of

the calcd. values by the Kohlrausch formula. If 200.2 is the velocity of $OH^-$ $Mg^{++}$, $Sr^{++}$, $Ca^{++}$, $Ba^{++}$, $Ag^+$ and $Tl^+$ have values of 56, 60.1, 60.3, 65.05, 63.3 and 78.7. The conductance coeffs. ($f_\mu = \lambda v : \lambda_\infty$) differ by 0.5-1% from those calcd. by the M. Onsager formula, and the order of magnitude is the following: $NH_4OH < HgOH < Mg(OH)_2 < Ca(OH)_2 < Sr(OH)_2 < Ba(OH)_2 < TlOH < LiOH < NaOH < KOH < RbOH < CsOH$.

CA 30, 1645-7

NaOH Solutions. Heat of Dilution at 68°F
J. W. Bertetti and Warren L. McCabe
Ind. Eng. Chem. 28, 247-8 (1936)

Heats of diln. of solns. contg. 13.6 to 48% by wt. NaOH were measured and corrected to 68°F. The enthalpies at 68°F. relative to infinitely dil. solns. were calcd.

CA 30, 1956-2

Purifying Caustic Soda Solutions
VanderCook and A. M. Lawson
U. S., 2,028,898, Jan. 28

$Na_2SO_4$ is added to form a substantially insol. complex salt with NaCl and NaOH, the complex salt is removed and $Na_2SO_4$ is recovered from it. For preventing accumulation of $Na_2CO_3$ in the system, recovered $Na_2SO_4$ is dissolved in water, $H_2SO_4$ is added and the complex salt is treated with the soln. to dissolve NaCl and NaOH from it, leaving at least a portion of the $Na_2SO_4$ undissolved, the undissolved $Na_2SO_4$ is sepd. from the soln., and at least a portion of the recovered $Na_2SO_4$ is reused in purifying further amounts of NaOH soln. Cf. CA 29, 3790-5.

CA 30, 2119-8

Caustic Soda
Hugh K. Moore
U. S., 2,031,844, Feb. 25

For purifying a body of NaOH soln. contaminated by dissolved complex impurities tending to blacken the solid NaOH recovered by evapg. the soln., the body of the soln. is exposed to cathodic electrolyzing action while only a small fraction of the body is kept exposed to anodic electrolyzing action and out of circulatory communication but in elec. communication with the rest of the body so that impurities are converted into insol. products colloidally suspended in the soln. and giving it an inky appearance, the soln. is then heated to ebullition to coagulate such suspended impurities in coarsened condition and they are removed. App. is described.

CA 30, 2333-4

Purifying Caustic Soda
Elledge and Hirsch
U. S., 2,030,694, Feb. 11

For removing silica, alumina, and Fe from NaOH liquor, it is treated with $SrSO_4$, pptd. impurities are removed; substantially all the Sr is recovered in the form of $SrCO_3$, and the recovered $SrCO_3$ is used for treating an addnl. portion of the NaOH liquor of such concn. as to dissolve the $SrCO_3$. An arrangement of app. is described.

CA 30, 3173-9

The Preparation of Sodium Hydroxide from Soda Solution by Granular Lime
V. E. Voronchikhin
J. Chem. Ind. (Moscow) 13, 154-8 (1936); cf. (CA 29, 1215-3)

When 200% excess $H_2O$ is added, rapidly or slowly, to CaO, the $Ca(OH)_2$ produced is dense and settles in the soln. at a moderate speed. If cold $H_2O$ is added rapidly, the $Ca(OH)_2$ is porous, but settles slowly. The best lime for the prepn. of NaOH obtained by slow addn. of cold $H_2O$. The $Ca(OH)_2$ which is formed is porous and settles rapidly.

CA 30, 3307-5

Specific Heats of NaOH Solutions
John W. Bartelli and Warren L. McCabe
Ind. Eng. Chem. 28, 375-8 (1936)

Exptl. results on the sp. heats of NaOH solns. over the concn. range 4.08-51.15% NaOH by wt. and a temp. range 3.1° to 88.5° were detd. Above 60° the heat capacities of the solns. were practically independent of temp. but the temp. coeff. of the heat capacity near 0° was of considerable magnitude. An adiabatic calorimeter controlled within 0.01° was used and the solns. were analyzed gravimetrically with an accuracy of ± 0.005%.

CA 30, 3308-3

Critical Transformation Points of High-Melting Oxides and of their Hydrates within the High-Temperature Range
P. N. Lachchenko and D. I. Kompanskii
J. Applied Chem. (U.S.S.R.) 8, 628-52 (in French 652-3) (1935)

The dissocn. temps. at atm. pressure were $Ca(OH)_2$ about 560°, MgOH 410-420°.

CA 30, 3598-3

The Economic Production of Caustic Soda by Chemical Means
Yu. Yu. Gessen
J. Chem. Ind. (Moscow) 13, 204-8, 259-62 (1936)

CA 30, 3604-9

NaOH
Hiroski Tanaka
Japan, 113,583, Dec. 9, 1935

$H_2SiF_6$ (or $Na_2SiF_6$) is decompd. with $NH_4OH$, to produce $SiO_2$ and $NH_4F$ (or $SiO_2$ + NaF + $NH_4F$). $NH_4F$ is treated with a Na salt (e.g., $NaNO_3$, $Na_2HPO_4$), to form NaF and $NH_4$ salt. NaF is causticized with $Ca(OH)_2$ to form NaOH and $CaF_2$. The $CaF_2$ is converted to $H_2SiF_6$ (or $Na_2SiF_6$) with $SiO_2$ and an acid or with $SiO_2$, NaF and an acid. The last product is used again in the process.

CA 30, 4634-5

Purifying Concentrated Solutions of Caustic Soda
Earl Sweetland and Raymon E. VanderCook (to Pa. Salt Mfg. Co.)
U. S., 2,040,717, May 12

For removing NaCl, the soln. is heated to at least 60° and very finely divided $Na_2SO_4$ is added at such temp. to form relatively large crystals of an insol. double salt of $Na_2SO_4$ with at least a portion of the NaCl present, and the materials are mechanically mixed slowly without appreciable breaking down of the crystals formed, at the temp. mentioned, until the formation of the complex salt is substantially complete; the soln. and suspended solids are then cooled to below 45° and are further agitated at such temp. until the supersatd. soln. is substantially completely broken down, and the soln. is then sepd. from the crystd. solids. An arrangement of app. is described.

CA 30, 4731-8

Evaporating Liquids such as Acids or Alkalies
Casimir Theiler
U. S., 2,042,488, June 2

An auxiliary gas such as one inert to the liquid undergoing evaporation, is brought into intensive contact with the liquid in an evaporator with consequent reduction of the partial pressure of the liquid and of its evapn. temp., and the gas and the assocd. produced vapor are evacuated from the evaporator and passes in heat-exchange relation to gas introduced into the evaporator. App. and various operative details are described.

CA 30, 5139-4

Preparation of Sodium and Potassium Hydroxides from their Sulfates
Gino Gallo
Ann. Chim. Applicata 25, 620-8 (1935)

NaOH and KOH are prepared from their sulfates, obtained from leucite, by treating with a boiling solution of $Sr(OH)_2$ contg. about 2% excess Sr. The soln. must be filtered hot, about 95° or better, to prevent reversion. The use of $Sr(OH)_2$ is more economical than Ba compd., because the $Sr(OH)_2$ can be regenerated by passing $NH_3$ and $CO_2$ into the $SrSO_4$ suspension, and then igniting the $SrCO_3$ formed at 1200°.

CA 30, 5511-6

Purifying Alkali Metal Hydroxide Solutions
Overdick and Gorke
U. S., 2,044,888, June 23

Chlorate and heavy metal compds. are removed from solns. such as those of NaOH by subjection of the soln. first to its electrolytic treatment with use of iron anodes and then to a second electrolytic treatment with indifferent anodes such as those of Ni or graphite. An arrangement of app. is described.

CA 30, 5735-6

Acids and Alkali Metal Salts
Silbermann
Fr., 796,088, Mar. 28, 1936

$HNO_3$ or HCl and alkali metal hydroxides or salts are made by treating nitrates, chlorides or other alkali metal salts with HF or an acid of the type $H_2SiF_6$ and $HBF_4$, the HF or other F acid being regenerated during the process and used again. Thus, $NaNO_3$ is treated with HF to form $NaHF_2$ and $HNO_3$. The $NaHF_2$ is treated with $CaCN_2$ and form $NaHCN_2$ and $CaF_2$. The $NaHCN_2$ is hydrolyzed to NaOH, $NH_3$, and $CO_2$, and the $CaF_2$ is treated with $H_2SiO_3$ to form $CaSiO_3$ and HF. Several examples are given.

CA 30, 5905-3

Rapid Determination of Sesquioxides in NaOH
Sokolov and Bartashevich
Zavodskaya Lab. 5, 500 (1936)

Neutralize 10 g. NaOH in $H_2O$ with HCl (methyl orange), add 0.5 cc. $HNO_3$ and boil for 10 min. Treat the hot soln. with 4 - 5 cc. of 20% $H_2SO_4$ and 2 cc. of 10% $(NH_4)_2S_2O_8$. After 15 - 20 min. ppt. the sesquioxides with $NH_4OH$; filter, ignite the filter, evap. the ppt. with 2 - 3 cc. HF, ignite and weigh.

CA 30, 6145-6

Purifying NaOH
Standard Oil Co. (Ohio)
Fr., 796,424, Apr. 7, 1936

Aq. solns. of NaOH contg. mercaptides are purified by washing with a soln. of S in an org. solvent, e.g., naphtha, which is insol. in the NaOH soln. and a solvent for the reaction products of S and mercaptides.

CA 30, 7795-3

Sodium Hydroxide from Sodium Sulfide
Lundin and Bitner
U. S., 2,054,727, Sept. 15

$Na_2SO_4$ is reduced with a carbonaceous reducing agent such as "black liquor," and the resulting Na sulfide is converted into NaOH by treating it with ZnO to form ZnS, roasting the latter to form ZnO and $SO_2$, and the NaOH formed is recovered. Various details of sequential procedure are described.

CA 30, 8540-3

Fusing KOH
P. G. Rudenskii
Russ., 42,043, March 31, 1935

Alkali metal nitrates and nitrites are introduced into the cast-iron melting pot at the beginning of the operation together with KOH, so as to reduce the effects of corrosion.

CA 31, 956-1

Alkalies
Soc. anon. Krebs and Co.
Brit., 453,517, Sept. 14, 1936

Alkali metal amalgam produced in an electrolytic cell is passed through a succession of vessels contg. alkali lye at 40-120°, wherein the amalgam is decompd. with formation of caustic alkali, the reaction being assisted by the action of contact electrodes of graphite resting on the amalgam.

CA 31, 1168-3

Purifying Caustic Soda Solutions
The Penn. Salt Mfg. Co.
Brit., 452,218, Aug. 18, 1936

See U. S., 2,040,717 (CA 30, 4634-5)

CA 31, 1749-2

Corrosion
Goldowski
Pub. Sci. Tech. Ministere Air (France) No. 64, 138 pp. (1935)
Cf. CA 30, 6691-3

The theoretical and math. foundations of corrosion are reviewed and discussed in detail. A math. analysis of the corrosion of Al in NaOH is given. 144 References.

CA 31, 2577-2

Aluminum Bronze
Mansfeld
Fr., 803,545, Oct. 2, 1936

Alloys resistant to hot corrosive liquids, e.g. KOH soln. containing Cu 83.8, Fe 4.18, Ni 4.78 and Al 7.2% or Cu 83.25, Al 7.87, Fe 3.55 and N 5.25%.

CA 31, 3764-9

The Thermodynamics of Aqueous Potassium Hydroxide Solutions from Electromotive Force Measurements
Harned and Cook
J. Am. Chem. Soc. 59, 496-500 (1937)

Measurements were made of the emf. of the cell, $H_2$/KOH (aq., M/$K_xHg$/KOH) (aq., M = 0.05/$H_2$, from 0° to 35° and from M = 0.1 to 4. From these data were calcd. for aq. KOH values of the activity coeff. and the relative partial molal heat content and heat capacity. The latter values are in fair agreement with existing calorimetric data.

CA 31, 4460-8

Alkali Metal Compounds
Consolidierte Alkaliwerke
Fr., 805,490, Nov. 20, 1936

Complex fluorides of alkali metals, such as $K_2SiF_6$ or $Na_2SiF_6$ are treated in aq. suspension at raised temp. with difficulty sol. or insol. carbonates of alk. earths, Mg or heavy metals, in proportion such that the complex fluoride is decomposed with formation of the fluorides or carbonates. These fluorides or carbonates are extd. and converted to caustic alkalies by reaction with $Ca(OH)_2$.

CA 31, 4462-8

Sodium Hydroxide from Sodium Sesquicarbonate
MacMullin and Cunningham
U. S., 2,078,092, Apr. 20

Decarbonation of the sesquicarbonate is effected by subjecting it to an amount of water limited to effect the pptn. of $NaHCO_3$, the pptd. $NaHCO_3$ is sepd. and the remaining liquor is causticized with lime.

CA 31, 5519-9

Alkali Metal Fluorides and Hydroxides
Consolidierte Alkaliwerke
Brit., 461,597, Feb. 19, 1937

Alkali metal hydroxides are obtained by making a mash of an alkali metal chloride, e.g., rock salt, with a quantity of $H_2O$ insufficient to dissolve it, treating the mash with a concd. nongaseous HF containing more than 40% HF and treating the alkali metal fluoride obtained with CaO to obtain caustic alkali and $CaF_2$. HCl is also obtained. The $CaF_2$ may be treated with $H_2SO_4$ to obtain HF for use in the process.

CA 31, 5520-1

Concentrated Alkali Metal Hydroxide Solutions
Gorke
U. S., 2,083,648, June 15

Concd. alkali metal hydroxide solns. are prepd. by trickling a stream of an alkali metal amalgam downwardly through a tower over and in contact with a mass of relatively small pieces of a solid catalyst so arranged in the tower in the path of said stream as finely to subdivide the stream while a stream of water is passed upwardly through the mass of catalyst and a temp. of about 60 - 100° is maintained within said mass and the resulting alkali metal hydroxide soln., H and Hg are separately withdrawn from said tower. App. is described.

CA 31, 6423-7

Caustic Alkali
Erwin Holland-Merten and C. E. Dreyer
Fr., 808,655, Feb. 12, 1937

A soln. of NaOH is heated in a thin layer in a high vacuum so that the NaOH seps. as a solid or powder. App. including heated rollers on to which the soln. flows is described.

CA 31, 6977-9

Electrochemical Protection of Iron from Corrosion in Alkalies
Stender and Artamonov
Trans. Electrochem. Soc. 72, 19 pp. (preprint) (1937)

Detns. were made of the rate of corrosion of electrolyte Fe, cast Fe and sheet Fe in concd. alkali fusion, (NaOH and KOH), fused alkalies, and in alkali lyes during the process of fusion. The rate of corrosion depends on the temp., the concn. of alkali, and the concn. of Cl ions and $ClO_3$ ions in the soln. The effect of cathode polarization on the rate of corrosion of sheet Fe and cast Fe in alkali solns. of different concns. at various temp. and various Cl and $ClO_3$ ion concns. was studied. It is shown that for the electrolytes examd., cathode polarization ensures protection of the Fe against corrosion, and that the ratio between cathode c.d. without applied cathodic polarization and c.d. with applied cathodic polarization (completely protected cathode) varies between the limits 0.20 to 0.37 amp./sq.m. During the process of fusion of the alkali in an Fe container and also after fusion, cathodic polarization gives only a partial protection against corrosion.

CA 31, 7031-6

Corrosion-Resistant Chromium-Nickel-Iron Alloys
Carius (to Fried. Krupp A.-G.)
U. S., 2,090,105, Aug. 17

Alloys which are resistant to alkalies and to HCl contain C 0.02-1.0, Cr 10-25, Ni 20-40, Mo 1-10, Sb 0.5% to less than 2%, and Cu 0.1-10%, the balance being iron with or without "normal impurities." Cf. CA 30, 7535-1.

CA 31, 7203-9

Sodium Hydroxide
Clifford and Imperial Chemical Industries, Ltd.
Brit., 464,834, Apr. 26, 1937

NaOH or solns. thereof are obtained in a process comprising the following steps, (1) reaction between NaCl and $Ba(OH)_2$ in aq. medium at not above

40° to form basic Ba chloride, which is removed from the reaction mixture; (2) evapn., with or without carbonation or sulfonation, of the mother liquor from (1) to remove as solids the remaining Ba content and the NaCl. Step (1) may be conducted in an aq. alc. medium, e.g., MeOH - $H_2O$ mixt., or in an aq. ammoniacal medium. The evapn. of (2) may be followed by cooling or flash evapn. may be employed, if desired, in several stages with intermediate removal of solids.

CA 31, 7375-4

Some Special Cast Irons of Interest in Chemical Engineering
Everest
Chemistry and Industry 1937, 657-66

Alloy cast irons suitable for service requiring resistance to: hot caustic, $H_2SO_4$, raw sewage, wear or heat are described.

CA 31, 7771-5

Electrolysis
I. G. Farbenindustrie A.-G.
Brit., 466,946, June 8, 1937

Alkali metal sulfate solns. are electrolyzed to produce alk. lyes and $H_2SO_4$ with use of anodes of Pb-Ag alloys, the temp. thereof being maintained below 50°. A suitable alloy contains Pb 96, Ag 3 and As 1 parts.

CA 31, 8411-9

Amorphous and Crystalline Oxide Hydrates and Oxides. XXXVI. Is Lithium Hydroxide Amphoteric? Heteropolybases.
Alfons Krause and S. Krzyzanski
Ber. 70B, 1975-9 (1937)

The soly. curve of LiOH in NaOH solns. up to 20N shows a min. for 12.7N NaOH. Below this concn. the solid phase is $LiOH \cdot H_2O$; above it, LiOH. Hydroxide compd. formation in the form of heteropolybases is postulated.

CA 31, 8841-8

Alkali
I. G. Farbenind. A.-G. (Werner Honsberg, inventor)
Ger., 648,981, Aug. 12, 1937 (Cl. 121 12)

A process of prepg. alkali lye or salts by treating water with alkali amalgam in the presence of a contact agent is described. App. is indicated.

CA 31, 8842-3

Alkali Metal Hydroxides
Clifford and Imperial Chemical Industries, Ltd.
Brit., 467,209, June 14, 1937

The hydroxides or solns. thereof are obtained by the reaction of alkali metal chlorides with $Ba(OH)_2$ in an aq. medium at above 40° to form basic $BaCl_2$, which is removed from the reaction mixt. The reaction may be effected in an aq. alc. medium, e.g., a MeOH-$H_2O$ mixt. or in an aq. ammoniacal medium. The mother liquor after the removal of the basic salt may be cooled and (or) evapd. to remove unreacted $Ba(OH)_2$ with or without some alkali metal chloride, for return to the process. The evapn. may be accompanied by carbonation of sulfonation. If carbonation is effected prior to the evapn., $BaCO_3$ is pptd. and, after calcination, returned to the process, the alkali metal chloride being returned separately.

CA 32, 34-1

Specific Heat of Molten NaOH
V. R. Terashkevich and A. I. Vishnevskii
J. Gen. Chem. (U.S.S.R.) 7, 2175-82 (1937)

Av. sp. heats of molten NaOH contg. 2.0, 3.92, 8.45, 15.20 and 19.7% $Na_2CO_3$ in the temp. intervals 344-597°, 357-647°, 340-558°, 367-571° and 361-554°, resp., are given as 0.4828, 0.4641, 0.4854, 0.4704 and 0.4532 Cals., resp.

CA 32, 738-6

Caustic Soda
Henri Lawarree
Fr., 810,789, March 30, 1937

A soln. of a Na salt (NaCl) contg. $NH_3$ is mixed with a metal oxalate (Cu oxalate) sol. in the soln. and the sol. salts of which are capable of double decompn. with Ca oxalate (I). The $(COONa)_2$ (II) formed is filtered off and treated with CaO to produce NaOH and I. The Cu oxalate is regenerated by double decompn. of I with the soln. resulting from the filtration of II, and the $NH_3$ is recovered by distn.

CA 32, 867-2

Electrically Heated Rotary Drum for Fusing Caustic Soda and Potash
Appareils et evaporateurs Kestner
Fr., 814,574, June 25, 1937

CA 32, 1059-7

Caustic Soda
Solvay and Cie
Fr., 812,492, May 11, 1937

See Brit., 464,834 (CA 31, 7203-9)

CA 32, 1190-9

Purifying Caustic Alkali Solutions
I. G. Farbenind. A.-G. (Fritz Overdick and Herbert Gorke)
Ger., 651,240, Oct. 9, 1937 (Cl. 121 15)

Caustic alkali solns. which have been prepd. by electrolysis are freed from chlorates and heavy metal impurities by electrolytic treatment first with an anode of Fe, whereby chlorates are reduced to chlorides, and then with an anode of an inert material, e.g., Ni or graphite, whereby heavy-metal impurities are eliminated. Both treatments may be effected at a raised temp. e.g. 80-110°. The first treatment may be effected with a cathode of Fe, and the direction of the current may be changed from time to time. Alternatively, a.c. may be used. Examples are given.

CA 32, 1873-9

Lowering the Content of Sodium Chloride in Technical Caustic Soda
A. D. Kats
J. Chem. Ind. (U.S.S.R.) 14, 1410-16 (1937); cf. CA 26, 5388

A 50° Bé, soln. of NaOH contg. NaCl is allowed to stand at 23-5° until all solids have settled, then decanted and treated with 50 kg. of solid $Na_2SO_4$ per cu. m. of soln., the mixt. stirred for 30 min., allowed to stand 3 hours, stirred again for 5 min. and allowed to stand for 3 more hours. This is twice repeated and the soln. is filtered. The $Na_2SO_4$ absorbs almost all the NaCl, which, in NaOH solns. more concd. than 46° Bé, is present as a colloid.

CA 32, 1876-5

Purifying Caustic Soda Lyes
I. G. Farben Industrie A.-G.
Brit., 472,754, Sept. 29, 1937

In purifying NaOH lyes by the formation and sepn. of 2 NaOH · 7 $H_2O$ (I), the I after mech. sepn., e.g., by centrifuging, is freed from adhering mother liquor by displacement with $H_2O$ at 10-14°.

CA 32, 2295-7

Determination of the Viscosity and Density of Aqueous Solutions of Technical Alkalies
Sevtsov
J. Applied Chem. (U.S.S.R.) 10, 1500-3 (in French 1503) (1937)

Viscosity and d. determinations for concns. 5.38, 6.40, 7.60, 9.00, 10.62, 12.47, 17.90, 21.40, 25.35, and 28.45% by wt. ($NaOH + Na_2CO_3$) at temps. of 15°, 19°, 25°, 35°, 45°, 55°, 65°, 75°, 85°, and 95° were detd. An empirical formula for detn. of d. of the solns. is given.

CA 32, 2415-4

Pressure of Water Vapor Over Molten NaOH and KOH
Bauman
J. Applied Chem. (U.S.S.R.) 10, 1165-72 (in German 1172) (1937)

Air of known partial press. of water vapor was passed over the substance under investigation until equil. was established. The $H_2O$ content was detd. by drying at 450-500° in a current of dry $CO_2$-free air and absorbing $H_2O$ in $P_2O_5$. Tab. data given the percentage water absorbed by KOH 93 + $K_2CO_3$ 7%, KOH 85 + $K_2CO_3$ 15%, KOH 88.35 + $K_2CO_3$ 6.65 + KCl 5%, NaOH 96.5 + $Na_2CO_3$ 3 + NaCl 0.5%, NaOH 84.5 + $Na_2CO_3$ 15 + NaCl 0.5%; and NaOH 80 + $Na_2CO_3$ 15 + NaCl 5% at temps. varying from 300° to 400° and $H_2O$ vapor pressures varying from 100 to 500 mm. From these data the heats of hydration of KOH and NaOH were calcd. by the van't Hoff, e.g.: $\ln(P_2/P_1) = [(\Delta H/R) - T_2 - T_1)/T_2T_1]$. For init. mixture KOH 93 and $K_2CO_3$ 7% on absorpn. of 7% $H_2O$ $\Delta H_{650 - 610°K.} = 18.1$ Cal.; for 6% $H_2O$ $\Delta H_{664 - 620°K.} = 17.1$ Cal. For mixt. NaOH 84.5, $Na_2CO_3$ 15 and NaCl 0.5% of absorption of 1.5% $H_2O$ $\Delta H_{625 - 574°K.} = 12.9$ Cal.

CA 32, 2431-9

Decomposition Potentials of Fused Electrolyte
Tverdovskii and Molchanov
J. Phys. Chem. (U.S.S.R.) 9, 239-51 (1937) CA 32, 1582-5

The following decompn. potentials have been derived from current - p.d. curves: NaOH 2.32 volts (393°), 2.02 (543°); NaCl 3.06 (840°), 2.91 (945°); NaBr 2.88 (765°), 2.85 (800°); KCl 3.22 (800°), 3.00 (925°); KBr 3.00 (782°), 2.38 (842°); $BaCl_2$ 3.14 (1005°), 2.99 (1070°); $MgCl_2$ 2.55 (910°), 2.46 (800°); $CaCl_2$ 3.23 (852°), 2.90 (945°).

CA 32, 2867-4

Analysis of Caustic Liquors for Traces of Impurities
Duffendack, and Wolfe
Ind. Eng. Chem. Anal. Ed. 10, 161-4 (1938)

The technic for the spectrochem. analysis of caustic alkali solns. for traces of Al, Ca, Cr, Cu, Pb, Fe, Mg, Mn, Si, and Sr have been developed at the U. of Michigan and is here described. Same method has been used in the testing of electroplating solns., inorg. and pharmaceutical chemicals and plastics. Urine and saliva have been analyzed for Na, K, Ca, Mg, and Pb, as well as in beverages and org. tissues.

CA 32, 3104-8

Purifying Caustic Soda Solutions
The Penn. Salt Mfg. Co.
Brit., 473,984, Oct. 25, 1937

See U. S., 2,028,898 (CA 30, 1956-2)

CA 32, 3917-8

Purifying Sodium Hydroxide
Domingo Lopez (to Westvaco Chlorine Products Corp.)
U. S., 2,112,813, March 29

A method of removing Fe and salt comprises prepg. a solution contg. about 63% NaOH, cooling the soln. to about 60° to crystallize the caustic as monohydrate, and sepg. the crystals from the mother liquor carrying Fe and salt.

CA 32, 4289-2

Purifying Solutions of Alkali Metal Hydroxides
Solvay and Cie
Belg., 422,539, Aug. 31, 1951

A 45-50% by wt. soln. of alkali metal hydroxide is treated with reagents at least one of which is selected from each of the following groups: (1) hydrated oxides, (2) hydroxides and salts of ferric Fe, (3) oxides, hydroxides and salts of Ca.

CA 32, 4291-5

Caustic Soda
Lawarree
Brit., 477,230, Dec. 24, 1937

NaOH prepd. by causing a suitable metal oxalate, e.g., of Cu, Zn, Ni, Ag, Co, or Cd, and a sol. Na salt, the acid radical of which forms a sol. Ca salt, e.g., NaCl, $NaNO_3$ to react in presence of $H_2O$ and a volatile alkali, e.g., $NH_3$,$NMe_3$, to ppt. $(COONa)_2$, causticizing this with CaO + NaOH + $(COO)_2$ Ca↓ , and causing this ppt. to react with mother liquor from first stage after at least part of volatile alkali has been removed and acid added to dissolve sol. constituent of resulting ppt., to ppt. original metal oxalate. In modifications, the pptd. $(COO)_2$ Ca is added to mother liquor prior to removal of volatile alkali or the alkali is removed, the resulting ppt. sepd., treated with acid and caused to react with the $(COO)_2$ Ca. Cf. CA 32, 738-5.

CA 32, 4734-8

Caustic Soda
Henri Lawarree
Fr., 47,512, May 24, 1937

Addn. to 810,789 (CA 32, 738-5). In the process of Fr., 810,789 the $NH_3$ is recovered by injecting steam into the soln. of ammoniacal metal salt, with pptn. of the insol. metal salt. The remaining soln. is acidified.

CA 32, 5588-5

Purifying Caustic Soda Lye
I. G. Farbenind A.-G.
Fr., 824,145, Feb. 1, 1938

See 472,754 (CA 32, 1876-5)

CA 32, 6405-1

The Causticizing of Soda and Settling from the Caustic Solution
Sevtsov
J. Chem. Ind. (U.S.S.R.) 15, No. 4, 14-20 (1938)

When soda is causticized 2 hrs. with lime from Karshinskii limestone contg. not less than 80% CaO, the yield of NaOH is 82%. The process can go on at 75-95°, but the temp. should be kept const. to avoid convection currents during settling. Excess lime is not necessary and good results are obtained if the lime is present in theoretical amt. or as little as 5% less than theory.

CA 32, 6415-7

Effect of Alkalies on Refractories
Hartmann
Stahl. u. Eisen 57, 1017-21 (1937)

Even at low temp. alkali vapors attack fine-grained $SiO_2$ refractories, large grains are more resistant. At 1000° alk. vapors soften fireclay, and a glass of low m.p. is formed on surfaces in which blow holes quickly form. Magnesite is fairly resistant; chrome-magnesite is strongly attacked, due to alkali reacting with Cr oxide. Molten $Na_2CO_3$ quickly attacked ladle lining of fatty clay, but one high with $Al_2O_3$ was fairly resistant. High Mn and Fe contents of slag counteracted effect of alkalies, such slags more viscous and hence more reactive. Highly basic blast furnace slags were not made appreciably more fluid by addns. of $Na_2CO_3$.

CA 32, 6612-4

Coating Aluminum or Its Alloys
Aluminum Labs. Ltd.
Brit., 482,028, March 22, 1938

A protective coating resistant to acids and alkalies is produced on Al or Al alloy article by first heating article to about 100°, and treating with an alkali silicate soln. at about 50-70° then treating with a pptg. soln. at about 30-40° and then heat-treating at 100-300° to render film irreversible and firmly adherent. Solns. of $NH_4Cl$, $NH_4OH$ and alkali carbonates, bicarbonates, sulfates, bisulfites and chlorides may be used for pptn. A wetting agent, e.g., soap may be added to the alkali silicate soln.

CA 32, 7353-3

Purifying Caustic Alkali Solutions
I. G. Farbenind. A.-G.
Ger., 662,449, July 13, 1938 (Cl. 12*l* .15)

Caustic solns. contg. traces of Hg are purified by subjecting them to electrolysis by method Ger., 542,781 (CA 26, 3191), the cathodes were made of metal capable of alloying with Hg. Process may be effected at 40-60°, and the cathodes should first be freed from oxide impurities. An example is given in original lit.

CA 32, 7686-9

Purification of NaOH Solutions
Earl Sweetland and Raymon E. VanderCook (to Canadian Ind. Ltd.)
Can., 375,587, Aug. 9, 1938

Concd. NaOH solns. are heated to at least 60°, passing continuously to a mixing chamber, continuously treated with very finely divided $Na_2SO_4$ to form relatively large crystals of an insol. complex salt contg. $Na_2SO_4$ and at least a portion of the NaCl impurity. The soln. and $Na_2SO_4$ are mixed slowly without appreciable breakage of the crystals and at 60° until the reaction involving the formation of the insol. complex salt is about complete. The overflow is cooled to below 45°, the mass continuously slowly agitated in a mixing chamber until a supersatd. soln. is substantially completely broken down without appreciable breakage of the crystd. solids. The overflow is passed to a sepg. app. and the solids are sepd. from the soln. An app. is described.

CA 32, 7880-6

Corrosion of Pots Used in the Fusion of Caustic Soda
Ugo Perret
Chimica e industria (Italy) 20, 133-6 (1938)

While investigating the causes of corrosion of cast-iron pots used for fusing NaOH, it was noted that NaOH made in Hg cells caused more rapid corrosion than NaOH made in diaphragm cells. This difference was found to be due to the presence of $NaClO_3$ in the latter cells. Addn. of $NaClO_3$ to NaOH produced in Hg cells reduces the rate of corrosion as much as 90%. Less than 1% $NaClO_3$ is required.

CA 32, 8086-1

Alkali Metals and their Hydroxides
Thomas Wood
Brit., 484,997, May 12, 1938

The metals are prepd. by distn. in an induction furnace of the sulfate or chloride mixed with a nonvolatile base, e.g., CaO, and solid reducing agent, e.g., coke, that is a conductor of elec., the distn. being conducted with exclusion of air and under reduced pressure. The metal may be condensed as metal or absorbed in $H_2O$ or dil. alkali to produce the hydroxide. App. is described.

CA 32, 8087-2

Purifying Caustic Soda
Waldeck
U. S., 2,127,496, Aug. 23

For removing dissolved salts from NaOH liquor of a concn. at least sufficient to form the heptahydrate, and which is substantially satd. with a Na salt such as NaCl, the soln. is cooled until a mixt. of substantial amounts of fine crystals of the salt and coarse crystals of hydrated NaOH is formed in the liquor, and the material is then filtered through a foaminous body having interstices of size sufficient to permit passage of the salt crystals, while retaining NaOH crystals.

CA 32, 9412-7

Alkali Metal Hydroxides and (or) Carbonates
Opatowski and Adamoli
Brit., 487,362, June 20, 1938

Extg. alkali metal hydroxides or carbonates together with $Al_2O_3$ from alkali Al silicates, e.g., leucite, feldspar, by thermal reaction of the silicate with alk. earth metal oxide, hydroxide or carbonate, e.g., CaO, limestone, a fluoride, e.g., fluorspar, is added to the charge, whereby reaction occurs below the m.p. of the mixt., e.g., 900-930°. The calcined mixt. after cooling, is powdered and lixivated with $H_2O$ to ext. alkali aluminate, from which in the known manner $CO_2$, $Al(OH)_3$ and an alkali carbonate soln. may be prepd., the latter being converted to caustic alkali if desired. The residue from the lixivation, comprising silicates, fluosilicates and alumino silicates of the alk. earth metals, may be used for the production of cement.

CA 33, 43-6

Chlorine and Caustic Soda from Salt of the Ocean
John H. Baker
Pacific Chem. Met. Ind. 2, 3-8 (1938)

A description of the electrolytic plant of the Penn. Salt Mfg. Co., at Tacoma, Wash.

CA 33, 923-9

The Production of NaOH and $H_2SO_4$ by Electrolytic Decomposition of Sodium Sulfate
G. Grube and St. Stainoff
Z. Elektrochem. 44, 640-8 (1938)

In the com. electrolysis of aq. $Na_2SO_4$ soln., NaOH and $H_2SO_4$ must be removed from the cell before neutralization by diffusion takes place and

before heavy losses in yield of lye occur due to recombination of H and OH ions. Flowing electrolytes in a 3-compartment cell with 2 filter diaphragms are required, the $Na_2SO_4$ soln. flowing from the center compartment through the diaphragms to the two outer compartments from which alkali and acid are removed, resp. Expts. are described with a cell having vertical diaphragms, and with a cell having horizontal diaphragms; in the latter case the cathode chamber was empty. With either type of cell the production of concd. NaOH soln. at the cathode is difficult since the soly. of $Na_2SO_4$ in $H_2O$ decreases sharply with increasing alky. and consequent clogging of the pores of the cathode diaphragm by $Na_2SO_4$ crystals. A cell for continuous operation with a flowing Hg cathode was designed in which only one diaphragm is required. Favorable results with this cell are reported.

CA 33, 1110-4

Caustic Soda Lye
I. G. Farbenind A.-G. (Hermann Heres, inventor)
Ger., 665,851, October 5, 1938 (Cl. 121. 15)

NaOH lye is purified by forming the heptahydrate, sepg. this from the mother liquor by a centrifuge, and washing off the adhering mother liquor by a small amt. of water at 10-14°. The amt. of water used is preferably less than the amt. of adhering mother liquor.

CA 33, 1177-9

The Filtration of Conc. Lye in the Laboratory
R. Scholder and G. Hendrich
Chem. Fabrik, 1938, 541-3

Expts. to show the corrosive action of NaOH solns. on sintered filters of various kinds of Jena glass, of SiC filter plates, porcelain crucibles, Ni, Ag, and syn. org. products. Solns. of 50-60% at 90-160° were used. The gen. result with glass filters was that the stronger the solution and the higher the temps. the shorter the life, but up to 100° they were satisfactory. The use of acid instead of hot $H_2O$ to clean them was much more destructive. SiC and porcelain filters were not satisfactory. Ni was unaffected, but fine-mesh Ag gauze filters did not give clear filtrates. A "Flexolith" filter, made from I.G.'s "Luvican" was unaffected by 60% soln. at 160°. Also a plate made by G. Siebert from a syn. prod. was satisfactory up to about 150°, so these materials give promise of usefulness in tech. filtration.

CA 33, 1250-1

The Effect of Treating Cast Iron with Caustic Soda
T. L. Joseph, F. W. Scott and M. Tenenbaum
Metals and Alloys 9, 329-35 (1938)

The method of applying NaOH to cast iron and the chemistry of the treatment are described. The effects of NaOH on chem. analysis, silicate content,

transverse strength and microstructure of Fe are discussed. The transverse strength of cast iron is increased by addn. of NaOH; this is largely attributed to the rapid removal of S by the NaOH. The graphite flakes of cast iron show a tendency to be thinner and less blocky after treatment.

CA 33, 1458-6

The Resistance of Glasses to Acids and Alkalies
Kozo Tabata, Tatuo Yokoyama and Tamotu Kusama
J. Japan Ceram. Assoc. 45, 897-905 (1937)

Alkali borosilicate glasses contg. alumina, lime or zinc oxide together with some commercial glasses were examd. for the resistance to acids and alkalies by a powder method. Glass resists so well $H_2SO_4$ and HCl that there is hardly a definite relation between its compn. and the resistance. As to the resistance to Na carbonate soln., both alumina and zinc oxide are beneficial, while lime is injurious, the replacement of 0.75 mol of boric acid by 0.75 mol. of lime makes the resistance considerably poorer. As for the resistance to NaOH soln., oxides of Al, Ca and Zn are advantageous; however, in the case of lime, more than 0.5 mol. of boric acid must be replaced. Action of NaOH soln. is severest, that of Na carbonate soln. next, and that of the two acids is at least.

CA 33, 1891-4

Dialysis of Aqueous Caustic Solutions
Arthur W. Saddington and Arlie P. Julien (to Solvay Process Co.)
U. S., 2,138,357, Nov. 29

A process for the prepn. of a 20-30% aq. soln. from an aq. KOH soln. of about 50% concn. involves passage of the latter soln. in counter-current dialytic relation with aq. liquid. The more concd. soln. is passed through a series of alternate dialytic zones and cooling zones, and the cooling is so regulated that the max. temp. in the dialytic zones is maintained below about 30°.

CA 33, 1891-5

Purifying Caustic Soda Solutions
R. M. Law and H. C. Britton (to Solvay Process Co.)
U. S., 2,138,347, Nov. 29

The soln. to be purified (an aq. concd. soln.) is mixed at an elevated temp. (suitably about 60°) with a $Na_2CO_3$ suspension obtained by addn. of an aq. alkali carbonate soln. to an aq. concd. NaOH soln. at an elevated temp., followed by cooling the mixt. and filtering to sep. the ppt. from the NaOH soln.

CA 33, 2057-5

Potassium Uranates
R. Flatt and W. Hess
Helv. Chim. Acta 21, 1506-12 (1938)

A systematic study of the system $UO_2(NO_3)_2$-KOH-$H_2O$ was made to det. the reaction of uranyl salts with bases. The hydrate, $UO_2(OH)_2$ is not pptd., but a K uranate is obtained to which the formula $K_2U_7O_{22} \cdot m\ H_2O$ is given; with excess KOH this uranate is transformed into a second uranate, $K_4U_5O_{17} \cdot nH_2O$. It is preferable to introduce the uranyl nitrate into the KOH in order to maintain a basic medium. The hydrolysis of basic uranyl nitrate is formulated as: $16\ UO_2(OH)^+ + 2\ K^+ \longrightarrow K_2U_7O_{22}$ (ppt.) $+ 9\ UO_2^{++} + 8\ H_2O$.

CA 33, 2061-5

The Fundamental Reactions in Analytical Chemistry. I. Reactions of Caustic Soda with Metallic Ions
Yosinaga Oka
J. Chem. Soc. Japan 59, 971-1013 (1938)

II Reactions of sodium carbonate with metallic ions. 2. Ibid 1385-9

CA 33, 2457-2

Chemical Resistance of Silicon and Chromium Irons Produced in the U. S. S. R.
I. Ya. Klinov
Khim. Machinostroenie 6, No. 6, 40-4 (1937)
Chimie and Industrie 40, 680

Best resistance to $H_2SO_4$ is exhibited by cast iron contg. 14.6% Si. Cast iron contg. 49.3% Cr is less resistant under these conditions, but is the material which best resists $H_2SO_3$ solns., for which Si iron is not suitable. Cr iron is less attacked by $SO_2$ gas than is Si iron; but even the former should be used in presence of only low $SO_2$ concns. Both of these irons exhibit enhanced resistance to NaOH, hypochlorites and lactic acid.

CA 33, 2458-1

Selection of Steel for Autoclaves in Contact with Alkali at High Temperatures
A. V. Smirnov
Khim. Mashinostroenie 1938, No. 2, 22-30

Various steels, soft Fe, Fe-Ni, and monel were tested at 200° under a pressure of 12 atms. for period of 150 hrs. The best results were obtained with Fe-Ni contg. $< 0.10$ C, 0.30-0.60 Mn, 0.15-0.30 Si, $< 0.020$ S, $< 0.030$ P, 4.75-5.25 Ni, and $< 0.25$ Cr.

CA 33, 3083-2

Dehydrating Alkali Metal Hydroxides
Geo. L. Cunningham (to Mathieson Alkali Works)
U. S., 2,144,364, January 17

An alcoholate derived from the same alkali metal and an alc. having not more than 4 C atoms is treated with the aq. component of the alkali metal hydroxide, and the alc. formed is removed by distn. Operative details are described involving reaction of an alc. such as MeOH with an alkali metal amalgam in the presence of an electrode such as a graphite grid.

CA 33, 3545-8

Caustic Soda
Henri Lawarree
Ger., 671,319, Feb. 6, 1939 (Cl 121.13)

This corresponds to Fr., 810,789 (CA 32, 738-5) and 47,512 (CA 32, 4734-8) but includes additional description.

CA 33, 3663-3

The Second Dissociation Constant of Barium Hydroxide
Cecil W. Davies
J. Chem. Soc. 1939, 349

Based on the activity measurements of Harned and Mason (CA 26, 2913-2), the second dissocn. const. for $Ba(OH)_2$ is 0.23, as compared with 0.031 for that of $Ca(OH)_2$.

CA 33, 4151-1

Preparation of Calcium Hydrosilicates by Hydrothermal Synthesis
A. I. Kryagova
J. Applied Chem. (U.S.S.R.) 11, 1103-7 (in German, 1107) (1938)

. . . .The curves obtained by thermal analysis showed the dehydration of $Ca(OH)_2$ at 370-520°. Data are tabulated.

CA 33, 5234-3

Sintered Metal Filters for the Purification of Conc. Alkali Solutions
L. Schlecht and G. Trageser
Chem. Fabrik, 1939, 243-4

The filters are formed from metal powders derived, preferably, from carbonyl compds., and it is possible to regulate the pore size and vol. to suit special conditions. They may be shaped as pipes, plates, crucibles, etc., which

may be strengthened by sintering in a wire gauze, and they may be welded to solid metals. A filter of 14 tubes 1 m. long and (presumably) 150 mm. diameter, working at 0.3 - 2.0 atm. pressure, varying with thickness of cake, will handle 32 tons of 50% NaOH liquor at 60° - 70° in 6 - 8 hrs., and is easily cleaned by backwashing with $H_2O$ or blowing with N. Under such conditions, a tube will last several months, which is increased by exclusion of air and O.

CA 33, 5416-8

Acetylene
Charles Ness and Hugo Viljo Kojola (to Linde Air Prod. Co.)
Brit., 500,302, Feb. 7, 1939

$C_2H_2$ and substantially dry $Ca(OH)_2$ are obtained by a process wherein $H_2O$ is introduced at the bottom of a reaction vessel to which $CaC_2$ also is fed at a point below the point of removal of the $Ca(OH)_2$, the introduction of the $CaC_2$ causing an upward displacement of the $Ca(OH)_2$. App. is described.

CA 33, 5611-7

Caustic Soda
Compagnie Nationale de Matieres Colorantes et Manufactures de produits chimiques du Nord reunies, establissements Kuhlmann
Fr., 836,742, Jan. 25, 1939

NaOH free from Cl, or contg. only traces thereof, is prepd. by washing with water, preferably with agitation, the amalgam coming from the electrolysis of an alkali chloride with Hg cathode, before its passage into the app. for decomposing the amalgam.

CA 33, 5728-1

The Density of Aqueous Solutions of NaOH
Gosta Akerlof and Gerson Kegeles
J. Am. Chem. Soc., 61, 1027-32 (1939)

For NaOH, 1-26 molal, dens. 0°-70° was det'd. When the app. partial molal vol., $\phi$, is plotted against (concn.)$^{0.5}$ a straight line is formed up to a point where for each concn. a break occurs and beyond which another straight line appears. For concns. below the break: $\phi_1^\circ = -10.580 + 0.2863\ t - 0.00470\ t^2 + 0.0000266\ t^3$, and $k_1 = 5.3342 - 0.8788\ t + 0.001603\ t^2 - 0.00000994\ t^3$. For concns. above the break: $\phi_2^\circ = -3.798 + 0.1030\ t - 0.001312\ t^2 + 0.000008563\ t^3$, and $k_2 = 3.181 - 0.0155\ t + 0.000201\ t^2 - 0.00000145\ t^3$. Tables of ds. and partial molal vols. are included.

CA 33, 6007-7

Removing Sodium Chloride from Caustic Soda Solutions
James L. Jamieson (to Pittsburgh Plate Glass Co.)
U. S., 2,155,269, Apr. 18

For removal of NaCl, a sol. B compound, such as borax or boric acid, is added to a soln. having a NaOH concn. of 40-70% and the pptd. NaCl is sepd.

CA 33, 6007-8

Caustic Soda Solution
Brazier K. Beecher and Wm. F. Waldeck (to Pittsburgh Plate Glass Co.)
U. S., 2,155,252, April 18

A water white soln. is prepared by treating an aq. soln. of $Na_2CO_3$ with lime to form a soln. of NaOH contg. manganic coloring matter of green tint, treating the soln. with sufficient Zn to remove the green coloration, with formation of a solid dispersed product from the manganic coloring matter, and then removing this solid material by use of an adsorbent.

CA 33, 6130-4

Enthalpy Concentration Charts from Vapor-Pressure Data
Wm. Haltenberger, Jr.
Ind. Eng. Chem., 31, 783-6 (1939)

The thermodynamic relations are given whereby an enthalpy-concn. chart for a soln. can be constructed from the sp. heat of the soln. at one concn. over the entire temp. range, and vapor pressure data on the soln. over the entire temp. and pressure range. The Duhring plot of temps. at which soln. and solvent have the same v.p. is used to facilitate the required differentiation of the equil. data. The method is applied to the system NaOH-$H_2O$ over the range 68-160°F. and 0-50% NaOH by wt. and the results are compared with exptl. data. At low concns. an error of 0.01 in the slope of the Duhring lines may cause an error of 10 BTU in the change in enthalpy corresponding to a change of 10% in concn.; this is cumulative as the concn. change is increased.

CA 33, 6536-4

Caustic Alkalies
Consolidierte Alkaliwerke (Fritz Gewecke, inv.)
Ger., 644,074, May 22, 1939 (Cl. 121.13)

Concd. or anhyd. HF, produced from $CaF_2$ and $H_2SO_4$, is treated with an alkali chloride in the presence of an amt. of $H_2O$ not exceeding that required to dissolve the chloride. An alkali fluoride and HCl are obtained, and the former is treated with $Ca(OH)_2$ to yield an alkali hydroxide and $CaF_2$, which is used for the production of HF.

CA 33, 6547-3

The Action of Alkalies on Refractory Materials. An Examination of the Reaction to NaCl vapor with Refractory Materials at 1000° and the Condition Leading to the Volatilization of the Brick Constituents
F. H. Clews, H. M. Richardson, and A. T. Green
Inst. Gas. Engrs., Copyright Publ., 193/76, 9-17 (1938)
Cf. CA 32, 6820[1,3]

A refractory material can react with NaCl vapors at 1000° without the presence of any other agent; the extent of the reaction is small. The chlorides of Fe, Cu, and Al so formed were volatilized from fireclay, $SiO_2$ and china-clay specimens in the absence of large amounts of Cl and HCl gases. When O and $H_2O$ vapor was added to NaCl vapor, greater reaction was obtained by the following equations, but smaller volatilization resulted: $4\ NaCl + O_2 = 2\ Na_2O + Cl_2$, $NaCl + H_2O = NaOH + HCl$. The chlorides of Fe, Ca, and Al formed, migrated to the surface and oxidized in dry air; in moist air, the oxides remained in the test pieces. Oxidation of NaCl needed a reactive surface to obtain appreciable reaction; $SiO_2$ surfaces were not effective.

CA 33, 7968-5

Liberation of Alkali Metals from Their Compounds
Burritt S. Lacy (to E. I. duPont de Nemours and Co.)
U. S., 2,162,619, June 13

An alkali metal compd. such as NaCl is heated with a reducing agent such as Ca carbide to produce alkali metal vapor and the vapor is rapidly cooled to a temp. not higher than 700° by mixing it with a cooling gas such as CO to condense the vapor to a liquid metal. App. is described.

CA 33, 7968-6

Alkali Metal Hydroxides
Pittsburgh Plate Glass Co.
Fr., 839,518, April 5, 1939

Aq. alkali metal hydroxides, e.g., NaOH, are concd. and also purified if they contain impurities such as chloride and chlorate by treatment with a liquid amine sol. in water, e.g., liquid $NH_3$, having a concn. such that it is capable of absorbing water from the hydrate and elimination of the amines and absorbed water, along with impurities if present. Practically anhyd. or partially hydrated liquid $NH_3$ is used. App. is described. Fr., 839,519. Impurities are extd. by liquid amine, e.g., liquid $NH_3$, contg. sufficient water to prevent appreciable concn. of the NaOH soln. Thus, a 40-50% soln. of NaOH or solid NaOH is treated with liquid $NH_3$ contg. about 25% of water.

CA 33, 8061-4

Filtering App. Suitable for Treating Caustic Alkali Solns., etc., to Separate Precipitates
Hugh K. Moore (to Brown Co.)
U. S., 2,164,142, June 27

Operative and structural details are described of a filter structure adapted to remove extremely finely divided ppt. from aq. suspension, comprising a medium such as metal-sprayed wire cloth whose pores and openings are of such fine size as to retain thereon pptd. $CaCO_3$ of the character of lime sludge while permitting free flow of aq. medium there through and a layer of pptd. $CaCO_3$ of the character of lime sludge deposited on such medium and capable of retaining ppts. of a particle size finer than itself.

CA 33, 8463-2

Nomographic Chart for the Temperature Correction of Caustic Soda Solution Densities and Interconversion of Physical Data
Ernst Berl
Chem. and Met. Eng. 46, 527 (1939)

CA 33, 8938-1

Caustic Soda
Henri Lawarree
U. S., 2,167,404, July 25

See Brit., 477,230 (CA 32, 4291-5)

CA 33, 9152-9

A Simple Experimental Arrangement for the Electrolysis of Alkali Chlorides
P. Gruber Rehenburg
Z. Physik. Chem. Unterricht, 52, 156-7 (1939)

A sintered-glass suction filter is set on a wire gauze cathode which rests on a glass plate and is fitted with a graphite stick for an anode. When a soln. of NaCl is electrolized in this app., NaOH soln. drips from the cathode.

CA 33, 9558-5

Soda Ash and Caustic Soda; Lime, Salt, Heat and Power Join Forces
Jessie Coates
Southern Power and Ind. 57, No. 10, 45-50 (1939)

Sixteen plants supply domestic demands for NaOH and soda ash, with ammonia-soda process plants supplying 95% of domestic requirements for soda ash.

The nine soda ash plants probably have a combined capacity considerably in excess of present requirements. A flow sheet and further details of the ammonia-soda process are given, and a flow sheet and descriptions of the lime-soda and electrolytic processes for NaOH.

CA 33, 9562-6

Calcium Hydroxide
I. G. Farbenindustrie A.-G.
Brit., 505,890, May 18, 1939

$Ca(OH)_2$ masses obtained in the prepn. of $C_2H_2$ from $CaC_2$ are purified by treatment with alkali metal hydroxide solns.

CA 34, 310-4

Apparatus for Investigation of Oxidation Equilibrium of Metals by Water Vapor
Kokiti Sano
J. Chem. Soc. Japan 60, 758-62 (1939)

The dissocn. pressures of $Sr(OH)_2$ were detd. The results:

$$\log p_{H_2O} \text{ (mm)} = (-5405.9738/T) + 8.3846.$$

CA 34, 653-1

The Ability of Monel to Withstand Corrosion in the Oil and Fat Industry
R. Muller
Fette u. Seifen 46, 346-8 (1939)

Tabulated data show the excellent resistance of monel to corrosion by fat acids, caustic, $H_2SO_4$ and fats. Since monel also has very high mech. strength and good weldability, it is very desirable, as a material for construction in the oil and fat industry.

CA 34, 1446-8

Anhydrous NaOH Production by Partial Pressure Evaporation
D. F. Othmer and J. J. Jacobs, Jr.
Ind. Eng. Chem. 32, 154-60 (1940)

Anhyd. NaOH was prepd.continuously from 50% aq. solns. on a pilot scale, with kerosene as diluent in the evapn. Kerosene remaining on the solid NaOH was removed by centrifuging and solvent washing. The total, calcd. heat cost was about 350 lb. of coal per ton of 50% NaOH soln., or about 150 lb. from a 70% NaOH soln., i.e., 1/3 the present cost. Because of the protective film from the kerosene, no corrosion of equipment was found. Steel

equipment might be used. The NaOH produced was a fine, cryst. powder, free-flowing and of rapid chem. activity because of great surface area. "Carborundum is inert to caustic."

CA 34, 1448-5

Purifying Caustic Soda
Irving E. Muskat and W. F. Waldeck (to Pittsburgh Plate Glass Co.)
U. S., 2,178,694, Nov. 7

An impure aq. soln. of NaOH substantially satd. with NaCl is concd. so that monohydrate will crystallize, cooled to crystallize a substantial quantity of both relatively coarse hydrated NaOH and relatively fine NaCl crystals, and such coarse and fine material are sepd. by passing the resulting liquor with which they are assocd. through a filter of suitable porosity.

CA 34, 1454-8

Impervious Clay Pots Resistent to Acids and Alkalies
Sandor Bleier
Hung., 121,783

Clay is suspended in water, neutralized, diluted and sedimented. The pptd. layers are mixed in given ratios, ground to fine powder, neutralized and dried. Pots are made as usual and fired on biscuit ware. The surface is cleaned with a strong alkaline solution and enamel, m. 600-850°, applied by galvanoplasty. A final enamel is applied and the pot fired in the usual manner.

CA 34, 1827-2

Ammonia-Soda Process with Production of a Pure Caustic Soda
John C. Garrels and Howard Roderick (to Michigan Alkali Co.)
U. S., 2,180,755, Nov. 21

In the operation of the ammonia-soda process in which carbonic acid compds. are formed and lime is treated with $NH_4Cl$ soln. for recovery of $NH_3$, leaving a $CaCl_2$ soln., the latter is clarified, the carbonic acid compd. of the process is treated with the $CaCl_2$ soln. to form $CaCO_3$, the $CaCO_3$ is calcined and the product is treated with $Na_2CO_3$ in the presence of water to form NaOH and $CaCO_3$, followed by filtering, drying, and returning the last produced $CaCO_3$ to the cycle and sepg. of the NaOH in pure form.

CA 34, 2728-3

Preparation of NaOH Reagent Free from Carbonate
A. M. Kellog
Chemist-Analyst 29, 4-8 (1940)

Various methods are reviewed and a suitable procedure for prepg. the soln. and for standardizing it against $KHC_8H_4O_4$ is described.

CA 34, 3157-9

The Reaction Mechanism at a Graphite Electrode
V. Sihvonen
Atti X° congr. intern. chim. 4, 404-13 (1939)
Cf., CA 30, 2871-1; 31, 2101-9

When a melt of pure alkali carbonate electrolyzed open to the air with a graphite anode, the reaction mechanism at first corresponds to the equation: $C + 2CO_3^{--} = 3CO_2 + 4\epsilon$. The cathodically deposited alkalies, however, react with O and the corresponding oxides diffuse to the anode so that the reaction soon becomes: $C + 2CO_3^{--} + 2\ Na_2O = CO_2 + 2\ Na_2CO_3 + 4\epsilon$. In melts of alkalies, the anodic process is: $C + 4OH^- + 2NaOH = Na_2CO_3 + 3\ H_2O + 4\epsilon$. If a small graphite anode is used, the max. c.d. values are related to the temp. as follows: $\ln$ c.d. $= (A/T) + B$, where T is the temp., A is a function of potential, and B is a const.

CA 34, 4948-5

Crystal Structure of $LiOH \cdot H_2O$
Raymond Pepinsky
Phys. Rev. 55, 1115

CA 34, 4958-2

The Lattice of the High-Temperature Form of KOH
Wolfram Teichert and Wilhelm Klemm
Z. anorg. allgem. Chem. 243, 138-44 (1939)

KOH crystallized at high temps. in the NaCl system with a = 5.78 A. at 300°. The OH group has a radius of 1.53 A.

CA 34, 5257-4

Sodium Hydroxide from Sodium Chloride
Ivor L. Clifford
U. S., 2,195,917

An arrangement of apparatus is described and a process which involves: (1) treating NaCl with $Ba(OH)_2$ in the presence of a limited amt. of water

at a temp. not exceeding 40° and with a chloride-ion conc. within the range within which basic Ba chloride can exist as a stable solid phase, removing such solid basic Ba chloride from the liquor; (2) concg. the mother liquor from step (1) by evapn. and removing sepd. solid NaCl with assocd. Ba compds. U. S., 2,195,918 relates to a similar process in which reaction is effected at a temp. above 40° and the sepd. basic Ba chloride is split up by water treatment and the resulting $Ba(OH)_2$ is further used in the process.

CA 34, 5604-4

Anhydrous Caustic Alkalies
Irving E. Muskat (to Pittsburgh Plate Glass Co.)
U. S., 2,196,593

An aq. alkali metal hydroxide of not less than about 50% conc. is treated with substantially anhyd. liquid $NH_3$ in the amt. sufficient to absorb substantially all the water present. Fluffy, porous particles of NaOH are thus obtained. U. S., 2,196,594 relates also to app. and operative details of use of liquid $NH_3$ and aq. $NH_3$ mixtures for concg. and purifying solid hydrated NaOH. U. S. 2,196,595 relates to a method of purifying solid hydrated NaOH contg. an impurity of the group consisting of chloride and chlorate which comprises extg. the same while in the solid state with liquid $NH_3$ contg. sufficient water to prevent substantial dehydration of the solid by the liquid $NH_3$, the amount of $NH_3$ present during treatment being sufficient to ensure the existence of a liquid phase contg. a major portion of the $NH_3$ and a second phase contg. a major portion of the hydroxide. U. S., 2,196,596 relates to the purification of hydrated impure hydroxides of the alkali metals by treatment with water-sol. org. amine, such as methyl-or ethylamine at temps. such as to maintain the amine in liquid state.

CA 34, 6030-7

30th Report of the Refractory Materials Joint Committee. Inst. Gas Engr., Commun. No. 218, 119 pp; Gas World III, 403-4; Gas J. 228 and 229. XII. The Effect of Heat on Refractory Materials Impregnated with $Na_2CO_3$ and NaOH
F. H. Clews, H. M. Richardson and A. T. Green
Inst. Gas Engrs., Commun. No. 218, 49-55

Fireclay and $SiO_2$ refractories impregnated with $Na_2CO_3$ and NaOH solns., then heated to 1000° for 5 hours with repetition of the process several times, expand because of evolution of gases ($CO_2$ and $H_2O$), an effect very different from that caused by alkali chlorides.

CA 34, 6042-2

The Production of Acetylene with the Recovery of Dry Calcium Hydroxide from the Byproducts
P. A. Rodionov, A. L. Veisman and P. A. Ivanov
Avtogennoe Delo 8, No. 11, 26-30 (1937); Chem. Zentr. 1938, II, 2840

Two modifications of an improved app. for the production of $C_2H_2$ are described. Advantages over other equipment for production of the gas are greater capacity and ease of handling, decreased space requirements, and the possibility of simultaneous recovery of the CaO.

CA 34, 6419-4

Alkali Metals and Their Hydroxides
Thomas Wood
U. S., 2,200,906, May 14

App. is described and a method of alkali metal production involving the use of a chloride or sulfate such as NaCl, a non-volatile base such as lime, and a solid reducing agent such as coke which is a conductor of electricity, in a mixture in which eddy currents are generated sufficient to raise the temp. to a point at which reaction takes place with liberation of alkali metal, air being excluded and a reduced pressure maintained and the vapors of alkali metal removed from the reaction zone. NaCl, lime, and coke may be heated together by high-frequency induction with exclusion of air and under reduction of pressure, and the Na vapors liberated withdrawn and brought into contact with water to form NaOH.

CA 34, 6948-3

Reactions Such as the Production of Acetylene and Calcium Hydroxide
Hugo V. Kojola and Maurice O'Brian (to Prest-O-Lite Co.)
U. S., 2,204,184, June 11

App. used is described, and a process for the continuous and simultaneous production of a gas and a substantially dry residue by the exothermic reaction of a solid and a liquid, which comprises continuously introducing the solid into a reaction chamber, bringing the solid in the reaction chamber into contact with only suff. liquid, in excess of the theor. amt. necessary completely to react with the solid, to absorb only that por. of the heat of reaction nec. to maintain the products of reaction at a temp. substantially above the b.p. of the liquid, introducing the liquid directly into the solid to prevent its coming into contact with the generated gas, continuously conveying the unreacted solid and the solid products of reaction along a predetd. path in the reaction chamber, and simult. agitating the unreacted solid and solid products of reaction so as to cause the solid to react comp., continuously discharging the generated gas from the chamber at predetd. points in the path of the solid and solid products of reaction, and continuously discharging the substantially dry residue from the reaction chamber at the end point of the path.

CA 34, 7170-7

The Heat of Dilution of Aqueous Sodium Hydroxide Solutions at 25°
Julian M. Sturtevant
J. Am. Chem. Soc. 62, 2276-80 (1940)

Calorimetric data are given for the integral heats of diln. of NaOH solns. at 25° up to 4 molal; the data are shown graphically. The apparent and partial relative molal heat content of solute and partial relative molal heat content of solvent in aq. NaOH solns. at 25° are calcd. The heats of diln. are compared with previous work at 20°.

CA 34, 7270-4

Corrosion Testing of Silver
J. M. Thomas and Allison Butts
11th Progress Rept. Am. Silver Producers' Research Project 1940, 8 pp.
J. Inst. Metals 66, Pt. 8, Met. Abstracts 7, 352

Data are recorded showing the rate of attack of HCl and $H_2SO_4$ of various conc., PhOH and fused NaOH on Ag. In HCl, protective films are formed even in fairly concd. acid, and these remain stable while the metal is completely immersed and the acid is satd. with AgCl. Attack by hot $H_2SO_4$ becomes severe at the waterline with 60% acid. Phenol is almost inert to silver, while 70% caustic soda at 110° attacks silver much less readily than it does Ni.

CA 35, 462-7

Purifying Calcium Hydroxide Obtained in Acetylene Production
Karl Wintersberger and Walter Spormann (to I. G. Farbenind A.-G.)
U. S., 2,213,131, Aug. 27

The residue from $C_2H_2$ production from Ca carbide is treated with an alkali metal hydroxide soln. such as one of NaOH (4% at 60°) and the solids are sepd.

CA 35, 586-3

Purifying Sodium Hydroxide Solutions Containing Mercaptides
Everett C. Hughes (to Standard Oil Co. of Ohio)
U. S., 2,211,695, Aug. 13

Mercaptide-contg. solns. are mixed with elemental S, passed in contact with a sulfide of Pb or Cu, and extd. with an org. solvent, such as naphtha, in which the reaction product of S and the mercaptide is sol., and the soln. is sepd.

CA 35, 1586-4

Calcium Carbonate and Sodium Hydroxide
Brooks and Rafton
Can., 392,967, December 3, 1940

Lime is slaked in a substantial excess of water, vigorously agitated, treated with $Na_2CO_3$ in the presence of water at not above 70° and maintained at this temp., the soln. sepd. from the ppt., the ppt. treated with further $Na_2CO_3$ in the presence of water, and the slow-settling, finely-divided $CaCO_3$ sepd.

CA 35, 1948-5

Sodium Hydroxide
Kenzi Matuo
Japan, 129,711, April 11, 1939

A method based on the poor soly. and easy decompn. of $MgSO_3$ for making NaOH at low cost from $Na_2SO_4$ depends on the reaction:

(1) $MgSO_3 \longrightarrow MgO + SO_2$
(2) $CaSO_3 + Na_2SO_4 + H_2O + SO_2 \longrightarrow 2NaHSO_3 + CaSO_4$
(3) $2NaHSO_3 + MgO \longrightarrow Na_2SO_3 + MgSO_3 + H_2O$
(4) $Na_2SO_3 + Ca(OH)_2 \longrightarrow 2NaOH + CaSO_3$

CA 35, 2288-3

Barium Hydroxide, etc.
Lyle O. Hill and Sampson Isenberg (Isenberg 6% to
Lyle O. Hill and 20% to the Firm of McLaughlin and Wallenstein)
U. S., 2,225,633, Dec. 24

$Ba(OH)_2$ is produced by providing a fused mass of NaOH contg. dissolved barytes, allowing the mass to cool, pulverizing it, dissolving out $Ba(OH)_2$ with a solvent at least a substantial part of which comprises ethylene glycol, and treating the soln. with water to ppt. $Ba(OH)_2$. Similarly, $Sr(OH)_2$ may be formed from $SrSO_4$.

CA 35, 2386-6

Crystal Structure of Lithium Hydroxide Monohydrate
R. Pepinsky
Z. Krist. 102, 119-31 (1940) (in English)

$LiOH \cdot H_2O$ from Merck is cryst. monoclinic: a = 7.37, b = 8.26, c = 3.19A., $\beta$ = 110°18', a:b:c = 0.892:1:0.386 (Groth gives a:b:c = 0.8184:1:0.3750, $\beta$ = 94°29'). The d., 1.51 g.cc., indicates 4 mils. per unit cell. Space-group $C_{2h}^3$-C2/m. Two-dimensional Fourier analyses gives the at. positions:

Li = (4h) with y = 126° = 0.350, sym. = $C_2$-2;O = (4g) with y = 76° = 0.211 and (4i) with x = 103° = 0.286, z = 140° = 0.389, sym. = $C_2$-2, $C_s$-m. Each Li is at the center of a tetrahedron of O. Two such tetrahedra share an edge in a reflection plane and at an angle of 12.5° with the a axis. Upper and lower corners of all tetrahedra are shared with tetrahedras in the cells immediately above and below, the edges between these shared corners being parallel to the c axis. Thus paired tetrahedra form unending chains in the c direction. O of the shared tetrahedral edges in reflection planes ($C_s$-m) are in OH groups, and O of upper and lower tetrahedra are linked sideways by OH-bonding between the hydroxyls and waters. Distances within a tetrahedron: Li-$O_{OH}$ = 1.95, Li-$O_{H_2O}$ = 1.97, $O_{OH}$-$O_{OH}$ = 2.99, $O_{OH}$-$O^{(1)}_{H_2O}$ = 3.14, $O^{(1)}_{H_2O}$-$O^{(2)}_{H_2O}$ = 3.19, $O_{OH}$-$O^{(2)}_{H_2O}$ = 3.34A. Sepns. for nearest atoms in adjacent tetrahedra: Li-Li = 2.48, $O_{OH}$-$O_{H_2O}$ = 2.68, $O^{(1)}_{H_2O}$-$O^{(1)}_{H_2O}$ = 3.48, $O^{(1)}_{OH}O^{(3)}_{OH}$ = 3.74A. Relations between the structures of $LiOH \cdot H_2O$ and those of $Li_2O$ and LiOH are discussed.

CA 35, 3178-4

Apparatus for Electrolysis of Caustic Alkalies
Sei-iti Inoue
Japan, 132,341, Oct. 2, 1939

Into the bottom of a cell having channels for Hg, are introduced blocks similar in shape to the Hg container to save Hg and to effect its smooth circulation.

CA 35, 3404-9

Action of Alkalies on Refractory Materials. VI. Action of the Vapor from a Potash-Silica Glass on Refractory Materials at 1200°
Clews, Richardson, Chadeyron and Green
Trans. Brit. Ceram. Soc. 39, 289-96 (1940) Cf. CA 34, 7079-9

Silica and siliceous refractories formed a fluid surface glaze which began to drip when the alkali content was about 5%. Fireclay products were not modified after the absorption of over 12% $K_2O$ in 300 hrs. at 1200°. The rate of absorption of $K_2O$ varied inversely with the intensity of the previous firing and directly with the apparent porosity. Surface coatings of $Al_2O_3$ decreased the absorption by 2 fire brick specimens.

CA 35, 3577-3

Alkali Effect on Unalloyed and Alloyed Steel
Ubrich, Wellinger and Muller
Mitt. Ver. Grosskesselbesitzer Nos. 74-5, 274-80 (1940)
Met. Eng. Digest (in Metals and Alloys) 12, No. 6, 824

For the different German brands of com. superheater-tube materials (plain carbon steel, Mo-Cu steels and Cr-Mo steels) tested, variations in types and strength of alky. present, including the presence or absence of Na silicate, were without much effect on the relative corrosion sensitivity of the various steels.

CA 35, 3775-6

The Theory of the Lowig Process (of Caustic-Soda Production)
V. R. Terashkevich, R. E. Shtok and E. G. Gurova
J. Chem. Ind. (U.S.S.R.) 17, No. 12, 18-24 (1940) Cf. CA 34, 4868-4

Photomicrographs and d. studies of the $Fe_2O_3$ used in the process show that the reaction between $Na_2CO_3$ and $Fe_2O_3$ to form $Na_2O \cdot Fe_2O_3$ and its subsequent hydrolysis take place on the large internal surface created by the porosity of the $Fe_2O_3$. The optimum reaction temp. is 850°, since above this the porosity decreases. If the process is run under ideal conditions, the supporting skeleton of the $Fe_2O_3$ remains unchanged through a large no. of cycles.

CA 35, 3866-9

Superheated Water Vapor as a Solvent
Fuchs
Z. Elektrochem. 47, 101-10 (1941)

Expts. at temps. up to 400° and pressures up to 300 kg./sq.cm. show that NaCl, KCl and NaOH volatilize appreciably with superheated steam. The concn. of salt in the vapor increases greatly with increased pressure. The solns. of the salts in the vapor show no elect. cond. of importance. Concns. in the vapor are nearly independent of liquid concns. over a considerable range.

CA 35, 4292-6

Electrolytic KOH
Christo D. Lambieff
Ger., 692,414, May 23, 1950 (Cl. 121.9)

CA 35, 4329-6

Intercrystalline Cracking in Boiler Places. III. Exposure of Iron and Steel Specimens to Sodium Hydroxide Solutions at High Temperatures and Pressures
Adcock,
J.Iron Steel Inst.(London) Advance copy May, 1941, 25-41

With small pressure bombs, intercryst. cracking was found in boiler plate steel immersed in a soln. of pure NaOH at 310°. Other expts. in a steel pressure vessel lined with Ag showed no intercryst. cracks in annealed samples at 410° but in cold-worked samples cracks similar to those produced by H at high temp. were formed in 17 days at 300°. With highly concd. caustic solns. intercryst. cracks penetrating from the surface become filled with oxide. These oxidizing type cracks penetrated annealed or cold-worked steel with equal facility. Pure Fe developed crack of the oxide type. It is probable that both forms of intercryst. cracking contribute to the caustic cracking of boiler plates under service conditions.

CA 35, 4329-7

Intercrystalline Cracking in Boiler Plates. II. Prolonged-Stress Tests on Iron and Steel. Specimens Immersed in Hot Sodium Hydroxide Solutions
Jenkins and Adcock
J. Iron Steel Inst. (London) (Advance copy May, 1941, 10-24)

Specimens with or without notches or drilled holes were kept under tension in concd. NaOH at 225°. The typical intercryst. crack was not obtained. In regions of concd. stress breakdown was caused by growth of nonmetallic inclusions. Heavily cold-worked steel resisted better than annealed.

CA 35, 4557-1

Barium Hydroxide
Athole G. Allen, Ltd., and Daniel Tyrer
Brit., 514,583, Nov. 13, 1939

Cryst. $Ba(OH)_2$ is produced by heating a mixt. of Ba sulfate or carbonate with 10% of its wt. of $Al_2O_3$ as free from silica as possible, together with C, to a temp. below that at which fusion occurs, dissolving in hot water and cooling to crystn.

CA 35, 4942-2

Acetylene and Dry Calcium Hydroxide
Charles Ness and Hugo V. Kojola (to Linde Air Products Co.)
Ger., 693,064, June 6, 1940 (Cl. 26b. 41)

See Brit., 500,302 (CA 33, 5416-8)

CA 35, 6156-7

Heat-Transfer Coefficients in Natural Circulation Evaporators
Jenness and Caulfield
Paper Trade J. 112, No. 21, 37-42 (1941)

The evapn. of $H_2O$, together with sucrose solns. and NaOH solns. of a range of concns. of 4.4-41.6%, was studied in 2 small-scale natural circulation evaporators with different types of submerged heating coils. The over-all coeff. was found to vary inversely with the power function of temp. difference, and of the groups $(\rho/\mu)$ and $(c\mu/k)$. The general equation followed was: $U \Delta t^m = a/[(\rho/\mu)^n (c\mu/k)^p]$ The exponential value of $\Delta t$ was const. in all cases, while those of the groups were found to be const. for 2 solns. in 2 different machines provided the type of liquid circulation remained the same. The constant a varied between different types of heating surface. Materially larger exponents of the groups and values of the const. a were found when turbulent flow was believed to exist.

CA 35, 6400-4

Sodium Hydroxide
G. V. Marchenko
Russ., 56,293, Jan. 31, 1940

$Na_2CO_3$ is heated with crude iron ore contg. at least 95% of $Fe_2O_3$.

CA 35, 6491-4

Alkali Resistant Containers and Utensils
Rath
Ger., 697,791, Sept. 26, 1940 (Cl. 80b. 8.13)

Alkali-resistant ware is made from a body consisting in the main of $TiO_2$ and alk. earth titanates. Alumina and sillimanite may be added, but clay, etc., should be kept very low. As plasticizers it is advantageous to use org. substances such as: starch, dextrin, glue, gum arabic, as well as bentonite.

CA 35, 6492-7

Generating Acetylene
Paul Goebels (to G. Polysius Akt.-Ges.)
Ger., 698,704, Oct. 17, 1940 (Cl. 26b. 4)

The container for $CaC_2$ is provided with porous plates. Through those plates the acetylene is blown under pressure. This results in the sepn. of a dry $Ca(OH)_2$; the water can come in contact with the $CaC_2$ more easily, thus speeding up the generating of the gas.

CA 35, 7127-7

Converting Alkaline Earth Metal Oxalates into Oxalates of Other Metals
Clifford
Brit., 517,455, Jan. 30, 1940

Solns. of oxalates of metals such as Cu, Zn, Ni, Ag, Co, Cd (or of the ammines of such oxalates) are obtained by treating an alk. earth metal oxalate, such as $CaC_2O_4$, with an oxide or hydroxide of the metal whose oxalate is to be obtained, and with a sufficient quantity of $CO_2$ to convert the whole of the alk. earth oxalate into alk. earth carbonate, in presence of an aq. medium contg. sufficient $NH_3$ or other volatile alkali to render the desired metal oxalate (or oxalate ammine) sol. The reaction is, preferably, carried out by treating first the oxide or hydroxide with $CO_2$ in an aq. medium contg. volatile alkali and adding then the alk. earth metal oxalate. The obtained oxalates or oxalate ammines may be used for the manuf. of alkali metal hydroxides by treatment with an alkali metal salt and causticization of the obtained alkali metal oxalate according to $2\ NaCl\ (brine) + 3\ NH_3 + CuC_2O_4 \cdot NH_3 = Na_2C_2O_4 + CuCl_2 \cdot 4NH_3$ and $Na_2C_2O_4 + Ca(OH)_2 = CaC_2O_4 + 2NaOH$.

CA 35, 7129-5

Washing of Precipitated $Mg(OH)_2$
Ocean Salts (Products) Ltd.
Brit., 527,139, Oct. 2, 1940

The hydrous floc material is dried prior to washing to produce a granular material which readily yields up impurities in the washing operation without reassuming its hydrous floc form. The drying is effected by heating the material rapidly to a temp. exceeding 90° in a rotary or other drier to expel the bulk of the $H_2O$ of hydration.

CA 35, 7666-4

Powdered Dry Calcium Hydroxide
G. and W. H. Corson, Inc.
Brit., 529,481, Nov. 21, 1940

Quicklime is caused to react with an excess of $H_2O$. The resulting, wet, slaked quicklime is dried by effecting a finely divided particle dispersion thereof under conditions causing the conversion of the excess $H_2O$ into steam which vaporizes off leaving a substantially dry lime hydrate....

CA 35, 8220-8

Twenty Years of Progress in Caustic Soda
J. C. Leppart
Soap 17, No. 7, 28-30, 67, 69-70 (1941)

CA 35, 8220-9

Potash
Dale C. Kieffer
Mineral Ind. 49, 505-19 (1940)

Production in the U. S. and foreign countries, imports and exports and market are discussed.

CA 35, 8224-9

Recovery of Lithium from Minerals
Gruvaktiebolag
Brit., 530,028, Dec. 3, 1940

Lithium minerals are lixiviated with aq. solns. of salts such as alk. chlorides or alk. nitrates which do not augment the soly. of $Li_2CO_3$. In the lixiviation of spodumene with a $NaNO_3$ soln., it will thus be possible to obtain a concn. of Li in the lixivium of 8-10 gm. of Li per $\ell$ which concns. may easily be lowered below 1 g. per $\ell$ by the admixt. of $Na_2CO_3$ with the boiling liquor. The LiOH is recovered from the Li-contg. liquor.

CA 36, 228-7

Concentrating Aqueous Alkali Metal Hydroxides
Brit., 519,416, March 27, 1940

An aq. alkali metal hydroxide having a concn. of at least about 50% is concd. by treating the hydroxide soln. with a liquid, water-sol. amine having such a concn. that it is capable of absorbing water from the hydroxide and removing the amine and the absorbed water. Brit., 519,616, April 1, 1940. Addn. to Brit., 519,416 (above). A process of concg. aq. alkali metal hydroxide, such as aq. NaOH, consists in treating the hydroxide with a quantity of liquid, water-sol. amine, or $NH_3$, having such a concn. that it is capable of absorbing water from the hydroxide to produce a liquid concentrate of the hydroxide and a second layer comprising dild. amine, regulating the temp. and the amine-hydroxide ratio in a manner as to cause the pptn. of solid hydroxide and removing the amine with its absorbed water.

CA 36, 734-4

Corrosion Resistant Materials for the Manufacture of NaOH
A. I. Sheskin
Korroziya i. Borba s. Nei 5, No. 3-4, 106-107 (1939)

The tubes of vacuum evaporators used in NaOH manuf., when made of C steel, or of cast-iron contg. much C, or Cr-Ni metals wear out in 15-90 days. Steel contg. 5% or more of Ni does not corrode even when the concn. of

NaOH soln. reaches the limit of 1000 g/ℓ. Steel with 4.5-5% Ni corrodes more the less Ni is present. Steel with 1.7% Ni and 0.3% Cr corrodes slightly, yet is 30 times more resistant than C steel (with 0.01-0.1% C). Steel contg. C 0.1-0.16, Ni 1.7-2.3 and Cr 0.2-0.5% is recommended as protective material in NaOH manuf.

CA 36, 740-1

Alkali-Resistant Coating for Metals
Brit., 522,077, June 7, 1940

A method of preventing contamination of an alkali metal hydroxide by a metal with which it is in contact consists in coating the metal surface to be exposed to the alkali metal hydroxide with a water-insol. ether of cellulose admixed with a plasticizing agent consisting of an alkyl naphthalene or benzylnaphthalene.

CA 36, 1745-2

Sodium Hydroxide
Alex Rudner
Can., 401,440, Dec. 16, 1941

$Ag_2O$ is dissolved in $NH_3$, treated with a soln. of NaCl to produce NaOH and AgCl, the NaOH sepd. from the AgCl, the AgCl dissolved in $NH_3$, treated with $H_2S$ to form $Ag_2S$ and $NH_4Cl$, the $Ag_2S$ filtered off, the $NH_4Cl$ treated with $H_2SO_4$ to form $(NH_4)_2SO_4$, and HCl and the HCl gas are recovered. An app. is described.

CA 36, 1829-7

Adsorption by Strontium Salts of Traces of Iron from Caustic Soda Solutions
Wm. E. Caldwell and Charles A. Boyd
Ind. Eng. Chem. 34, 230-3 (1942)

The iron impurity in com. caustic soda solns. prepd. by electrochem. methods is chiefly in the form of the $FeO_4^{--}$ ion, and possibly also of $FeO_3^{--}$ and $Fe_2O_4^{-}$ ions. The removal of this iron impurity by finely ground $SrSO_4$ and $SrCO_3$ may be represented by the Freundlich adsorption isotherm, and therefore is essentially an adsorptive process. $SrSO_4$ is a better adsorbent than $SrCO_3$ at 30°, and both are better than Ca and Ba sulfates and carbonates. At higher temps. $SrCO_3$ approaches $SrSO_4$ in effectiveness but both improve in ability to remove iron impurity with increasing temp. The proposed mechanism for the adsorption is an exchange reaction at the surface of the adsorbent with the resulting formation of Sr ferrate, perferrate or ferrite on this surface. According to this mechanism the efficiency of the iron removal depends chiefly on the soly. of the Sr mineral and the soly. of the resulting Sr ferrate, perferrate or ferrite.

CA 36, 2095-4

Alkali Hydroxides
Max Enderli, Hermann Sutter and Helmut Keller
Ger., 707,152, May 15, 1941

Alkali hydroxides are produced by heating the alkali formates with $Fe_2O_3$ to 700-800° and leaching the alkali ferrite with hot water. Before decompg. the ferrite any alkali carbonate that may have formed is leached out with cold water. Roasted pyrite is used as a source of $Fe_2O_3$.

CA 36, 3325-9

Twenty Years of Progress in Caustic Soda
J. C. Leppart
Pittsburgh Plate Products 50, No. 1, 9, 21 (1942); CA 35, 8220-9

Historical discussion of manufg. operations in the U. S.

CA 36, 3327-8

Purification of Alkali Hydroxide Solutions
Deutsch Solvay-Werke Akt.-Ges.
Ger., 682,454, Sept. 28, 1939

Dissolved Si is removed from alkali hydroxide solns. by heating them at approx. 95° in the presence of $Al_2O_3$ and an alk. earth compd. to form an insol. alk. earth aluminosilicate. The $Al_2O_3$:$SiO_2$ ratio is considerable; thus, if a Ca compd. is used the ratio is 1:3. Suitable sources of $Al_2O_3$ are minerals contg. it, e.g., bauxite. The alk. earth can be supplied as CaO, $Ca(OH)_2$, $CaCO_3$, $CaSO_4$, etc.

CA 36, 3421-7

Specific Heats and Heats of Dilution of Concentrated Sodium Hydroxide Solutions
Howard R. Wilson and Warren L. McCabe
Ind. Eng. Chem. 34, 558-66 (1942) Cf. CA 30, 1645-7, 3307-5

The sp. heats of NaOH solns. were measured calorimetrically over a concn. range of 50.2-75.9% by wt. and a temp. range of 30-122°. The heats of diln. were detd. over a concn. range of 48.64-75.51% by wt. at 200°F. An enthalpy-concn. chart covering the range of 0-80% by wt. and 32-400°F. is given. The enthalpies at the higher temps. were obtained by extrapolating the sp.-heat data.

CA 36, 3768-4

The Effect of Corrosion of the Apparatus on the Purity of Chemical Reagents
E. Malakhovskaya
Trans. Inst. Pure Chem. Reagents (USSR) No. 17, 80-9 (1939);
Khim. Referat. Zhur. 1940, No. 5, 84-5

The use of rustproof steel in making app. used in the production of chem. reagents was investigated. The resistance to corrosion was detd. from the amt. of Fe and Ni dissolved in the reaction mixt. Ag can be replaced by the Russian steel EYal for the production of cryst. soda. Steel EYalT is resistant to NaOH soln. at room temp.; it begins to corrode at 80-85°. Corrosion decreases with increasing NaOH concn., owing to the passivation of Fe. Cathodic protection of the steel (at c. ds. up to 3 amp/sq.m) preserves the steel somewhat from corrosion during the evapn. of NaOH solns., but does not resist fused NaOH. None of the steels tested is suitable for use in evapn. of NaCl soln. to dryness. Steel EYalT and furodite (cf. CA 35, 5079-5) can be used in the manuf. of $NaH_2PO_4$. Steel EYaZS is recommended only if $H_3PO_4$ is added to the soda soln. instead of the soda soln. to $H_3PO_4$.

CA 36, 3917-3

Solid Caustic Alkali
Irving E. Muskat and Dwight R. Means
U. S., 2,273,722, Feb. 17

A process is employed for dehydrating an aq. soln. of an alkali metal hydroxide, at a pressure below 16 in. of Hg, to insure pptn. of granules of alkali metal hydroxide during dehydration, which involves preventing substantial corrosion of the dehydrating equipment by the hydroxide and contamination of the hydroxide by mixing a nonreactive liquid coating agent, which is substantially nonvolatile at the temp. of dehydration, with the aq. hydroxide and dehydrating the hydroxide, the concn. of the agent in the mixt. being of sufficient magnitude to cause formation of a corrosion-resistant film upon the walls of the evaporator and upon pptd. granules of the hydroxide.

CA 36, 4015-9

The Solubility of Sodium Carbonate in Fused NaOH
Ralph P. Seward
J. Am. Chem. Soc. 64, 1053-4 (1942)

F.-p. data are given for NaOH-$Na_2CO_3$ mixts. up to 35% carbonate. The f.p. of NaOH is 320° and the transformation point 294°. The addn. of $Na_2CO_3$ reduces the f.p. until a eutectic at 286° with a $Na_2CO_3$ content of 22% is reached. The heat of fusion of NaOH was calcd. to be 1670 cal. per mole.

See also (1) Neumann and Bergve, Z. Elektrochem., 20, 271 (1914); "International Critical Tables," Vol. IV., p. 67.
(2) Halla and Tompa, Z. anorg. Chem., 219,321 (1934)
(3) Von Heversy, Z. Physik. Chem., 73,667 (1910)
(4) Antropoff and Sommer, Ibid. 123,165 (1926)

TABLE I

Temp. Compn. Data

| $Na_2CO_3$ Wt.% | Freezing Temp. °C | Transition Temp. °C | Eutectic Temp. °C |
|---|---|---|---|
| 0.4 | 319 | 294 | --- |
| 2.4 | 316 | 294 | --- |
| 4.3 | 313 | 294 | 286 |
| 7.1 | 307 | 294 | --- |
| 9.7 | 301 | 294 | 286 |
| 12.2 | 295 | --- | --- |
| 14.6 | 292 | --- | 286 |
| 19.0 | 288 | --- | 286 |
| 22.8 | 292 | --- | 286 |
| 25.3 | 320 | --- | 286 |
| 26.6 | 333 | --- | --- |
| 27.9 | 342 | --- | 286 |
| 29.4 | 354 | --- | --- |
| 30.8 | 367 | --- | --- |
| 33.1 | 381 | --- | --- |
| 35.1 | 395 | --- | 286 |

| | Fr. pt., °C | Trans. pt., °C |
|---|---|---|
| Ref. 1 | 296 | --- |
| 2 | 328 | 295 |
| 3 | 318 | 299 |
| 4 | 322 | 304 |
| This Report | 320 | 294 |

CA 36, 4296-8

Caustic Soda
Wm. C. Moseley (to the Mathieson Alkali Works)
U. S., 2,275,792, March 10

In treating $Na_2CO_3$ with lime, a max. concn. of $Na_2SO_4$ is maintained, not substantially exceeding 0.0025% of the NaOH present after causticization, and pptn. and settling of $Na_2CO_3$ and $Na_2SO_4$ are effected from the causticized liquor while maintaining such max. concn. of $Na_2SO_4$.

CA 36, 4763-7

Purification of Alkali Metal Hydroxide Solution
Edward T. Ladd
Can., 405,161, June 2, 1942

By electrolysis-chlorides and hypochlorites in alkali soln. are converted to chlorates, substantially insol. in the soln., and metal impurities are deposited on the cathode.

CA 36, 5760-5

Investigations of the Inhibiting Action of Potassium Permanganate and Sodium Chromate in the Attack of Al by NaOH
Lilli Reschke and Heinrich Neunzig
Aluminum 23, 358-62 (1941)

The inhibitory action of $KMnO_4$ and $Na_2CrO_4$ solns. in the attack of NaOH on 99.6% Al, as rolled and soft annealed, and on 99.99% Al, as rolled, was detd. at room temp. for 1,5 and 24 hrs. duration of the attack with concns. of 0.3, 0.5 and 1%; the amt. of the addns. was 0.1-3%. A permanent protective surface is obtained on 99.6% Al if the ratio NaOH:$KMnO_4$ is about 1:3 in the solns. A complete stoppage of the reaction is, however, obtained in very few cases. The inhibitory effect of $KMnO_4$ is stronger than that of $Na_2CrO_4$. The conditions are similar for purest Al, but with $Na_2CrO_4$ as inhibitor, often a slighter loss of wt. is found than for $KMnO_4$ addn. although the surface showed a stronger action of the NaOH.

CA 36, 6761-4

Purifying Alkali Metal Hydroxide Solutions
Muskat and Ayres
U. S., 2,285,299, June 2

For purifying a soln. such as one of NaOH contg. a substantial amt. of silica as an impurity, a treatment is employed which involves adding $NH_3$ to the soln. in an amount sufficient to cause pptn. of silica but insufficient to cause sepn. of 2 liquid phases, maintaining the temp. (suitably at about 60° under 240 lbs. per sq. in. pressure) such that pptn. of a substantial portion of solid hydroxide does not occur, removing pptd. silica from the soln., and sepg. the $NH_3$ from the purified soln.

CA 36, 6761-4

Concentration of Caustic Alkali
Muskat
U. S., 2,285,300, June 2

A method is employed for prepg. concd. NaOH which involves treating a soln. contg. at least about 40% of NaOH with a substantial amt. of $NH_3$

in such conc. that a sepn. of liquid phases does not occur and maintaining the temp. such that a solid hydrate of concn. higher than that of the soln. is pptd. Cf. CA 36,288

CA 37, 504-7

Purification of Concentrated Alkali Liquors
Kali-Chemie Akt.-Ges.
Ger., 707,175 (Cl. 12*l*)

Concd. alkali liquors contg. Fe are purified by adding to them alkali ferrite or substances forming it in such amts. that the dissolved alkali ferrite separates at temps. above the crystn. point of solid alkali hydroxide. The cryst. slime contg. the alkali ferrite is then sepd.

CA 37, 1917-1

Surface of Contact of the Phases as the Main Factor of Chlorination of Sodium Sulfate
B. A. Kopylev and L. P. Svyatnaya
J. App. Chem. (U.S.S.R.) 14, 783-9 (1941)

The reaction of $Na_2SO_4$ with Cl was investigated and shown to be a surface interaction. Optimal conditions for chlorination are: temp. of 950-1000° and max. surface of the reacting materials. Treatment of $Na_2SO_4$ with Cl combined with the process of electrolysis of NaCl is a basis for a new method of utilization of the sulfate for production of NaOH and $H_2SO_4$.

CA 37, 2277-6

Electrolytic Process for the Preparation of Alkali Hydroxide Solutions
Hubert L. Stewart
Ger., 706,834, May 8, 1941

The hydroxides are prepd. electrolytically from solns. of alkali salts of polybasic acids. The app. is described.

CA 37, 2287-8

Reaction of Columbium Pentoxide with Sodium Hydroxide. I.
V. I. Spitsyn and A. V. Lapitskiĭ
J. App. Chem. (U.S.S.R.) 15, 194-203 (1942)

The action of solns. of NaOH upon $Cb_2O_5$, anhyd. Na metacolumbate and hydrated Na metacolumbate, and of $H_2O$ upon the melt of NaOH and $Cb_2O_5$ was studied. Calcined $Cb_2O_5$ can react with NaOH solns., forming a salt $Na_{14}Cb_{12}O_{37}\cdot 32H_2O$. Anhyd. metacolumbate is practically insol. in $H_2O$ and does not react with NaOH solns. Hydrated metacolumbate readily reacts

with NaOH, giving the above salt. The observations made by Bedford (J. Am. Chem. Soc. 27, 1216 (1905) were confirmed, in that treatment with $H_2O$ of the melt of $Cb_2O_5$ with NaOH forms the above salt. The melt cannot contain anhyd. Na metacolumbate. It is proposed that upon melting together of $Cb_2O_5$ with excess NaOH there is formed a columbate more rich in NaOH than the above, and by hydrolysis, or simple addn. of $H_2O$, it is convertible into the above salt. Soly. data are given for the above salt in water and NaOH solns. (from 0 to 1g./100 cc. concn.).

CA 37, 2666-6

Electrolytic Production of $Mg(OH)_2$
Deutsche Solvay-Werke A.-G.
Ger., 719,169, March 5, 1942 (Cl. 12m. 3)

$Mg(OH)_2$, practically free of chlorides, is produced electrolytically from alkali-poor $MgCl_2$ solns. using a diaphragm between the anode and cathode compartments. Particularly suitable are K end liquors. The sulfate-contg. solns. with at least 0.5 g. of $SO_3$ per liter are electrolyzed at a cathodic c.d. of 60-90 amp. per sq. m. and an initial concn. of 200-100 g. of $MgCl_2$ per liter. The catholyte is preferably stirred.

CA 37, 2673-6

Chemical Interaction of Metallic Antimony with Water and Alkalies
B. A. Nekleevich
Khim. Referat. Zhur. 4, No. 2, 26 (1941)

Metallic Sb was heated with water and with alkali in the absence of air at ordinary and higher pressures. Stibine and O compds. of trivalent and quinquevalent Sb are found in the reaction products. On heating with solid alkali, Sb reacts completely, forming H, stibine, antimonite and antimonate.

CA 37, 2673-7

Chemical Interaction of Elementary Arsenic with Alkali
B. A. Nekleevich
Khim. Referat. Zhur. 4, No. 2, 27 (1941)

Arsenic in mixts. with water (in some of the expts.) and with alkali (in other expts.) was heated in the absence of air at ordinary and higher pressures. The As reacted especially energetically with anhyd. alkali. The reaction products contained arsine and O compds. of trivalent and quinquevalent As.

CA 37, 3235-1

Sodium Hydroxide
Ivor L. Clifford
Ger., 708,764, June 19, 1941

The sol. salt, especially Cu salt, produced in the course of the process is treated with $Ca(OH)_2$; thus $NH_3$ is liberated and CuO formed, which is filtered off and treated with Ca oxalate in the presence of $CO_2$ and excess $NH_3$ to form Cu oxalate complex and $CaCO_3$. The latter is filtered off and the soln. returned to the circuit.

CA 37, 3888-9

Concentrating Aqueous Solutions of Alkali Metal Hydroxides
Irving E. Muskat
U. S., 2,309,412, Jan. 26

A soln., such as one of NaOH having a concn. substantially below 65% is heated through a carbon wall for a time sufficient to concentrate the soln. to a concn. above 65% but not substantially above 75-80%.

CA 37, 4309-7

Alkali Amalgam Decomposition Cell Suitable for the Production of Sodium or Potassium Hydroxide
Wm. C. Gardiner (to the Mathieson Alkali Works)
U. S., 2,311,744, Feb. 23

In an app. in which an alkali metal from an anode of an amalgam of the alkali metal is caused to react with a superposed body of aq. electrolyte such as NaOH or KOH soln. in contact with the anode to form H and alkali metal hydroxide in a compartment thru which the amalgam moves, use is made of an approx. level grid composed of a plurality of cathode bars of "carbon" or graphite and a plurality of spacer strips each provided with holes into which the bars project in good elec. contact with the strips, the bars being held side by side but spaced from each other by the strips in the body in contact with the amalgam but out of contact with the bottom of the compartment, with the strips resting on the bottom in contact with the amalgam.

CA 37, 4309-9

Alkali Amalgam Decomposition Cell Suitable for the Production of Sodium or Potassium Hydroxide
Wm. C. Gardiner and J. L. Wood (to the Mathieson Alkali Works)
U. S., 2,311,745, Feb. 23

In an app. in which a moving body of an amalgam of Hg and an alkali metal such as Na is treated with an aq. body, such as NaOH soln. overlying the

amalgam, to produce H and alkali metal hydroxide, use is made of a cathode in the form of a series of upwardly projecting plates of graphite in contact with the amalgam and sepd. from each other by substantial but narrow spaces, these plates projecting upwardly into the aq. body for a substantial distance and to a level above any attained by the amalgam during its normal movement and being several times as high as the spaces are wide and disposed with their major surfaces in the direction of movement of the amalgam, and a massive metallic grid member resting on and in good elec. contact with the plates and formed of a metal such as Fe having a lower overvoltage with respect to H than does the graphite and which is resistant to the action of the aq. body but tends to amalgamate with Hg and become coated with it, and being disposed in contact with the aq. body but spaced a substantial distance from the amalgam and entirely above any level attained by the amalgam during its normal movement.

CA 37, 4537-6

Prevention of Contamination of Sodium Hydroxide Solution in Tank Cars
Arlie P. Julien and Otto Kay
Can., 412,463, May 11, 1943

To prevent contamination of a hot NaOH soln. in tank cars, Ni surfaces in contact with soln. at about 100° are made anode and an av. c.d. of 0.01-0.02 amp./sq.ft. of Ni surface is maintained between a Ni anode immersed in the NaOH soln. and the Ni surfaces. An app. is described.

CA 37, 4616a

Polymorphism of Bi Trioxide
W. C. Schumb and E. S. Rittner
J. Am. Chem. Soc. 65, 1055-60 (1943)

....The soly. of $Bi_2O_3$ in NaOH is found to be proportional to the NaOH concn. up to 2.46N, from which the mol. species present in the soln. is shown to be $NaBiO_2$.

CA 37, 4671-8

Laboratory Vessels of Gold-Platinum Alloy
K. W. Frohlich
Chem. Ztg. 66, 161-3 (1942)

So far as its phys. properties are concerned an alloy of 90 Au and 10 Pt is appreciably inferior to Pt only in its lower m.p. (1100-1190°). The alloy is resistant to $HNO_3$, $H_2SO_4$ and HF in all concns.; it is more resistant than Pt to hot concd. $H_3PO_4$, but is attacked more readily than Pt by aqua regia. Neither Pt nor the alloy is appreciably attacked by $KHSO_4$ below 400°, but at 600° a 50-cc. crucible of the alloy contg. 11 g. of $KHSO_4$ loses approx. 4 mg. in 20 min., as compared with 1.9 mg. for a

similar Pt crucible. Aq. alkalies do not attack the alloy except in the presence of oxidizing agents, in which case a slight action is observed. The alloy is several times more resistant than Pt to $Na_2CO_3$ or $K_2CO_3$ at 720° and to NaOH at 600°; the loss in wt. with NaOH is, however, much greater than that with the carbonates. Below 600° NaOH-$KNO_3$ mixts. have practically no effect on the alloy. Fused KCN attacks it badly. Blood ashing also attacks it, probably as a result of the intermediate formation of cyanides. All other ordinary ashing and igniting procedures can be carried out without damage. The alloy is less sensitive than Pt to P. Alloy electrodes can be used for the electrolysis of Cu in acid soln., Ni in $NH_3$ soln. and Zn in NaOH soln., although there is some loss in wt. of the anode in the Zn detn. Alloy electrodes cannot be used in the anodic Pb detn.; the reason for the loss in wt. in this case has not been found.

CA 37, 5224-2

Large Scale Simultaneous Production of Acetylene and Practically Dry Calcium Hydroxide
Edward Kalb (to Alexander Wacker Gesellschaft fur elektrochemische Industrie G. m. b. H.)
Ger., 722,909, June 4, 1942 (Cl. 26b. 41)

CA 37, 6418-2

$Mg(OH)_2$
Ocean Salts (Products) Ltd.,
Basil A. Adams and Theodore R. E. Kressman
Brit., 547,769, Sept. 10, 1942

Pure $Mg(OH)_2$ suitable for pharmaceutical requirements is prepd. from Mg-bearing material by converting the Mg into sol. Mg-bicarbonate and filtering it from the insol. residue from the Mg-bicarbonate soln. Mg basic carbonate is pptd., which is treated with NaOH to yield pure $Mg(OH)_2$ with the formation of $Na_2CO_3$. Cf. CA 36, 1447-5.

CA 37, 6827-2

NaOH and $Na_2CO_3$
Deutsche Solvay-Werke
Ger., 728,323, Oct. 22, 1942

In a continuous process, alk. earth carbonate is made to react with $K_2SiF_6$. The KF produced in this reaction is made to react with NaCl, thus obtaining NaF which in turn is converted to NaOH. The by-products, alk. earth fluoride, $SiO_2$ and KCl, are regenerated with HCl and returned to the circuit.

CA 38, 3-5

Filters Suitable for Use with Strongly Acidic, Alkaline or Oxidizing Materials
Walter Harz, Herbert Rein, Emil Hubert and Carl Kayser
U. S., 2,324,838, July 20

A filtering material substantially stable against inorg. chemicals is prepd. by heating a fabric or layer consisting of filaments of a polyvinyl resin to a temp. sufficiently high "partially to soften" the resin to adjust the porosity of the fabric or layer. The resin used may be polystyrene or a polyvinyl chloride or polyvinyl ether (use of various other materials also being mentioned.

CA 38, 282-9

Evaporating Water from Solutions Such as Those of NaOH
Vaman R. Kokatnur and Joseph J. Jacobs, Jr. (to Autoxygen, Inc.)
U. S., 2,326,099, Aug. 3

App. is described, and a method of operation for removing water in a continuous process by evapn. from an aq. soln. of a nonvolatile material, such as NaOH, that is solid at ordinary temps. and at temps. of about 300-500°F but undergoes coalescence causing adherence of its contacting particles when heated in the presence of water vapor to a temp. between approx. 300-500°F., which involves passing the soln. downwardly through a fractionating column adapted to effect intimate contact between a liquid and a vapor, simultaneously passing upwardly through the column the vapor of a liquid, such as kerosene, that is immiscible with the soln., maintaining the soln., and vapor thus brought into contact at the temp. of boiling of the mixt., so that boiling and fractionating ensue, condensing the vapors in part and returning the condensate so formed down the fractionating column so that the immiscible liquid is in intimate contact with the aq. soln. in the column, withdrawing from the upper part of the column the remaining fractionated mixt. of vapors of water and the immiscible liquid, condensing the withdrawn mixt. of vapors, sepg. the resulting condensate into an aq. and a nonaq. layer, returning the nonaq. layer to the fractionating column, withdrawing from the lower part of the column a slurry contg. the immiscible liquid and the nonvolatile solid material in substantially completely dewatered condition, and sepg. the dewatered material from the slurry, as by centrifuging and washing with a selective solvent for the kerosene.

CA 38, 459-8

Caustic Alkali Purification
Irving E. Muskat (to Pittsburgh Plate Glass Co.)
U. S., 2,325,339, July 27

A process is employed for purifying NaOH which involves treating it in an aq. soln. also contg. NaCl, with a substantial amt. of $NH_3$ in a concn. such that a sepn. of a liquid phase does not occur, but sufficient to

cause pptn. of a solid hydrate under the temp. of operation (which may be about 10-25°) and maintaining the concn. of the remaining soln. such that at the end of the pptn. the soly. of NaCl is sufficiently high to retain at least most of the total quantity of NaCl in the initial soln.

CA 38, 461-6

Evaporator Suitable for Concentration of NaOH Solution Containing NaCl
James E. George (to Westvaco Chlorine Products Corporation)
U. S., 2,326,024, August 3

Various structural and operative details are described for reducing or preventing the deposition of incrustations on the upper tube sheet of a vertical-tube steam-heated calandria, this tube being above the normal liquid level in the evaporator.

CA 38, 922-7

Electrolytic Cell Suitable for Cl and NaOH Production from NaCl Solns.
Umberto Pomilio (to Pomilio Corp. Ltd.)
U. S., 2,329,726, Sept. 21

Various structural details of a cell having a porous graphite anode.

CA 38, 1154-8

Concentrating Solutions Depositing Crystals Such as Solutions of Electrolytically Produced NaOH Containing NaCl
Martin J. Kermer (to Buffalo Foundry and Machine Company)
U. S., 2,330,221, Sept. 28

Numerous details of app. arrangement and operation are described, for a process of sepg. a crystallizable material, such as NaCl, from its solution in a solvent, such as aq. NaOH solution, in which process of a stream of the solution is passed progressively through a plurality of evaporator units of a multipleunit evaporator in which the solution is progressively concd. and crystals are formed. The process involves preconcg. the solution in the stream in one stage of its transfer to the evaporator, heating the solution in the first unit of the evaporators through which the solution passes by heat exchange with the vapors generated from the solution while in a subsequent unit in the progression through which the solution passes, heating the solution in such subsequent unit, cooling the preconcd. solution before it passes to the mentioned first unit, sepg. a slurry of the crystals from the solution in the units and washing the slurry of crystals so sepd. with the cooled and preconcd. solution.

CA 38, 1330-6

Alkali Hydroxides or Carbonates
Fritz Gewecke
Ger., 734,216, March 11, 1943 (Cl 121.13)

The continuous process involves a reaction between alkali fluosilicates and alk. earth carbonate. This yields alkali fluoride in soln. and a ppt. The alkali fluoride is used for converting it into a hydroxide or carbonate. The ppt. is changed into a fluosilicate and returned into the circuit. The reaction between the fluosilicate and the carbonate is done under conditions such that the resulting soln. contains at least 120 g. per l. of KF.

CA 38, 1614-4

Transportation of NaOH in Tank Cars
Robert B. MacMullin
U. S., 2,332,242, Oct. 19

A method of operation is employed which involves substantially filling a tank car with solid caustic soda in the form of relatively cool, free-flowing particles contg. about 65-85% NaOH, and discharging the tank car by first introducing relatively cool water into the bottom of the car in an amount sufficient to form an aq. NaOH soln. liquid at ordinary atm. temp. but insufficient to cause a temp. rise of more than about 100°F. and insufficient to cause the temp. to rise above about 147°F. and thereafter, without further diln., running off the resulting liquid soln. of the NaOH from the tank car. App. is described.

CA 38, 2457-5

Intensification and Rationalization of the Preparation of NaOH by the Löwig Method
P. G. Laskaviĭ
J. Chem. Ind. (U.S.S.R.) 18, No. 6, 1-4 (1941); Chem. Zentr. 1942, II, 2629

Improvements are suggested in the construction of the app. and the treatment and regeneration of the reagents.

CA 38, 2573-6

Hg Cathode Electrolytic Cell Suitable for Electrolyzing Aqueous NaCl Solutions
Chester N. Richardson (to the Mathieson Alkali Works)
U. S., 2,334,354, Nov. 16

Various details of a cell having a compartment, an electrode of Hg amalgam contg. an alk. metal such as Na on the bottom of the compartment, an aq. electrolyte such as NaCl soln. overlying the amalgam electrode and a second

electrode such as one of graphite disposed in the electrolyte; use being made of a steel bottom consisting of a plate section, and various structural details of its attachment to side members being described.

CA 38, 3097-7

Decomposing Alkali Metal Amalgams to Form Alkali Metal Hydroxides and Alcoholates
Maurice C. Taylor
U. S., 2,336,045, December 7, 1943

App. is described, and a process is employed which involves the reaction of alkali metal from an amalgam with water or an alc. contg. not more than 3 atoms of C per mol., by passing the amalgam and liquid in countercurrent contact with each other through a space contg. an electrode in the form of a packing of electrically conductive material, such as graphite in small pieces, with which Hg does not amalgamate substantially and which is preferentially wetted by the liquid, the packing being maintained submerged in a pool of the amalgam, and the liquid moving through the amalgam and passing over the packing in the form of a thin film.

CA 38, 3111-7

The Effect of Additives, Especially of Ash Components, on the Alkali-Activated Water-Gas Process at Atmospheric, Reduced and Superatmospheric Pressure
C. Kroger and R. Schbert
Oel u. Kohle 39, 756-69 (1943)

Since in the water-gas reaction only a slight retarding effect of some metal oxides was noticed, it is assumed that in this case no compd. formation between alkali and oxide takes place. The equil. of this reaction was studied by detg. the vapor pressure of the water formed in the reaction 2 KOH + metal oxide = $K_2O$ · metal oxide + $H_2O$. Pressures are given for LiOH at 600-800°, 2 LiOH and PbO at 400-800°, 4 LiOH and PbO at 500-700°, 2 LiOH and CaO at 500-650°, 2 LiOH and CuO or $SnO_2$, resp., at 400-550°. The formation of the following compds. is assumed from these data: $Li_2O \cdot PbO$, $Li_2O \cdot CuO$, $Li_2O \cdot CaO$, $Li_2O \cdot SnO_2$. The investigation of KOH by the same method showed the highest pressures on addn. of CdO, MnO and PbO. The existence of the following compds. is probable: $K_2O \cdot CdO$, $K_2O \cdot MnO$, $K_2O \cdot CuO$, $K_2O \cdot PbO$, $K_2O \cdot Cr_2O_3$, $K_2O \cdot SnO_2$, $K_2O \cdot ThO_2$. The promoter effect of $Cr_2O_3$ for the steam conversion is due to incomplete compd. formation with KOH at 700° and activation of the steam decompn. by K and also the increased sorption effect of the coal contg. the oxide. The retarding effect of $MoO_3$ results from the formation of a compd. that is not reduced by C. Similar conditions prevail in the case of $TeO_2$, $U_3O_8$, $La_2O_3$, $CeO_2$ and $ThO_2$ probably do not form compds. with KOH under the conditions investigated and are effective by interaction with metallic K. The easily reducible oxides, CdO, PbO, $Tl_2O$, MnO and PtO, form alloys with K; these alloys then react with steam.

CA 38, 3913-9

Electrolytic Production of NaOH and Bicarbonate from Sodium Carbonate in Solution
Hubert L. Stewart (to Koppers Co.)
U. S., 2,340,254, Jan. 25, 1944

App. is described and a mode of operation is employed which involves continuously and repeatedly circulating a soln. of $Na_2CO_3$ (suitably of about 1.5-2 lb. per gal. initial strength) within a temperature range of about 60-80°, thru the anolyte chamber of an electrolytic diaphragm cell, such temp. being employed for maintaining in soln. $NaHCO_3$ electrolytically produced in the anolyte chamber, and while withdrawing from the latter chamber the resultant soln. contg. the electrolytically produced completely dissolved $NaHCO_3$ and converted $Na_2CO_3$ subjecting the anolyte chamber and catholyte chamber to controlled differential pressure by means of separately entrapped gases from the chambers so as to effect passage of some of the anolyte soln. thru the diaphragm and generating NaOH soln. in the catholyte chamber of the cell to concns. up to about 25% and thus avoiding caking out of solid NaOH on the cathode and, in the course of the process, separately withdrawing from the cell so-formed soln. contg. the NaOH, lowering the temp. of withdrawn soln. contg. $NaHCO_3$ and $Na_2CO_3$ to effect solidification of $NaHCO_3$ while maintaining the $Na_2CO_3$ in soln., and returning the $Na_2CO_3$ soln. to the anolyte chamber for the generation of addnl. $NaHCO_3$ and NaOH.

CA 38, 4389-8

Dewatering Alkali Hydroxide Liquors
Paul Ernst, Hans Scheidemandel, Matthias Thoma and Hugo Zoebelein
Ger., 738,657, July 22, 1943

For dewatering alkali hydroxide liquors containers are used made of e.g., C, graphite, fused magnesia, etc. This container is placed within a heated metal kettle. The space between is filled with alkali hydroxide.

CA 38, 4860-2

The Process of Fusion. II. The Molar Entropy of Fusion of Inorganic Salts
Chr. Finbak
Tids. Kjemi Bergvesen Met. 2, 67-8 (1942); Chem. Zentr. 1943, I, 933-4; Cf. CA 35, 7775-2

The molar entropies of fusion of the halogen salts of univalent metals (Li, Na, K, Rb, Cs, Tl) and of their nitrates and hydroxides are of the same order of magnitude (2.57 - 15.5 cal. $mole^{-1}$ $degree^{-1}$). The av. entropies for the ions are larger in the first case and particularly small for alkali hydroxides. The general rule results that in all substances in a group approx. the same amt. of translational energy must be made available to a

particle (atom, ion or mol.) for the transition from the solid to the liquid state. This holds if the particle cannot absorb rotational energy in the melting process.

CA 38, 6057-5

Losses in Recovery of NaOH in Causticizing Operations
L. Grunberg
Ind. Chemist 19, 628-32 (1943)

The losses due to incomplete conversion and the formation of pirssonite and gaylussite in $Na_2CO_3 + Ca(OH)_2 \longrightarrow 2\ NaOH + CaCO_3$ have been studied. Conversion fell from 95% to 80% and recovery ($NaOH + Na_2CO_3$) from 98% to 90% with rise of original $Na_2CO_3$ concn. from 10% to 23%. For continuous causticization, with NaOH make-up, recoveries are improved because of the build-up of $Na_2CO_3$.

CA 38, 6140-9

Receptacles Such as Tank Cars for Holding Caustic Alkali Solutions of about 50% or Higher Concentration
Irving E. Muskat
U. S., 2,354,824, August 1, 1944

A metallic receptacle such as a tank or tank car is provided with an interior surface coating of a compn. comprising a benzene-sol. ethylcellulose or the like and polystyrene, with a pigment if desired, such as mica or $TiO_2$, or various other admixts.

CA 38, 6428-7

Agents for the Transmission of Heat at High Temperatures
J. Spangler
Z. Ver. deut. Ing. 87, 356, (1943)

Water, glycerol and mineral oils of high b.p. are no longer used for the transmission of heat at high temps. Biphenyl, phenyl ether and a mixt. of the 2 sepg. as a eutectic have proved to be satisfactory for continuous operation up to 350° and for short periods up to 400°. The thermal properties of the eutectic mixt., which is liquid at room temps., are reported. This mixt. is stable in the vapor state and can be used in that state. Its thermal transmission nos. are 1/4 and 1/5 those of water between 250 and 350° but they are high enough. Org. substances which are premanently stable above 400° are not known. Of inorg. substances, Hg is most suitable, although its use is difficult for practical reasons. The use of salt melts at high temps. (up to 600°) is discussed. A eutectic mixt. of KOH and NaOH (both anhyd.) is recommended for high temps.

CA 39, 26-6

Continuous Concentration of Electrolytic NaOH
Martin J. Kermer
Trans. Electrochem. Soc. 86, 11 pp. (preprint) (1944)

A process for concg. electrolytic NaOH cell liquor by a high-pressure pre-evaporator of the natural-circulation type, producing vapors at comparatively high pressure, to be used in the steam chest of the first-effect evaporator of a double-effect, forced-circulation backflow-type machine. The cell liquor is concd. in the pre-evaporator below the crystg. point of the NaCl. This liquor is then flashed into a flash chamber, producing vapors for the steam chest of the second effect of the double-effect evaporator, while the liquor produced in the flash chamber is cooled to a lower temp. and produces a soln. with a small quantity of NaCl crystals in suspension. This soln. is to be used for washing the salt slurry produced by the double effect. The salt slurry produced in the double effect is continuously removed. The salt slurry removed from the salt separator of the first effect is pumped into the lower part of the second-effect evaporator. This slurry is washed in the lighter NaOH soln. contained in the second effect and mixed with the salt pptd. in that effect. This is the total amt. of salt produced in the double-effect evaporator, which in turn is now washed with the lighter NaOH soln. produced by the flash chamber, which is accomplished in an especially designed salt separator known as the main slurry tank. Nearly all the salt is now contained in crystal form in a satd. NaCl soln., with a comparatively low alkali content, which in turn is filtered and washed. The clear caustic liquor produced is fed to the evaporator storage tank from where the second-effect evaporator is fed. The clear liquor produced by the salt separator of the second-effect evaporator is pumped into the first-effect evaporator, while the clear concd. liquor is removed from the salt separator of this effect and fed into a flash chamber, where it is exposed to a higher vacuum resulting in cooling and evapn., while a small quantity to salt is pptd. This is the final product which can then be further cooled, if desired.

CA 39, 591-3

Production of Highly Concentrated Alkaline Liquors by Decomposition of an Alkaline Amalgam
I. G. Farbenind A.-G.
Belg., 445,474, June 30, 1942

The amalgam is heated to about 100° by countercurrent heat exchange with the Hg resulting from the decompn. The rates of flow of the amalgam and Hg and the amt. of water fed to the decompn. tower are regulated so as to obtain a highly concd. liquor.

CA 39, 593-4

Treatment of $Na_2SO_4$
R. O. Meyer
Belg., 444,489, March 31, 1942

$Na_2SO_4$ is decompd. in the pulverized state at 100° into $SO_2$ and NaOH liquor in presence of $CO_2$ and $H_2O$.

CA 39, 791-4

Treatment of $Na_2SO_4$ Obtained from Viscous Precipitation Baths and other Industrial Alkali Sulfate Solutions
Zellwolle-and Kunstseide-Ring G. m.b. H.
Belg., 445,862, July 31, 1942

A mixture of sulfate and $Al_2O_3$ (in the proportion of 1:2) is calcined at 800-1000° in a current of a reducing gas and, at the end of the operation, in an oxidizing atm.(air). The $SO_2$ is converted into $H_2SO_4$ and the Na aluminate is used as such or hydrolyzed to NaOH and $Al_2O_3$, which is returned to the cycle.

CA 39, 875-2

Solution of Soda and S, with or without $H_2SO_4$, From $Na_2SO_4$
Belg., 447,103, Oct. 31, 1942

$Na_2SO_4$ is reduced to $Na_2S$, which is dissolved and made to react with $Na_3Fe(CN)_6$. The S formed is sepd. and the solution is reconverted electrolytically into an $Na_3Fe(CN)_6$ solution (which is returned to the cycle) and NaOH.

CA 39, 1027-7

Purification of Caustic Soda
Irving E. Muskat (to Pittsburgh Plate Glass Co.)
U. S., 2,349,596, May 23, 1944

As an illustration of the process, anhyd. NaOH (contg. about 2% by wt. of NaCl) 1 is agitated with a mixt. (contg. $NH_3$ 55 and $H_2O$ 45%) 2.4 parts at 60°. The mixt. is allowed to settle into 2 layers. Upon withdrawing the lower layer and removing $NH_3$, a soln. was obtained contg. 55% NaOH; 0.2% of NaCl was also secured. The process may be continued; the mixt. is allowed to cool to 25°, whereupon the liquid phases are merged and a solid hydroxide is pptd. which contains NaOH 64 and NaCl 0.3%. The amt. of $NH_3$ and $H_2O$ used in the process is not critical but it is preferred that the ratio should be approx. 1:3. Cf. CA 38, 459-7.

CA 39, 1967-1

Producing K salts from Swedish Raw Material
J. A. Hedvall and Sven Nordengren
The Swedberg (Mem. Vol.) 1944, 113-39

Alum slate, treated to give shale oil, leaves a residue contg. 5% $K_2O$. This is the cheapest source of K in Sweden. This raw material and limestone in equal parts, plus 1/20 part pyrites, heated to 1200°, gives a 70% yield of K as $K_2SO_4$. The residue, limestone and NaCl, heated to 900°, gives a K yield of 90% as KCl. A still better yield of K results if the residue is mixed with $Ca(OH)_2$ and subjected to a steam pressure of 12-20 kg. per sq. cm., giving KOH.

CA 39, 3129-8

Concentrating Alkali Metal Hydroxide
Irving E. Muskat (to Pitts. Plate Glass Co.)
U. S., 2,373,257, April 10, 1945

Concd. NaOH is obtained by treating aq. solns. contg. at least 40% NaOH at 45° with $NH_3$ in amts. sufficient to cause the formation of a liquid phase contg. most of the NaOH, adding more $NH_3$ while cooling until the 2 phases merge into a single liquid phase, whereupon solid NaOH of about 68% is pptd. Higher temps. and larger amts. of $NH_3$ increase the concn. of the resulting NaOH.

CA 39, 3636-4

Purification of Alkali Hydroxide Solutions
Gardner W. Vose
U. S., 2,364,882, Dec. 12, 1944

Add to an aq. alkali hydroxide soln. to be purified a 1-10% Ni salt soln. in such a quantity that the Ni salt equiv. is 0.1-0.5% of the hydroxide. Allow the soln. to settle out and sep. all the insol. impurities from the hydroxide soln.

CA 39, 4000-6

The Melting Point and Heat of Fusion of $Ba(OH)_2$
Ralph P. Seward
J. Am. Chem. Soc. 67, 1189-91 (1945)

The m.ps. of $Ba(OH)_2$ and of solns. of $BaCO_3$, $BaCl_2$, $BaBr_2$, and NaOH in fused $Ba(OH)_2$ were measured by the cooling-curve method. The observed m.p. of $Ba(OH)_2$ was 408 ± 1°, and its heat of fusion calcd. as 3400 ± 100 cal. per mole. The observed f.p. lowerings are consistent with complete dissocn., with ion activities proportional to their mole fractions.

CA 39, 4238-6

Corrosion-Resistant Coating Compositions
Irving E. Muskat (to Pittsburgh Plate Glass Co.)
U. S., 2,379,246, June 26, 1945

A metallic container is internally protected by a coating of an alkali-insol. cellulose ether and an ester contg. 2 unsatd. groups in which the unsatn. is in an aliphatic straight C chain and is attached to the second C atom from a carbonyl group. The coating is used to protect metallic containers for storing 65-80% NaOH at over 150°F. and also for the manuf. of soap. Ethyl cellulose gives satisfactory protection against corrosion except at over 220°F. and in 3-20% NaOH at lower temps., but is seriously deteriorated when the container is washed with water. The heat and water resistance of the cellulose ether is materially improved by the addn. of an organic compd. with at least 2 polymerizable groups such as diethylene glycol bis (allyl carbonate) or glycol dimethacrylate. A peroxy polmerization catalyst may be added. The coating compn. is dissolved in a suitable solvent applied, allowed to dry and then polymerized by heat and (or) light. 73% NaOH may be stored in Fe tanks so coated for long periods without corrosion. Many of these compns. will withstand boiling 3% NaOH for days.

CA 39, 5137-3

Transportation of Caustic
Dwight Means
U. S., 2,384,111, September 4, 1945

Tank cars for the shipment of high concn. caustic (I) (greater than 50% NaOH) are protected by the application of compounded rubber latex (contg. vulcanizer, accelerator, and antioxidant) to the metal wall and then "conditioning" or curing the rubber film by filling the tank with I at 150-200°F. and holding for some 10-12 hours. This treatment produces a firmly adherent caustic-resistant film which effectively preserves the caustic from metallic contamination.

CA 39, 5197-6

Preparation of Standard Solutions of Sodium Hydroxide from Sodium Carbonate
V. J. Panasyuk and A. N. Peter
Legkaya Prom. 4, No. 12, 22 (1944)

30 g. $Na_2CO_3$ is dissolved in 1000 ml. boiling distd. water. To the soln. is added 35 g. CaO (made by calcination of pure chalk) or 46 g. $Ca(OH)_2$. After 1 hr. on the water bath the deposit of $CaCO_3$ is left to settle overnight, filtered off, and the NaOH soln. is dild. to 1000 ml. for an approx. 0.5 N concn.

CA 39, 5239-2

The Resistance of Nickel and Its Alloys to Corrosion by Caustic Alkalies
International Nickel Co., Development and Res. Division
Tech. Bull. T-6, 19 pp. (1945) Anon.

Corrosion rates of Ni and monel in dil. or intermediate concns. of NaOH, from room temp. to boiling, range under 4 mg. per sq. dm. per day (m.d.d.). The corrosion rate in 14% NaOH soln. was: Ni 0.13, monel 0.33, inconel 0.19, mild steel, 45, cast iron 41; and in 23% NaOH at 105°; Ni 1.0, monel 1.2, inconel 1.0 m.d.d. Plant tests in an evaporator concg. NaOH from 30% to 50% at 82° showed: Ni 0.6, monel 1.2, Cu-Ni-Zn (75-20-5) 3.1, Cu 14, mild steel 20, cast iron 35 and Cr steel (14% Cr) 180 m.d.d. Specimens exposed in an evaporator concg. NaOH solns. from 60 to 75% at 149° showed corrosion rates as follows: Ni 6.5, monel 29, Cu-Ni (70-30) 34, Cu-Ni (80-20) 38, arsenical Cu (0.43% As) 234, Ni-Cr steel (11-15) 55, Ni steel (18-19) 400 m.d.d. The paper contains 39 tables of test data for various concns. and temps. (The presence of oxidizable S compds. in the NaOH soln. tends to increase the corrosion of Ni at high temps., particularly with $H_2S$, mercaptans, and Na sulfide. This increase can be avoided by the addn. of $Na_2O_2$ to change the oxidizable S compounds to sulfate. Significant galvanic corrosion can occur in cast iron or steel in contact with Cu or Ni. It is desirable to use Ni tube sheets with Ni tubes in highly concd. NaOH solns. The use of Ni anodes in fused and highly concd. NaOH solns. was successful with a corrosion rate of 5 m.d.d. in 75% NaOH at 121° and 69.8 m.d.d. in the fused NaOH at 482°. A black oxide film protects the anode from corrosion. Under conditions of high-stressed metal, high temp. and high concn. of NaOH, Ni is subject to intergranular attack. Ni should be fully annealed before exposure. Ni and "L" nickel (a C-free wrought Ni) are not suitable for fusion pots where the fuel has a high S content. The presence of chlorates in the NaOH soln. increases the rate of corrosion. The addn. of Ni to cast iron greatly increases the corrosion resistance, 3 to 5% Ni nearly doubles the corrosion resistance. Tests with NaOH solns. contg. Na metasilicate, and Na sulfide showed Ni and Ni alloys superior to cast iron or mild steel. Tests were made in several industrial applications including: viscose rayon, soap, pulp and paper, and petroleum manuf.

CA 40, 1399-9

Products of Electrolysis of Molten Salts with an Iron Anode
Jean L. Andrieux and Georges Weiss
Compt. rend. 218, 615-17 (1944)

An Fe or amorphous C crucible is used as cathode, and an Fe rod as anode; as the anode is oxidized, it is further immersed in the bath to maintain a const. depth of 2 cm. Electrolysis of $Na_2O_2$ in an Fe crucible at 450-500° (12 v., 14 amp., for 1 hr.) gives Na ferrate and both magnetic and nonmagnetic $Fe_2O_3$; while NaOH (9 v., 10 amp., for 1 hr.) gives microcryst. $Fe_3O_4$; Na is found at the cathode. Electrolyzed $NaBO_3$ (C crucible, 950°, 25 amp., under 7 v., for 1-2 hrs.) cooled and treated with hot, dil. $HNO_3$ gives $Fe_3O_4$ and black, shiny needles of feebly magnetic $B_2O_3 \cdot Fe_2O_3 \cdot 4FeO$, sp. gr. 4.50. This compound, unaffected by $HNO_3$, is attacked by HCl, 1 to 1 $H_2SO_4$, and alkalies.

CA 40, 2275-8

Causticizing Bisulfite Solutions with Lime
J. L. Hofman and R. E. Osherovich
Khimicheskaya Prom. 1944, No. 12, 13-14; cf. CA 38, 5049-4

$CaSO_3$ was produced according to $2NaHSO_3 + Ca(OH)_2 \rightarrow Na_2SO_3 + CaSO_3 \cdot 2H_2O$. The ppt. was allowed to settle, filtered, and washed. To insure a complete transformation of the bisulfite the lime is taken in approx. 10% excess. $Na_2SO_3$ is recovered from the filtrate either by cooling to 10-15° or by evapn. Cooling yields $Na_2SO_3 \cdot 7H_2O$; evapn. at not below 34° yields anhyd. $Na_2SO_3$. The possibility of production of NaOH according to $4NaHSO_3 + 3Ca(OH)_2 + 2H_2O \rightarrow 2NaOH + Na_2SO_3 + 3CaSO_3 \cdot 2H_2O$ is discussed. Exptl. results are tabulated.

CA 40, 2278-2

Removing Water from Hygroscopic Inorganic Compounds by Partial-Pressure Distillation
Vaman R. Kokatnur
U. S., 2,394,244, Feb. 5, 1946

Aq. solns. of alkali metal hydroxides are dehydrated by distilling the soln. in the presence of excess kerosene or other inert hydrocarbons which are $H_2O$-immiscible and which have a b.p. in the range of 150-300°. The vapor pressures of the two immiscible liquids are additive, so that this process permits the removal of $H_2O$ from such compds. at a temp. much lower than that previously required. A superficial coating of the hydrocarbon remains upon the hydroxide and retards its corrosive effect. In addn. to the drying of alkali metal hydroxide solns., the process may be used for producing anhyd. $MgCl_2$ or $ZnCl_2$ from their solns.

CA 40, 2596-2

Caustic Alkalies
Vaman R. Kokatnur (to Autoxygen Inc.)
U. S., 2,393,108, Jan. 15, 1946

The prepn. of finely divided anhyd. NaOH or KOH by evapn. of solns. is improved by providing a heavy inert liquid to coat the crystals and isolate them from the mother liquor. 50% NaOH soln. is fed together with equal wts. of $C_6H_2Cl_4$ into a semicontinuous still operating at 22-28 in. vacuum and 75% NaOH in the water phase, i.e., at about 138° or safely above the transition temp. to monohydrate at 63°, and below the m.p. of anhyd. NaOH. The pptd. anhyd. NaOH coated with $C_6H_2Cl_4$ is withdrawn with the lower layer, sepd. from the liquid, and may be washed free of the coating with suitable solvents such as acetone or benzene. An enhanced partial-pressure evapn. effect is obtained by substituting for half of the high-boiling liquid, in this case $C_6HCl_5$, a low-boiling liquid hydrocarbon dilutent

(b.p. 140-200°). KOH may be similarly prepared at concns. above 86% in the water phase and at temps. above the transition point at 146° and below 282°. Suitable liquids, inert, immiscible with the alkali solns. and having ds. greater than 1.6-1.7 g/cc., are polychlorinated and brominated aromatic hydrocarbons and nitro compds. of same, also certain organometallics, e.g., dipropylmercury.

CA 40, 3239-8

Dehydrating Caustic Solutions
Edwin T. Ladd
U. S., 2,396,664, March 19, 1946

NaOH or KOH is dehydrated in an insulated graphite tower while cascading over trays countercurrent to steam at 260-425°. Pick-up of impurities is thereby minimized and oxidation of the graphite is avoided by maintaining the pressure slightly above atm. so as to exclude air.

CA 40, 3677-5

A Method for Comparative Calculation of the Entropy, Heat, and Free Energy of Formation of Chemical Compounds. I. The Entropy of Formation of Inorganic Compds. from Atoms Under Standard Conditions
V. Kireev (Kuibyskev Inst. Bldg. Eng., Dept. Chem., Moscow)
Acta Physico-Chim. U.R.S.S. 20, 905-22 (1945)

The attempt is made to establish some relations of a more general nature than the customary entropy of formation from simple substances. The concepts of atomic entropy of formation from free atoms, designated as $\Delta S_f^a$, and the ideal entropy of formation from elements in a hypothetical state of a monatomic ideal gas at the same temperature and pressure p = 1 atm., designated as $\Delta S_f^i$, are introduced. The method is valuable for the heat of formation and free energy of formation also. The possibility of calcns. is limited mainly by the incompleteness of data characterizing transition of various compds. to the ideal gas state, i.e., data on heat of vaporization, heat of sublimation, and satd. vapor pressure. The principal factor detg. $\Delta S_f^a$ proves to be the number of atoms in a mol. of a given compd. Structural effects and position in Mendeleev's periodic table modify the values of $\Delta S_f^a$. The following generalization holds: transition within a single subgroup of the periodic table from elements with a lower at. wt. to heavier elements for similar compds. is accompanied by a gradual decrease of $\Delta S_f^a$ in abs. value. This applies to binary salts and oxides, but H is an exception to the rule. Mean values of $\Delta S_f^a$ are already sufficient to calculate the entropy of many compds. to within 1 to 5 E.U. per mole, according to the type of compd. Calcd. values of $\Delta S_f^a$ are tabulated. In many cases the entropy values so calcd. are sufficiently accurate for equil. calcns. Values of $\Delta S_f^i$ show that the function depends upon the number of atoms in the mol. to a greater extent than does $\Delta S_f^a$ for cryst. substances. $\Delta S_f^i$ proves to be much more regular than the ordinary quantity $\Delta S_f$. New calcns. of entropy are given for NaBr, NaI,

$Ba(OH)_2$, HgI, $AgBrO_2$, $Mn(OH)_2$, $AgIO_2$, $KBrO_4$, $CsIO_4$, $Fe(OH)_2$, $CsBrO_4$, $Zn(OH)_2$, $CsMnO_4$, $Be(OH)_2$, $Sr(OH)_2$ and $KIO_4$. Entropy of CdO is calcd. as 55.05 ± 0.5 instead of the published value of 46.9, and for TlI 69.9 instead of 63.9.

CA 40, 6228-4

Purifying Caustic Alkali Solution
Claude A. Cummins
U. S., 2,403,789, July 9, 1946

Chlorate is removed from alkali solns. of 30 to 60% strength by heating in the presence of Fe at between 70° and the b.p., cooling to 30°, and adding Cl or a sol. hypochlorite with resultant pptn. of the dissolved Fe as hydroxide.

CA 40, 7012-9

The Purification of the Electrolyte of Mercury-Cathode-Cells for the Manufacture of NaOH. II.
Vincenzo La Pietra
Chemica e industria (Milan) 26, 101-3 (1944); Cf. CA 37, 2659-9

Absolute purification of the NaCl is not necessary. It is sufficient if the ratio $CaO/SO_3$ is slightly more than 1. The absence of Mg is useful. Purification is effected simply by washing NaCl.

CA 41, 1401f

Prevention of Contamination of NaOH by Ni in Tank Cars
Otto Kay
Can., 437,941, Nov. 12, 1946

In Ni-lined tank cars an anode of material resistant to attack by NaOH soln. is immersed in the soln. and a d.c. of an average cathode c.d. of 0.0003-0.001 amp./sq. ft. is maintained between the anode and the Ni surfaces.

CA 41, 1532h

Electrolytic Conductivity of NaOH in $H_2O$ and of NaOD in $D_2O$ at 25°. A Vacuum Distilling Apparatus for Deuterium Oxide
Enok Hetland (Oslo Univ., Norway)
J. Am. Chem. Soc. 68, 2532-5 (1946)

Conductivities of solns. of NaOH in $H_2O$ and of NaOD in $D_2O$ were measured at 25° and data are tabulated. By use of the equiv. cond. for Na ion in water or $D_2O$ given by MacInnes and Longsworth (Cf. CA 31, 8324-9; 32, 8890-3) the limiting values of the ion conductances of $OH^-$ and of $OD^-$ in ordinary and in heavy water, resp., were calcd.: $OH^-$ = 197.6 (in $H_2O$); $OD^-$ = 119.0 (in $D_2O$).

CA 41, 1974 g

Caustic Soda as a Quenching Medium for Steel
Kenneth Rose
Materials and Methods 25, 75-7 (1947)

The use of dil. NaOH solns. provides more rapid heat withdrawal from steel than $H_2O$ and gives more uniform hardening.

CA 41, 2340 b

The Preparation of Oxides by Electrolysis
Pierre Jolibois and Marthe Berges
Compt. rend. 224, 78-9 (1947)

By long-continued electrolysis of the appropriate salt soln. in an approx. W-shaped cell, oxides or hydroxides of high purity were prepd. The final conditions were 30 ma. and 2000v. The method was recommended for prepg. gram quantities of RbOH and CsOH, which were recovered from the catholyte. Insol. hydroxides, such as $Mg(OH)_2$ and $Be(OH)_2$, were also prepd. Dehydration of these hydroxides was followed by continuous weighing with a thermobalance. $Mg(OH)_2$ began to lose water at 340° and was totally dehydrated at 800°. For $Be(OH)_2$ the corresponding figures were 230° and 900° resp.

CA 41, 2377 i

Intercrystalline and Intracrystalline Corrosion and Their Causes
F. C. Althof
Z. Metallkunde 36, 177-86 (1944)

The mechanism of intercryst. and intracryst. corrosion of brass in $HgNO_3$, $NH_4OH$, sea water, and NaOH is described.

CA 41, 2541 c

Purification of Caustic Alkali Solutions from Chlorates
David J. Pye and Marc F. Leduc (to Dow Chem. Co.)
U. S., 2,415,798, Feb. 11, 1947

Caustic soda made by the electrolytic process generally contains 500-2500 p.p.m. of chlorate; its presence is objectionable because of corrosive action on the Ni evaporators. In the present process, chlorate is reduced by means of finely divided metallic Fe. The reaction at first produces Fe in the ferric state, up to the point where all of the chlorate is reduced. The continued action of the metallic Fe forms ferrosoferric oxide ($Fe_3O_4$), which forms a green solution in the caustic. This compd. is pptd. as a black sludge when the solution is cooled to room temperature and may be filtered out. If the reaction is allowed to continue, all of the Fe

compds. go to the ferrous form and cannot then be pptd. and removed. Accordingly, the process contemplates stopping the reduction when the caustic solution acquires the green color of the ferrosoferric compd. In carrying out the process, the caustic soda solution is heated to 115-135° and introduced into a Ni-lined tank. Powdered Fe of 100-200 mesh is added in 2 to 5 times excess, and the solution agitated until the reduction of chlorate is complete. The endpoint can be detd. conveniently by electrometric means. As soon as the endpoint has been reached, the liquor is filtered to remove Fe, cooled to about 35°, and allowed to stand until the ferrosoferric oxide ppts. It is then filtered. The electrometric control consists of a Pt-Fe couple, and the control point for these conditions is 130 mv., while the endpoint is 145 mv.

CA 41, 3003 f

Behavior of Iron Electrode in Various Solutions
A. I. Krasil'shchikov
J. Phys. Chem. U.S.S.R. 20, 1187-98 (1946) (in Russia)

Cathodic and anodic polarization curves of com. and pure Fe in various solns. satd. with air or $O_2$ were detd. at 17°. At a given c.d., pure Fe shows a greater polarization in the anodic, and a smaller polarization in the cathodic, range than com. Fe. The polarization is reversible in the region characterized by the evolution of H, and shows a "hysteresis" in the region of the reduction of O. Small concns. of alkali at the cathode do not alter the cathodic polarization. Passivity is achieved in 0.1 N NaOH, 0.01 N $NaNO_2$, or 0.01 M $K_2Cr_2O_7$.

CA 41, 3267 h

Alkali Hydroxides and Ammonia
H. C. M. Ingeberg
Norw., 71,231, Nov. 4, 1946

Alkali hydroxides and $NH_3$ are made by treating an alkali nitrate or nitrite with H or a mixt. of H and N in the presence of a catalyst at a temp. between 100° and 800°. Pt, Cu, Fe, Ni, and Co either as metals or as compds. are suitable catalysts. The yield may be raised by increasing the pressure of the H. The residual gas, after removal of steam and $NH_3$ may be used in a synthetic $NH_3$ plant.

CA 41, 3360 d

Ratio of Molecular Heat of Fusion to Melting Point for Chemical Compounds
Stefan Procopiu
Compt. rend. 224,264-6 (1947)

The ratio (K) of mol. heat of fusion to abs. m.p. (entropy change of fusion) was found to be approx. equal to the no. of atoms in the mol. (n) for compds. having at least 8 atoms per mol .... Values of K for the alkalies

NaOH, KOH, RbOH, and CsOH are 2.7, 2.6, 2.8 and 3, resp.; for the acids HCl, HBr, and HI, 3.2, 3.3 and 3.3; and for the salts NaF, NaCl, KF and KCl, 6.2, 6.8, 5.6 and 5.4, or approx. the sum of the entropies for the corresponding acid and base. Cf. CA 41, 1147 a.

CA 41, 3377 b

Production of Na-K Alloys by Electrolysis of Fused Alkalies
Yu. V. Baimakov
Trans. Lenigrad M. I. Kalinin Polytech. Inst. 1942, 124-38

The m.p. of the eutectic Na-K (which contains 78% K) is -12.6°. An electrolytic process of high efficiency was developed. The primary investigations covered the hydrolysis of molten NaOH in the light of ancient and modern techniques. Then the technological conditions of electrolysis of mixts. of NaOH and KOH were investigated and the following optimum conditions were established: compn. of the bath: 60% NaOH, temp. 230-260°, c.d. 1-10 amp./sq./cm. The construction and operation of the electrolytic bath, the manufg. technique, and safety precautions are discussed. Theoretical aspects of the electrochem. process involved, thermal equil., efficiency, and compn. of the final product are also discussed.

CA 41, 3426 a

Corrosion Resistance of Steel and Cast Iron
A. W. Spitz
Chem. Eng. 54, No. 2, 135 (1947)

Qual. values given for many chemicals including NaOH.

CA 41, 3590 f

Purification and Concentration of NaOH Soln., and Prepn. of a NaOH-Methylol Compd.
David F. Smith (to Wyandotte Chem. Corp.)
U. S., 2,418,372, April 1, 1947

To impure 50% NaOH soln. about 10% $CH_3OH$ is added at about 70°. Upon cooling the soln. to about 35°, 3 $NaOH \cdot 2\ H_2O \cdot CH_3OH$ crystals form which are removed and decompd. in a vacuum stripping column in the presence of purified 70-73% NaOH soln. More than 90% of the NaCl and $NaClO_3$ impurities are thus eliminated. The alc. and suitable treated mother liquor are recycled. The alc. compd. consists of white crystals, m. about 119°, b. about 128°. It is hygroscopic and quite stable at atm. pressure. Cf. CA 32, 8087-2.

CA 41, 4061 d

Determination of Water in Caustic Soda and Other Alkaline Materials. A Distillationtitrimetric Method
H. R. Suter (Wyandotte Chem. Corp., Wyandotte, Mich.)
Anal. Chem. 19, 326-9 (1947)

To det. 0.5-1.8% $H_2O$ in NaOH, it is recommended to mix 15-25 g. of sample with pyridine and distil off the water with the pyridine. Treat the distillate with MeOH and with Karl Fischer's reagent (a soln. of $I_2$ in MeOH and pyridine) and titrate the excess reagent with a standard soln. of water in MeOH. If numerous precautions are taken (these are described) the results should be within about 5% of the truth (e.g., 104.6% recovery of 1.48% $H_2O$ present.

CA 41, 6031 d

Apparatus for Decomposition of Alkali Metal Amalgam
Maurice C. Taylor (to the Mathieson Alkali Works, Inc.)
U. S., 2,423,351, July 1, 1947

A tower is packed with electrically conductive material with which Hg or the amalgam does not amalgamate; such packing is preferably graphite. Water or a lower alc. is admitted under pressure through the bottom, while e.g., Na amalgam is passed countercurrently. A pool of Hg collects at the bottom and is separately withdrawn from the resulting alkali metal hydroxide or alcoholate and H which are led through outlets near the top.

CA 41, 6160 h

Sodium Sulfate Electrolysis in the Application of Glauber's Salt as a Spinning Bath
Burgin (I.G.F.A.-G., Bitterfeld, Germany)
Reichsamt Wirschaftsausbau, Chem. Ber. Pruf-Nr. 93 (PB 52008), 128-34 (1940) (Pub. 1941)

On a lab. and semitech. scale, $Na_2SO_4$ soln. was electrolyzed in a 9000 amp. Hg cell with good current efficiency. Pure 50% NaOH solution was obtained, and 20% $H_2SO_4$ contg. sulfate and 0.0001% $O_3$. The cell cost was 150% above that for chloride electrolysis, and operation cost 30% higher. Further work is necessary on purification of electrolyte from heavy metals, earth alkalies, chloride, and viscose-decompn. products. The NaOH produced is used in the viscose process. The $H_2O$ solution from this together with acid forms further $Na_2SO_4$ for electrolysis.

CA 41, 6418 b

Caustic-Resistant Coatings
P. J. Gegner (to Pittsburgh Plate Glass Co.)
U. S., 2,424,813, July 29, 1947

Such metal containers as tank cars are coated with after-chlorinated (55-62% Cl) polychloroprene (I) to resist the action of 73% NaOH at 135°. The surface to be lined is cleaned and roughened by grit blasting and given 2 primer coats (100 parts of I in xylene compounded with 10 C black and 5 of ZnO) that are air dried 1 hr. each; then 12 coats of compounded I (latex 100, $TiO_2$ 20, hard clay 10, ZnO 5, Ph-β-naphthol 2, half Na sulfate ester of mixed higher fatty alcs. 0.75, casein 0.25, $NaSiO_3$ 0.25, and Me cellulose 0.25 parts by wt.) are applied, one per hr., and the resulting film is air dried 24-48 hrs. at room temp., then cured with 73% NaOH at 115°.

CA 41, 6473 f

Diaphragm vs. Amalgam Cells for Chlorine-Caustic Production
Robert B. MacMullin
Chem. Inds. 61, 41-50 (1947)

CA 41, 7276 d

Laboratory Preparation of Alkali Metal Hydroxides by Electrolysis
A. F. Winslow, H. A. Liebhafsky, and H. M. Smith (G. E. Co., Schenectady)
J. Phys. and Colloid Chem. 51, 967-72 (1947)

The work was undertaken to develop a method for making cesium and rubidium hydroxides for conversion into other salts, such as azides, chromates, or iodides. An oscillating Hg cell resembling Fetzer's (CA 23, 1354) modification of the Castner-Kellner type was constructed. Detailed operating instructions are included. With a current of about 20 amp., the elec. efficiency is 80% with NaCl. Two electrodes were required to obtain a hydroxide substantially free of chloride. With CsCl, 98% of the calcd. quantity of CsOH was obtained. The chief objection to the method--not serious in this case--was a contamination of the hydroxide by Na ions from the glass.

CA 41, 7689 e

Utilization of Glauber's Salt to Convert it into Sulfuric Acid and Sodium Hydroxide
A. Zieren
Belg., 453,088, Dec., 1943

The salt is dehydrated, converted into $Na_2S$, and the latter is then decompd. at 200-500° by means of a current of steam and $CO_2$. The resultant $Na_2CO_3$ is converted into NaOH, while the S in the form of $H_2S$ is removed and burned to $H_2SO_4$.

CA 42, 337 b

Washing Glass Surfaces
Walter F. Wegst, Leslie R. Bacon, et. al.
U. S., 2,425,907, Aug. 19, 1947

Tabulated data show that the addn. of approx. 5% by wt. of a sol. chloride of Sr, Ba, Bi, Sb, or Sn to NaOH (I) inhibits the tendency of dil. (3%) aq. solns. of I to attack glass surfaces.

CA 42, 1175 f

Resistance of Al to Corrosion in Solns. Contg. Various Anions and Cations
A. B. McKee and R. H. Brown
Corrosion 3, 595-612 (1947)

Al is significantly attacked in NaOH above 0.0004 N in the presence of absence of chloride, sulfate, nitrate and acetate salts of Na.

Al is resistant to NaOH solns. more dil. than 0.1 N contg. chromate anion at a concn. of 1.0 N.

CA 42, 1827 h

Production of Lithium Hydroxide by Electrolysis of LiCl Solutions
S. I. Sklyarenko and B. A. Sakharov
J. Applied Chem. (U.S.S.R.) 20, 406-21 (1947)

Expts. were conducted on a lab. scale between a Pt anode and a circulating Hg cathode (40 sq. cm) with circulating electrolyte; the amalgam was decompd. with $H_2O$ in contact with graphite.....

CA 42, 2150 h

Polytetrafluoroethylene for the Prevention of Bumping from Superheating of Boiling Fluids
H. S. Bennett (MIT)
Science 106, 646 (1947)

Polytetrafluoroethylene prevents bumping of boiling solns. of acids and alkalies.

CA 42, 2190 a

Electrolysis of Sodium Sulfate
Comptoir des Textiles Artificiels, S.A.R.L.
Brit., 594,443, Nov. 11, 1947

Carefully purified $Na_2SO_4$ solution (Brit., 594,442, CA 42, 2409 a) is passed continuously to a cell having the cathode conductors bathed in Hg and having Pb-Sb anodes placed horizontally in tubular porous filter elements. The layer of Hg, which is 10 mm. thick, moves along the floor of the cell at the rate of 125 cm. per sec. The layer of $Na_2SO_4$ electrolyte above the Hg is 20 cm. thick. Electrolysis takes place at 40° under 6 v. potential with a c.d. of 6 amp. per sq. dm. (based on Hg surface). $H_2SO_4$ is formed at the anode and is continuously removed through a vacuum line which extends into the elements housing the anodes. A Na-Hg amalgam forms on the surface of the layer of Hg and is continuously removed from the cell as the moving body of Hg passes out through a discharge line. The Hg-amalgam mixture goes to a shallow trough where it meets a countercurrent stream of water which causes decompn. of the amalgam. The Hg is purified and recirculated. The caustic soda solution is of very high quality.

CA 42, 2847 a

Kinetics of the Decomposition of Lithium Amalgam in Water and in Aqueous Solutions of Lithium Chloride and Lithium Hydroxide
S. J. Sklyarenko and B. A. Sakharov (Lomonosov Inst. Fine Chem. Technol, Moscow)
J. Gen. Chem. (U.S.S.R.) 17, 1385-400 (1947) (in Russian)

CA 42, 3276 i

Decomposition of Common Salt by Steam
P. Sen, M. L. Sen-Gupta, and H. N. Das-Gupta (Calcutta Univ., India)
Indian Soap J. 13, 102-6 (1947)

Between 500° and 810° slight decompn. of NaCl by $H_2O$ to form HCl and NaOH takes place. At 810° $CO_2$, $SiO_2$, kaolin, feldspar, KCl, and agitation promote the reaction; $Fe_2O_3$ has no effect.

CA 42, 3718 d

Corrosion of Iron in Sodium Hydroxide Solutions
M. Pourbaix (Univ. Libre, Bruxelles, Belg.)
Bull. Tech. A.I.Br. 1946, 67-86; 1947, 109-20

Corrosion studies on Fe (usually in the form of 0.2 mm. diam. piano wire) were made in solns. of NaOH at temps. between about 30 and 110° in an effort to det. the effect of temp., NaOH concn., and Fe potential on the corrosion rate. These data have been obtained both for electrically insulated Fe and

Fe used as an anode. Thermodynamic considerations permit a rapid prediction of the circumstances, under which the Fe will be corroded, from the p.d. between the Fe and a reversible H electrode in an O-free soln. The exptl. technique used is applicable to all O-free solns., to det. the effect of temp. and concn. The corrosion of Fe in pure NaOH solns. occurs only over a definite potential range, varying somewhat with temp. and NaOH concn. Curves are presented for temps. of 80, 95, and 105 and concns. of NaOH from 0 to 700 g. per l.; extreme potential values for the corrosion range fall between -0.7 and -1.0 v. At potentials within the corrosive range the corrosion progresses continuously and gives rise to a green solution of sodium hypoferrite ($Na_2FeO_2$); the latter can decomp. with the formation of a black oxide ($Fe_3O_4$ ?). The corrosion of soft annealed steel in NaOH solns. is not intercryst. At low temps. and low NaOH concns., oxidizing agents act as passifiers; at high temps. and high NaOH concns. they act as activators; in the latter case differential oxidation by air or other oxidizing agents will cause intense activation. Certain Fe alloys with a high percentage of another metal (such as the Cr-Ni steel alloy V2A) have a very nearly perfect resistance to hot concd. NaOH solns.

CA 42, 4194 d

Alkali Metal Methylates
Richard S. Robinson (to Allied Chem. and Dye Corp.)
U. S., 2,437,272, March 9, 1948

Alkali methylates prepared by treatment of the alkali amalgam with MeOH, may be reacted with pure water in stoichiometric proportions to give a pure NaOH.

CA 42, 4723 h

Alkali Metal and Alkaline Earth Hydroxides
Don B. Wicker (to American Viscose Corp.)
U. S., 2,439,404, April 13, 1948

NaOH is produced by the process described in a form which may be used directly in the prepn. of a viscose rayon. The steps in the novel cycle are: (1) $Na_2SO_4$, which may be excess salt removed from the acid spinning baths, is reduced to $Na_2S$; (2) $Na_2S$ is treated with $Cu(OH)_2(NH_3)_4$ to form NaOH, $NH_4OH$ and a ppt. of CuS; (3) the $NH_4OH$ is removed from the solns. in a boiler; (4) the pptd. CuS is removed and oxidized to the metal oxides; (5) the metal oxide is treated with the $NH_4OH$ from (3) to re-form the metal complex required in (2); (6) concn. of the NaOH formed in (2) to the desired strength.

CA 42, 4724 b

Sodium Hydroxide from Sodium Sulfate and Calcium Hydroxide
Koninklijke Nederlandsche Zoutindustrie N. V.
Dutch, 61,090, May 15, 1948

The conversion of $Na_2SO_4$ by $Ca(OH)_2$ and the sepn. of solids are effected under conditions when a double salt of $Na_2SO_4$ and $CaSO_4$ is stable. E.g., a satd. $Na_2SO_4$ solution at 35° contg. some solid $Na_2SO_4$ was stirred for 2 days at that temperature with an excess of lime, about 15 g./l. There was a yield of 3.5% NaOH and a concn. of 9.8 g./l. After sepn. of the ppt. the liquid was cooled at its freezing point, when 92% of the original $Na_2SO_4$ sepd. The yield of NaOH, calcd. on $Na_2SO_4$, is 44%. The liquid sepd. from the solid $Na_2SO_4$ has 25 g. NaOH and 22 g. $Na_2SO_4$/l. and is suitable for water-softening, straw decomposing, etc.

CA 42, 6259 i

Basic Nitrates of Uranium
B. C. Haldar and G. B. Choudhury (Univ. Coll. Sci. Tech., Calcutta)
Science and Culture 13, 427-8 (1948)

The system $UO_2(NO_3)_2$-NaOH was studied. Thermal studies indicated compounds formed of the type $4UO_2(NO_3)_2 \cdot UO_2(OH)_2$ in the concentration range of 0.02912-1.1648 mol. $UO_2(NO_3)_2$. Data also indicate the presence of the uranates $Na_4U_7O_{23}$ and $Na_2UO_4$. A break corresponding to the formation of $UO_2(OH)_2$ and $Na_2UO_4$ appears at the points 1 $UO_2(NO_3)_2 \cdot 2NaOH$.

CA 42, 6499 f

Alkali Metal Compounds
Arther F. Lowes, Robert Burnett and Imperial Chemical Industries Ltd.
Brit., 577,454

Alkali metal is formed by sundry means and amalgamated with mercury, which amalgam is then treated with water to give the hydroxide free from impurities.

CA 42, 7606 a

The Thermodynamics of Aqueous Solutions of Potassium Hydroxides
G. C. Akerlof and Paul Bender
J. Am. Chem. Soc. 70, 2366-9 (1948)

Thermodynamic functions for both solute and solvent computed.

CA 42, 7946-9

Purifying Aqueous Alkali Metal Hydroxides
George L. Cunningham (to Diamond Alkali Co.)
U. S., 2,446,868, Aug. 10, 1948

Alcohols such as butyl, amyl, propyl, etc., are used to extract NaOH from its aqueous solution in presence of impurities produced by electrolysis and the extract passed into contact with pure water which preferentially dissolves the caustic to form a pure NaOH solution.

CA 42, 8680 c

Electrolytic Production of Chlorine and Caustic Soda
J. J. Graham (Assocd. Pulp and Paper Mills, Burnie, Australia)
Australian Pulp and Paper Ind., Tech. Assoc., Proc. 1, 169-85 (1947)

The diaphragm and the Hg cells are discussed. A description is given of the Hg-cell plant of the author's mill.

CA 43, 541 d

High-Temperature Attack of Various Compounds on Four Heat Resisting Alloys
D. G. Moore, J. C. Richmond, W. N. Harrison
Nat'l. Advisory Comm. Aeronaut., Tech. Notes No. 1731, 19 pp. (1948)

While ceramic coatings should render heat resisting alloys capable of operation at higher gas temp. for longer times, some common coatings were found to react with Hastelloy B, S-816, S-590 and Haynes Stellite #21 when heated at 1500°F. for 17 hrs. Of the 4, Hastelloy B was most heavily attacked when heated in air. In general, the compds. most corrosive were alkalies, Pb compds., and some alk. earths. In a $CO_2$ or He atm. at 1500°F., Hastelloy B was not attacked by alkalies.

CA 43, 1158 i

Modern Production of Chlorine and Caustic Soda
Will H. Shearon, F. Chrencik and C. L. Dickinson
Ind. Eng. Chem. 40, 2002-10 (1948)

Production increases in Cl and NaOH, location of new production centers, uses of Cl, and general methods of manufacturing of Cl and NaOH.

CA 43, 2082 h

The Thermochemistry of Sodium
W. A. Roth and H. L. Kaule
Z. anorg. Chem. 253, 352-6 (1947)

The heat of solution of Na in $H_2O$ was detd. with 99.97% pure Na in an Ag calorimeter calibrated electrically before and after each measurement. Precautions were taken to let the H escape at the temperature of the water. The result of 5 detns. was 45.27 ± 0.15 kcal./g. atom Na at 22.4° and 4510 mols. $H_2O$/mol. NaOH. Similarly, the heat of solution of $Na_2O_2$ from 8 detns. on a sample of 92.77% $Na_2O_2$ was detd. as 34.85 ± 0.1 kcal./mole at 18.5° and 1200 mols. $H_2O$/mol. NaOH, and the heat of solution of $Na_2O$ from 6 detns. on a sample of 94.19% $Na_2O$ was detd. as 56.02 + 0.2 kcal./mol. at 21.0° and 825 mols. $H_2O$/mol. NaOH. These data, neglecting heats of diln., lead to the following values for the heats of formation of NaOH (aq.), $Na_2O_2$, and $Na_2O$ at about 20°: 113.62 ± 0.15, 124.84 ± 0.32, and 102.87 ± 0.32 kcal./mole, resp. The error is within 0.5%. The results are higher than the values given by Bichowsky and Rossini (CA 30, 6279-1).

CA 43, 2100 g

Types of Anodic Polarization of Pt
A. Rius and S. Terol Alonso
Anales real soc. espan. fis. y quim. 44B, 891-902 (1948)

In polarization concn., resistance or activation may be main factor. Passivation accomplished by thiocyanates, ferrous-ferric salts, chlorides, and KOH. A diffusion layer is evident with ferrous-ferric salts. An explanation based on oxide films is difficult with chlorides and KOH. Observations point to purely phys. cause of passivity.

CA 43, 2109 i

Action of Carbon Monoxide on Cesium Hydroxide (Synthesis of Cesium Formate)
L. Hackspill and G. Thomas
Compt. rend. 227, 797-9 (1948)

A Ag U-tube 25 cm. high, one side 2 cm. in diam., the other 0.5 cm. and wound for electric heating, is used as a reaction vessel. The larger side contains 0.5 x 0.5 cm. Ag Raschig rings. Place 10 g. CsOH (m. 272°) in the larger side, and heat to 280-300°. Pass 5 l. pure CO into the smaller side over a 1-hour period. The temperature may rise 10-20°. Yield about 90%. If the initial temperature is above 300°, $Cs_2C_2O_4$ is formed.

CA 43, 2378 f

Chlorine-Caustic Soda
J. V. Hightower
Chem. Eng. 55, 112-16, 136-9 (1948)

A description and flow sheet of the Diamond Alkali Company's newest plant for the production of Cl, 50 and 73% NaOH solutions, and HCl are given. Ten advantages over conventional electrolytic installations are discussed.

CA 43, 2535 i

The Formation of Peroxide in KOH
C. Kroger and W. Behr
Z. anorg. Chem. 253, 92-4 (1945)

$2\ KOH + 1/2\ O_2 = K_2O_2 + H_2O$ sets in at 210°, increases with temp., at first slowly and above 370° rapidly, reaches max. at 470°, corresponding to about 20% conversion of the KOH.

CA 43, 3158 h

Evaporating Caustic Soda Solutions
AGM Hedley, F. M. Joscelyne and J. C. H. McEntee
Brit., 612,530, Nov. 15, 1948

Granular, dry, substantially anhydrous NaOH obtained at lower temp. and with less corrosion by exposing large surface area of 80-95% NaOH soln. at 200-300°C to gas or vapor with partial press. of $H_2O$ less than 600 mm. of Hg abs., under adiabatic condns. such that not more than 80 ton cal/ton of product is gained nor more than 40 ton cal/ton product lost. Process consists of spraying liquid into vacuum, or through current of hot air, feeding into vessel of gran. NaOH which is being agitated while air passes through, or spreading liquid as thin film.

CA 43, 3766 h

Corrosion of Struc. Steels Operating Under Stress
Ya. Klinor, and G. Shvarts
Khim. Prom. 1947, No. 10, 13-17

Samples of steels tested at 120° at atm. and 2.5 atm. press. in NaOH 40-2%. Equally distributed stresses same as no load. Localized stresses caused low C steel to crack when stress exceeded elastic limit 35-40%.

CA 43, 4583 i

Anodic Oxidation of Au in Alkali Hydroxide Solutions
F. Jirsa
Collection Czechoslov. Chem. Communs. 13, 505-13 (1948) (in English)

Measurement of potential of Au anode in KOH at low c.d., Au dissolves in univalent state, but $Au_2O$ rapidly decompd. to $Au_2O_3$ and metallic Au, so that anode became more or less passive. At high c.d. in dil. KOH Au was momentarily passive. As concn. of KOH was increased O was liberated at lower voltage. Degree of passivity depended on soly. of $Au(OH)_3$ in KOH which increased with KOH concn. Between KOH concns. of 0.01-0.1 N and 4-7 N soly. of $Au(OH)_3$ was independent of KOH concn., but soly. rose between 1 and 4 N and between 7 and 8 N. Deducted that 4 diff. modifications of $Au(OH)_3$ exist.

CA 43, 4622 d

Use of Inhibitors for Controlling Metal Corrosion
G. T. Colegate
Metallurgia, 39, 316-18 (1949)

There is no good inhibitor against caustic alkalies, although glue, glucose, agar-agar, and gum arabic have been used. Silicates give good protection against carbonates and phosphates.

CA 43, 5914 g

Attack of Glasses by Alkaline Solutions
R. D. Smith and P. E. Corbin
J. Am. Ceramic Soc. 32, p. 195-8 (1949)

Typical borosilicate, lime, and lead glasses were subjected to attack by alk. hydroxide and alk. silicate solns. having $SiO_2$ to $Na_2O$ (or $K_2O$) ratios of 0-4. Solns. were 0-5 N. Below about 0.5 N $Na_2O$ or $K_2O$, the rate of attack by hydroxide solns. was greater than by alk. silicate solns., but at higher concns. the reverse became true, the attack by alk. silicate solns. being more than double that by corresponding alk. hydroxide solns. in some cases .....

CA 43, 6031 i

X-Ray Diffraction Studies of Sodium Chloride - Sodium Bromide Solid Solutions
J. R. Nickels, M. A. Fineman, and W. E. Wallace
J. Phys. and Colloid Chem. 53, 625-8 (1949)

Back-reflection powder photographs were made of the 2 salts and 9 solid solns. whose heats of formation had been detd. (CA 43, 2854 h). Lattice spacings and molar vols. show pos. deviations from additivity as large as 0.008 kX and 0.07 cc./mole.

CA 43, 6376 b

Lithium Chloride
Riichi Hikosaka
Japan, 158,610, Aug. 30, 1943

Powd. Li ores treated with $H_2SiF_6$ gives $H_2O$ sol. $Li_2SiF_6$ which in an alk. medium decomposes according to $Li_2SiF_6 + 6\ NaOH = 6\ NaF + Si(OH)_4 + 2LiOH$. LiOH is then sepd. by its greater soly. in $H_2O$ from $Si(OH)_4$, pptd. with $(NH_4)_2CO_3$ as $Li_2CO_3$ and chlorinated with HCl to LiCl.

CA 43, 6965 i

Heat-Treating Salt Bath
Artemas F. Holden
U. S., 2,474,674, June 28, 1949

A series of 2 liquid salt baths are used for heat-treating the following stainless steels: A.I.S.I. 305, 307, 312, 315, 320, 327, 343, 130, 418. Bath #1 contg. $BaCl_2$, KCl, $CaF_2$ and $BaF_2$, heats the steel to 1850-1950°F. Bath #2 contg. NaOH, KOH, and NaCN, quenches the steel to 600-900°F. A cold aq. bath provides a final quench. The treated steel is clean and shiny, and free of fluxes, paint and scale.

CA 43, 7305 e

The Rate of Solution of High Purity Aluminum in Various Bases
M. E. Straumanis
J. Electrochem. Soc. 96, 21-6 (1949)

A series of soln. expts. were made on high purity Al (99.998%) in KOH, $Ba(OH)_2$, $Sr(OH)_2$, $Ca(OH)_2$, $Mg(OH)_2$ and $NH_4OH$ solns. of different concns. .....In very dil. solns. all the strong bases act similarly, whereas at concns. higher than N the rate of attack decreases in the following order: NaOH, KOH, and $NH_4OH$.

CA 43, 8109 b

Caustic Soda
Hartmut W. Richter (to Metal and Thermit Corp.)
U. S., 2,474,916, July 5, 1949

$Na_2CO_3$ and $SnO_2$ are treated in stoichiometrical amounts at 1000-1100° and atm. pressure for about 30 minutes. The dry granular $Na_2SnO_3$ thus formed is dissolved in $H_2O$ in an autoclave, and the temperature is increased to a range of 180° to 374°. Sufficient pressure is maintained to assure a liquid phase at all times during heating. During the reaction in the autoclave $SnO_2$ ppts. and leaves a solution of NaOH. This period covers approximately 30 mins. The final slurry is filtered, and the $SnO_2$ is returned

for treatment with more $Na_2CO_3$. Caustic soda yields may average 80% of theoretical. This process may also be applied to a detinning operation in which the Sn scrap is treated with a solution of caustic soda contg. some oxidizing agent, such as $NaNO_3$. The resulting $Na_2SnO_3$ may be sepd. from the $Na_2CO_3$ formed by reaction of $CO_2$ in the air with excess NaOH, or the entire solution may be sent to the autoclave for the production of NaOH. A flow diagram is used in the explanation of the process.

CA 43, 8127 i

Some Metallurgical Means of Combating Corrosion in Petroleum Refineries
B. B. Morton
Journees Corrosion Metaux., Oct. 1947, 19-25 (Suppl. to Rev. Inst. Franc. Petrole at Ann. Combustibles Liquides 4, No. 1, 1949; Cf. CA 43, 3947 b)

.....In general, the resistance to corrosion by $H_3PO_4$, HF, HCl, NaOH, and naphthenic acids is achieved by using monel metal, while fuming $H_2SO_4$ demands Fe/Si or Ni/Si alloys.

CA 43, 8809 h

The Equilibria of $Ni(OH)_2$ in Solutions of HCl and NaOH at 25°
K. H. Gayer, A. B. Garrett
J. Am. Chem. Soc. 71, 2973-5 (1949)

The soly. of $Ni(OH)_2$ was detd. in dil. acid and base at 25° ± 0.02°. The data show $Ni(OH)_2$ to be a relatively strong base.....

CA 43, 8936 b

The Solution of Al in NaOH Solutions
M. A. Streicher
J. Electrochem. Soc. 96, 170-94 (1949); Cf. CA 43, 5264 f

The effect was investigated of impurities, concn. of NaOH, temp., agitation, and an external current on the soln. of Al specimens (99.2 to 99.998% pure) in NaOH soln. Increasing quantities of impurities (Fe being the most effective) increase the rate of solution. The largest increase is at the concn. of Fe representing the limit of soly. of Fe in solid Al. During the solution the impurities in Al accumulate on the surface and accelerate the rate of soln. An Al alloy contg. 2.5% Mg and 0.5% Cr(52S) has a constant rate of soln. The impurities in this alloy, together with the alloying elements, drop to the bottom of the soln. They do not ppt. on the surface of the metal. The electrode potential for the alloy having a const. rate is const., whereas the alloys whose rate of soln. increases as the impurities ppt. on the surface reflect this increasing rate in electrode-potential measurements, which change in the cathodic direction.

CA 44, 24 c

Dissociation Pressure of Alkali Hydrides
Albert Herold
Compt. rend. 228, 686-8 (1949); Cf. CA 41, 6457 f

Dissocn. pressure of KH, NaH, CsH and RbH was measured at the temp. of 245.5° to 415.5°. The values obtained fit the equations:

$$\log p = -6175/T + 11.69 \text{ for KH}$$
$$\log p = -6100/T + 11.66 \text{ for NaH}$$
$$\log p = -5900/T + 11.79 \text{ for CsH}$$
$$\log p = -5680/T + 11.80 \text{ for RbH}$$

The heat of formation was calcd. to be 12,980 cal. for RbH, 13,480 cal. for CsH, 13,940 cal. for NaH, and 14,110 cal. for KH with an error of $< \pm 1.5\%$.

CA 44, 292 f

$Mg(OH)_2$ from Brines
Leslie W. Scoles (to Dow Chemical Co.)
U. S., 2,479,138, Aug. 16, 1949

$Mg(OH)_2$ with a rapid settling rate may be produced from sea water by mixing the brine with aq. $Ca(OH)_2$ with slow speed paddles, passing the suspension into a turbulent mixer and then to a sedimentation chamber, from which $Mg(OH)_2$ may be sepd.

CA 44, 292 g

Potassium Hydroxide
Glen H. Morey and Everet F. Smith (to Commercial Solvents Corp.)
U. S., 2,479,691, August 23, 1949

Finely divided, highly active KOH may be prepd. by mixing aq. KOH with a liquid $H_2O$ immiscible alkyl acetal, such as 1,1-dibutoxyethane, 1,1-dimethoxybutane, 2-ethyl-2-methyl-1,3-dioxolane, 1,1-dimethoxy-2-ethylhexane, 1,1-dipropoxybutane, or 1,1-dibutoxy-butane, and distg. off the $H_2O$ while agitating vigorously. The KOH produced in this manner may be used in reactions involving the absorption of 1-alkynes, such as acetylene. In U. S., 2,479,692, KOH similar to the above may be produced by using diethers, such as 1-ethoxy-2-butoxyethane, 1,2-dipropoxypropane, 2,3-diethoxybutane, ethylene glycol diethyl ether, or 1,4-dioxane, as the org. vehicle. In U. S., 2,479,693, the org. vehicle may be a mixt. of a liquid hydrocarbon (such as toluene, xylene, aliphatic naphthas, tetrahydronaphthalene, and decahydronapthalene) and a monohydric alc., such as butanol, 2-butanol, tert-butanol, isobutanol, ethylene glycol, monoethyl ether, phenol, cyclohexanol, and methallyl, isoamyl, capryl, and tetrahydrofurfuryl alcohols. In U. S., 2,479,694, the org. vehicle may

be a mixt. of a monoether, such as butyl, phenyl, octyl, and ethyl phenyl ethers and a primary monohydric alc., such as butanol, isobutanol, n-amyl, isoamyl, and tetrahydrofurfuryl alcs., 1-octanol, and ethylene glycol monoethyl ether.

CA 44, 293 a

Sodium Hydroxide
Imperial Chem. Industries Ltd.
Brit., 625,750, July 4, 1949

A soln. of $Na_2CO_3$ is treated with a suspension of $Ca(OH)_2$ contg. between 1.5 and 2.5 equivs. of NaOH per equiv. of $Na_2CO_3$ in the initial reaction mixt. The NaOH used is obtained by recirculating a portion of the product of the reaction $Na_2CO_3 + Ca(OH)_2 \longrightarrow 2NaOH + CaCO_3$. Advantages are absence of free lime in the final ppt. and the fact that the $CaCO_3$ is pptd. in a coarse granules which are easily sepd. by settling or filtration. Diagrams are used in the explanation.

CA 44, 293 h

Removing Iron from Fused Alkali Hydroxides
Ya. M. Verblyunskii and A. S. Yusupova
U.S.S.R., 69, 611, Nov. 30, 1947

To fused hydroxide, e.g., NaOH, dewatered in the usual manner with an alkali metal, is added more of the same metal to reduce Fe oxides. The fusion is allowed to stand for the Fe to settle out.

CA 44, 463 c

Electrolysis of Aqueous Sodium Sulfate
Minoru Kunitomi
Japan, 174,457, Feb. 3, 1947

CA 44, 463 d

Caustic Soda
Bompei Yasui
Japan, 174,463, Feb. 3, 1947

Electrolysis of aq. NaCl is made, without diaphragm by addg. bentonite (I). $Cl_2$ at the anodic soln. is absorbed by I and NaOH in cathodic soln. is concd. by evapn. of water.

CA 44, 805 d

The Chlor-Alkali Industry in the U. S.
R. L. Murray
Ind. Eng. Chem. 41, 2155-64 (1949)

A review of world history and present position of the industry in the USA.

CA 44, 918 g

Reactions in a Melt. II. Measurements in Weakly Basic Alkali Sulfate Melts
Hermann Lux
Z. Electrochem. 52, 220-4 (1948); cf. CA 33, 5745-8

The behavior of several compds. able to produce a basic reaction in a molten eutectic of $Na_2SO_4$ - $K_2SO_4$ at 950° was investigated by means of a Au electrode. During addn. of $Na_2O$ or $Na_2O_2$ to the molten eutectic a strong neg. potential was observed, the reason for which is not now known. After a while the potential difference started to decrease in a linear fashion, which is explained by the vaporization of $Na_2O$. Extrapolation of the time vs. potential difference curve to zero time, i.e., the moment of addn. of $Na_2O$, shows that this extrapolated value is a log function of the $Na_2O$ or $O^{--}$ concn. The decompn. of $Na_2CO_3$, $Li_2CO_3$, $KNO_3$, $NaNO_2$ and NaOH could be traced exactly as a function of time. At small concns. these compds. formed the corresponding alkali oxide quantitatively. The decompn. of $Na_2CO_3$ or $Li_2CO_3$ can be stopped at the concn. of 0.1 mol.% of $Na_2O$ or $Li_2O$.

III. The Solubility of Magnesium Oxide. Ibid. 224-6

The increase of $O^{--}$ concn. due to soln. of MgO in the liquid eutectic of $Na_2SO_4$ - $K_2SO_4$ at 950° was followed by potential measurements. The log of concn. of $O^{--}$, and the soly. of MgO, resp., is a linear function of the log of the concn. of $Mg^{++}$. The following equation holds: $[Mg^{++}]^{0.44}$ $[O^{--}]$ = const. $MgSO_4$ reacts slightly acid in the eutectic liquid. The addn. of $Na_2O$ ppts. MgO. The soly. of MgO can be found from the relation: $[Mg^{++}] = [O^{--}]$ to 0.0066 mol.%. Data are presented for the 3 - component system: eutectic-$MgSO_4$-MgO at 950°.

CA 44, 2401 b

Precipitation of Some Heavy Cations by Sodium Hydroxide
Joseph Heubel
Ann. Chim. (12) 4, 699-744 (1949)

Cond. measurements are used to determine the nature of the ppt. formed when metal solutions are treated with NaOH, and when NaOH is treated with metal solutions. Under these conditions, $MgSO_4$ gives no basic salts, and pure $Mg(OH)_2$ ppts. $MnSO_4$ forms 2 $MnSO_4 \cdot Mn(OH)_2$ when a great excess of

$MnSO_4$ is present. The basic salt is stable when dry but is decompd. by $H_2O$, giving an equivalent mixture with its components. Higher temperature and diln. increase the degree of decompn. The salt is less soluble than $Mn(OH)_2$, and preparation of pure hydroxide is, therefore, difficult. It can also be obtained by adding NaOH to $MnSO_4$ at 100°. $FeSO_4$ gives $2FeSO_4 \cdot Fe(OH)_2$, which resembles the Mn compound but is even more difficult to decomp. Pure $Fe(OH)_2$ could not be obtained. Like many other ppts. of this type, Mn and Fe hydroxides are more soluble when pptn. begins than at the end of the pptn. $NiSO_4$ forms $NiSO_4 \cdot 4Ni(OH)_2$, relatively unstable in $H_2O$, which is difficult to decomp. completely to $Ni(OH)_2$ by NaOH, since it is less soluble than the hydroxide. $CoSO_4$ gives $CoSO_4 \cdot 5Co(OH)_2$, unstable in $H_2O$, and less resistant to the action of NaOH than the Ni salt, owing to the lower soly. of $Co(OH)_2$. Pure $Co(OH)_2$ can be obtained in this case, if enough time is allowed. $CuSO_4$ gives $CuSO_4 \cdot 3Cu(OH)_2$ and $ZnSO_4$ gives $ZnSO_4 \cdot 4Zn(OH)_2$. Both salts are stable in $H_2O$ and are easily decompd. to the hydroxides by NaOH. No zincate could be detected. When NaOH is added to concentrated $Pb(NO_3)_2$, 3 salts form, appearing in the order $PbO \cdot Pb(NO_3)_2 \cdot H_2O$, $2PbO \cdot Pb(NO_3)_2 \cdot H_2O$, and $5PbO \cdot Pb(NO_3)_2 \cdot 5/3\ H_2O$. The latter changes on aging into the monohydrate, which is more stable. Addition of nitrate to NaOH gives the pentabasic salt, which changes to the dibasic. It is very difficult to obtain pure $Pb(OH)_2$. No evidence of plumbite formation is found. The basic salts are complexes that are in equil. in the presence of $H_2O$ with the simple salt and the hydroxide. All the basic salts react with NaOH to give either the hydroxide directly, or intermediate salts, as with Pb. This ability to react with NaOH varies greatly with different metals and is probably related to the differences in soly. between salt and hydroxide. The action of $H_2O$ on the basic salts is not related to the action of NaOH on them. The ease of preparation of the salt depends on its stability in $H_2O$. In some cases, two forms of hydroxide may exist, a complex form, in which the free OH ion is derived directly from the basic salts by replacement of an anion, and the simple, or unimol. form. The latter is less active and less soluble than the former.

CA 44, 2674 g

Heat Transfer Fluids
Guy Corfield
Gas 26, No. 2, 19 (1950)

CA 44, 2712 e

Highly Concentrated Solutions of Alkali Hydroxide
Imperial Chemical Industries, Ltd.
Brit., 627,767, Aug. 16, 1949

A modification of the reference patent pretaining to the production of concd. solutions of alkali hydroxide by the decompn. of alkali metal amalgams. This process uses a series of horizontal cells in contrast to the vertical cells in the earlier patent. Cf. CA 43, 3986 a.

CA 44, 4322 b

Thermal Conductivity of Aqueous Sodium and Potassium Hydroxide Solutions at Various Concentrations and Temperatures
L. Riedel
Chem. Ing. Tech. 22, 54-6 (1950)

Extensive measurements are reported with consideration of the effect of dissolved ions on the cond. of $H_2O$. Data are presented graphically and in tabular form and a math. correlation is developed.

CA 44, 4768 a

Hi-Temp. Heat-Content, Heat-Capacity and Entropy Data for Inorganic Compds.
K. K. Kelley
U. S. Bur. Mines, Bull. No. 476, 241 pp. (1949)
U. S. Bur. Mines, Bull. No. 477, 147 pp. (1950)

CA 44, 5552 h

Preparation of Carbonate-Free Sodium Hydroxide
C. W. Davies & G. H. Nancollas (Edward Davies Chem. Labs., Aberystwyth, Wales)
Nature 165, 237-8 (1950)

Carbonate ion is removed from NaOH solns. by passing the solns. through a column of Amberlite IRA-400 resin.

CA 44, 5749 f

Higher Nickel Hydroxides
Oskar Glemser and Josef Einerhand (Rheinisch-Westfalische Tech. Hochschule)
Z. anorg. Chem. 261, 26-42 (1950)

Four higher Ni hydroxides are indicated in the calorimetric study of the oxidation of $Ni(NO_3)_2$ by alk. $K_2S_2O_8$ (CA 40, 4596-2) or by anodic oxidation ($NiSO_4 \cdot 7H_2O$ and NaOAc as electrolyte); $NiO_2 \cdot x\ H_2O$ (I), $Ni_2O_3 \cdot x\ H_2O$ (II), $Ni_3O_4 \cdot 2H_2O$ (III), and $NiO_{1.22-1.07} \cdot x\ H_2O$ (IV). I was detected only in the calorimetric study; because of instability it could not be isolated. II ($\beta$-NiOOH) is formed at room temp. both by pptn. with $K_2S_2O_8$ and by anodic oxidation. III ($Ni_3O_2(OH)_4$) is prepd. by anodic oxidation at 40-60° and by pptn. at 100°. It has the "double layer lattice" described by Feitknecht (CA 35, 2764-9). Fusion of metallic Ni with $Na_2O_2$ followed by careful hydrolysis yields a hydroxide of compn. II, considered to be $\gamma$-NiOOH (V). A third hydroxide of the compn. II is produced by pptn. of $K_2[Ni(CN)_4]$ by alk. $K_2S_2O_8$. This is designated $\alpha$-NiOOH (VI).

The Structure of the Higher Nickel Hydroxides. Ibid. 43-51

IV crystallizes in the C-19 lattice with unit cell dimensions a = 3.07 ± 0.01 A., c = 23.2 ± 0.1 A; parameter u = 0.370. NiOOH is irregularly embedded between normally developed $Ni(OH)_2$ layers. V is also of the C-19 type lattice, cell dimensions, a = 2.82 ± 0.01A., c = 20.65 ± 0.05A.; u = 0.377. VI has the C-6 type lattice, cell dimensions a = 2.81 ± 0.1A., c = 8A. II ($\beta$-NiOOH) crystallizes in the C-6 type lattice with cell dimensions a = 2.81 ± 0.01A., c = 4.84A. III. ($Ni_3O_2(OH)_4$) has a hexagonal lattice with a = 3.04 ± 0.02A., c = 14.6 ± 0.1A. X-ray and electron-optical diagrams show decided laminar development.

CA 44, 6587 f

Economic Handling of Caustic Soda with Variable-Area Flow Meter
Arthur Patureau
Petroleum Processing 5, 248-52 (1950)

Flow diagrams are given and equipment is described for handling 73% NaOH in the following applications: diln., metering within a plant, neutralization and pH control. Substantial savings in freight costs are obtained by shipping NaOH in the higher concn., but diln. during unloading is the key to this saving.

CA 44, 6752 g

Electrolytic Refining of Lead or Lead Alloys Containing Bi
Joseph C. Dittmer (to National Lead Co.)
U. S., 2,507,096, May 9, 1950

A process for removing Bi from impure Pb consists of electrolyzing the molten impure metal cathode in a molten NaOH electrolyte at 330-50° at a cathode c.d. of 100-400 amp. per sq. ft. and an anode c.d. of 200-1000 amp. per sq. ft. Bi is transferred from the cathode to the anode consisting of an iron pan contg. molten Pb. Cf. CA 33, 928-1.

CA 44, 7032 b

Anhydrous Caustic Potash
Arthur G. M. Hedley and Imperial Chem. Industries Ltd.
Brit., 635,175, April 5, 1950

A soln. contg. 94% KOH at a temp. of 330° is subjected to conditions in which the partial water-vapor pressure is below 150 mm. and in which a large surface area of soln. is provided. This may be accomplished by spraying the soln. into a vacuum or into a current of hot air.

CA 44, 7032 d

Sodium Carbonate
Andre G. E. Tardieu
Fr., 940,018, Dec. 1, 1948

A soln. of $NaNO_3$ [which may be prepd. from $Na_2SO_4$ soln. and $Ca(NO_3)_2$] is treated with $Mg(HCO_3)_2$ soln. under a pressure of 5 kg./sq.cm. of $CO_2$ and at a temp. of about 0°. The $NaHCO_3$ pptd. is calcined to give $Na_2CO_3$. The $Mg(NO_3)_2$ soln. formed in the reaction is treated with milk of lime to give $Mg(OH)_2$ (which is carbonated and used again in the process) and $Ca(NO_3)_2$. Limestone is roasted to provide the lime and $CO_2$ used.

CA 44, 7497 c

Crystalline Magnesium Hydroxide
Wm. C. Gilpin
Brit., 635,781, April 19, 1950

Water, contg. convertible Mg salts, is treated in a reaction vessel with powd. burnt, but unslaked lime, or dolomitic lime. The liquid contg. the pptd. $Mg(OH)_2$ in suspension is transferred to a settling vessel. Settled seed crystals of $Mg(OH)_2$ are then returned to the 1st vessel until their wt. is about 10-15 times the wt. of $Mg(OH)_2$ pptd. per hr. On filtering cold, a cake contg. 40% $Mg(OH)_2$ is obtained.

CA 44, 8740 h

Solubility of Hydroxides of Copper, Zinc, Nickel and Cobalt in Sodium Hydroxide and in Ammonia
M. I. Arkhipov, A. B. Pakshver, and N. I. Podbornova (Ivanov Chem. Tech. Inst.)
Zhur. Priklad. Khim. (J. App. Chem.) 23, 650-6 (1950); cf. Ibid. 23, 181 (1950)

Soly. was detd. at 20° after 24 hr. contact between the hydroxide and the soln. Selected data of equil. concns. of the hydroxide (g./l.) in terms of the concn. of $NH_3$ or NaOH (g./l.) are: in $NH_3$ 46.7, 130.5-139.0, 213.0, $Zn(OH)_2$ 10.6, 19.3 (max.), 18.7; $NH_3$ 36.4, 126.0, 193.0, $Ni(OH)_2$ 2.35, 9.0, 14.5; $NH_3$ 43.9, 123.7, 204.0, $Cu(OH)_2$ 3.75, 11.9, 15.5; in NaOH 68.4, 202.0, 360.0, $Zn(OH)_2$ 8.0, 45.5, 80.4; NaOH 68.4, 202.0, 360.0, $Cu(OH)_2$ 0.25, 2.87, 10.4; at 15° NaOH 56.4, 172.8, 240.0, $Cu(OH)_2$ 0.10, 0.89, 2.61; at 15° NaOH 86.4, 169.2, 209.2, $Co(OH)_2$ 0.57, 4.69, 9.26. The order of decreasing soly. in $NH_4OH$ is $Zn(OH)_2 > Cu(OH)_2 > Ni(OH)_2$; in NaOH, it is $Zn(OH)_2 > Co(OH)_2 > Cu(OH)_2 > Ni(OH)_2$. The stability of the solns. was tested by dilg. the satd. soln. with water until beginning pptn. at 18-20°, allowing to rest 48 hrs. in the dark, and analyzing the supernatant soln. From the exptl. data, the order of decreasing stability toward hydrolysis is, in solns. in $NH_4OH$, $Zn(OH)_2 > Cu(OH)_2 > Ni(OH)_2$ and in soln. in NaOH, $Zn(OH)_2 > Cu(OH)_2$. Solns. of the same hydroxide in $NH_4OH$

are more stable than in NaOH. Whereas $Zn(OH)_2$ is more sol. in NaOH than in $NH_4OH$, the soly. of $Cu(OH)_2$ and of $Ni(OH)_2$ is greater in $NH_4OH$. With regard to soln. of cellulose in an $NH_3$ or NaOH soln. of a metal hydroxide, the obvious requirement is high soly. of the hydroxide and low stability of the complex soln. in contact with the OH groups of the cellulose. If the latter action is considered to run parallel to the hydrolysis by water, the most suitable solns. are $Zn(OH)_2$ in NaOH or $Cu(OH)_2$ in $NH_4OH$, less active are solns. of $Ni(OH)_2$ in $NH_4OH$, and $Cu(OH)_2$ or $Co(OH)_2$ in NaOH. A soln. of $Zn(OH)_2$ in $NH_4OH$ cannot be used for dissolving cellulose because of its stability.

CA 44, 8808 d

Conditions for Precipitation and Stability in Aqueous Solutions of Ammonium, Sodium, and Potassium Uranates. Application to a Study of the Red and Orange Sulfides of Uranium
Gabriel Tridot (Faculty Sci., Paris)
Ann. Chim. (12) 5, 358-97 (1950)

By dets. pH and cond. vs. amt. of reagent added in titrations of standard solns. of $UO_2(NO_3)_2$ or $UO_2(OAc)_2$ with standard $NH_4OH$, NaOH, or KOH or vice versa, and by analyzing resulting ppts. and solns., T. finds certain general principles. Adding base to a salt produces first a basic salt and, eventually, when 1.5 moles of $NH_4OH$ or 1.6 moles of NaOH or KOH has been added per mole of $UO_2^{++}$, $UO_3 \cdot x\ H_2O$. Diuranates, $M_2O \cdot 2UO_3$, are formed by the addn. of bases to salts as well as by the addn. of salts to bases. Diuranate is the stable and common uranate. Starting with $UO_2(OAc)_2$, addn. of excess base yields monouranates, $M_2O \cdot UO_3$; under similar treatment $UO_2(NO_3)_2$ is transformed into diuranate. Monouranate forms incompletely when salts are added to basic solns., but is unstable, yielding diuranate in the presence of water or uranyl salts. With NaOH or KOH, unstable intermediates such as $M_2O \cdot 5UO_3$ or $M_2O \cdot 4UO_3$ can be formed. The addn. of $UO_2(NO_3)_2$ to $Na_2S$ gives NaHS and $M_2O \cdot 5UO_3$; further addn. of $UO_2(NO_3)_2$ produces $Na_2O \cdot 5UO_3 \cdot 2NaHS$, commonly known as uranium orange. Excess NaOH converts this into uranium red, $Na_2O \cdot 5UO_3 \cdot NaHS \cdot Na_2S$.

CA 44, 9127 g

Magnesium Hydroxide
Dorr Co.
Brit., 639,123, June 21, 1950

$Mg(OH)_2$ of desirable phys. characteristics can be manufd. from $MgCl_2$ brines treated with $Ca(OH)_2$ by controlling the pH (9.6-11.5 for sea water, 9.5-12.5 for brines of low Na content), the Mg-ion concn. (0.01-0.8 g./l.) with concns. towards the lower value giving the more desirable ppt., and the contact time (20-90 min., depending on agitation, particle size of lime-bearing solids, and degree of extn. of Mg ions from the brine). Cf. CA 36, 3991-8.

CA 44, 9274 b

Securing Pure Oxides by Electrolysis
Marthe Domine-Berges
Ann. Chim. (12), 5, 106-51 (1950)

Solutions were electrolyzed in an S-shaped cell under the following conditions: 20 - 2000 v., 25 - 30 ma., and 3 - 30 days. Hydroxides of Al, Mg, Be, Ni, Cr, Zr, Th, and U were obtained at the cathode when solutions of their salts were electrolyzed. Mixtures of hydroxide and metal were obtained at the cathode in the case of Ag, Cd, Cu, Fe, Pb, and Zn. Electrolysis of $Hg(NO_3)_2$ resulted in the formation of droplets of Hg which did not adhere to the cathode. The hydroxides of Al, Be, Mg, and Ni were obtained in the crystd. state. $Al_2O_3$ was recovered at the cathode when $Al(NO_3)_3$ was electrolyzed and at the anode when $NaAlO_2$ was electrolyzed.....

CA 44, 9274 g

Nickel Hydroxide
Shinzo Okoda, Tetsuo Shiraishi, and Keiichiro Watanabe (Kyoto Univ.)
J. Chem. Soc. Japan, Ind. Chem. Sect., 51, 129-30 (1948)

.....$Ni(OH)_2$ prepared with alkali hydroxides, was amorphous at first, gradually forming a laminar lattice structure, while $Ni(OH)_2$ prepared with concd. $NH_4OH$ and heated at high temperatures had sharp cryst. patterns.....

CA 44, 9642 g

Alkali Metal Hydroxide and Sulfur Dioxide
Caspar W. Dorbach
Brit., 639,855, July 5, 1950

Alkali metal hydroxides and $SO_2$ are produced by (1) causing a "metallate" as defined below, to react with an alkali metal sulfide to form the alkali metal hydroxide and a sulfide of the metal of the metallate; and (2) sepg. and roasting the sulfide to form the oxide of the metal and $SO_2$. The "metallate" is the chem. combination derived from the hydroxide of a multivalent metal, which forms an insoluble sulfide in alk. solution, in which 1 or more H atoms are replaced by an alkali metal. Metals forming metallates are Zn, Cu, Pb, Ni, Sn, Mn, and Fe. The alkali metal sulfide is produced by reduction from the corresponding sulfate, especially $Na_2SO_4$, for example, by calcination with coal or coke.

CA 44, 9844 i

The Properties of Aluminum Hydroxide and Alumina. I.
Koemon Funaki
J. Electrochem. Assoc. Japan 10, 103-11 (1942)

Curves of dehydration vs. temperature up to 800° are given for various samples of $Al(OH)_3$ obtained (1) by treating Na aluminate with $H_2O$, or (2) with $CO_2$ gas, (3) by treating solid $Al_2(SO_4)_3$ with $NH_4OH$, or (4) by treating $Al_2(SO_4)_3$ in solution with $NH_4OH$. Hydrargillite obtained by method 1 was more cryst. than bayerite obtained by method 2. Two types of $Al(OH)_3$ were obtainable by method 3. $Al(OH)_3$ prepared below 80° was very unstable and gradually became similar to bayerite, while that prepared above 80° was of the boehmite type, and $Al(OH)_3$ obtained at 150-200° had the exact compn. $Al_2O_3 \cdot H_2O$.

CA 44, 9845 b

II. Ibid. 134-46

From microscopic and rontgenographic studies the modification changes of $Al(OH)_3$ and $Al_2O_3$ are: $Al(OH)_3$ prepared from $Al_2(SO_4)_3$ and $NH_4OH$ is amorphous and of the boehmite type ($\gamma$-$Al_2O_3 \cdot H_2O$), $\gamma$-$Al_2O_3$ or $\alpha$-$Al_2O_3$, depending on whether the pptn. is carried out at 150, 450, or 1200°, resp. The amorphous $Al(OH)_3$ gel gradually changes into boehmite and then into bayerite ($Al_2O_3 \cdot 2H_2O$), which can be prepared by passing O into Na aluminate solution, but never into hydrargillite ($Al_2O_3 \cdot 3H_2O$), which can only be prepared by hydrolyzing Na aluminate. Amorphous $Al(OH)_3$ gel heated at 150, 450, or 1200° forms boehmite, $\gamma$-$Al_2O_3$, or $\alpha$-$Al_2O_3$, resp. By heating at 210° bayerite and hydrargillite form boehmite. Diaspore forms $\alpha Al_2O_3$ by heating at 650°.

CA 44, 9845 d

The Melting Point of Potassium Hydroxide
Ralph P. Seward and Kenneth E. Martin (State College, Pa.)
J. Am. Chem. Soc. 71, 3564-5 (1949)

About 50 g. KOH was melted in a Ni container brought gradually to 475-500° and kept there 10-12 hours. Further heating did not change the f.p. The f.ps. were detd. from cooling curves. When a stream of dry N was passed over the KOH during dehydration and cooling the f.p. did not differ from that obtained in contact with air. By extrapolation the f.p. of KOH with no carbonate present was estimated to be 410°. A transition point was found at 249°. The heat of fusion was calculated to be 1830 cal/mole.

CA 45, 6 a

Dowtherm-Heated Finishing Evaporator for Sodium Hydroxide
W. L Badger and D. J. Pye (Consulting Engineers, Ann Arbor, Mich.)
Chem. Eng. Progress 46, 486-9 (1950)

Historical development of the process with emphasis on equipment and materials of construction.

CA 45, 525 a

Caustic Cracking: Stress-Corrosion Tests in Sodium Hydroxide Solutions at Elevated Temperatures
C. D. Weir (Univ., Glasgow, Scot.)
Inst. Mech. Engrs. (London), Applied Mechanics Proc. 163, No. 55, 18-26 (1950)

Stress-corrosion tests were carried out with app. specially designed for these tests at high temperatures, and similar to that of Schroeder and Berk (CA 30, 2150-6). The specimens, of hollow form, were inserted into the base of an autoclave and loaded by means of a lever system, through a push rod inserted in the specimen. This arrangement permitted the production of accurate notch-forms on the external surface in contact with the NaOH solution. Failures, comparable with those in practice, may be produced under controlled laboratory conditions with considerable consistency, but are confined to non-homogeneously stressed specimens. Concd. NaOH solutions are more effective than dil. solutions, though failure has been obtained with less than 10% NaOH. Analytically pure NaOH solns. are as effective as solns. prepd. from the com. product; Si is not necessary to produce failure, nor does it stimulate it. The presence of tannin does not entirely prevent cracking, though it does so to some extent in practice. Anodic polarization does not prevent and may even stimulate intercryst. failure. Cathodic polarization is effective; in the only case where spontaneous failure occurred it was not accompanied by intercryst. cracks. A fine-grained steel of low C content was no more resistant to attack than a normal steel of the same C content, a fine-grained steel slightly enriched in C showed a remarkably improved resistance.

CA 45, 832 i

Magnesium Hydroxide
Jean C. Seailles
Brit., 640,348, July 19, 1950

An improved process for producing $Mg(OH)_2$ from Mg salts in aq. solutions consists of mixing lime-water with Mg brine, sepg. the formed ppt., and reinjecting continuously the ppt. from one operation into the reaction liquids used for the next operation. After a number of successive operations, a heavy ppt. is obtained; it is easily recovered, filtered and washed.

CA 45, 1740 c

Sodium Hydroxide
Wm. P. Dooley (to Am. Viscose Corp.)
U. S., 2,518,530, Aug. 15, 1950

A continuous cyclic process for the conversion of $Na_2SO_4$ to NaOH is described. An aq. solution of the former is carbonated, satd. with $NH_3$, and then further carbonated to produce a slurry contg. $NaHCO_3$. The latter compd. is then sepd. from the slurry and converted into NaOH.

CA 45, 2840 h

The Mechanism of Inhibition of the Corrosion of Iron by Sodium Hydroxide Solution
J. E. O. Mayne, J. W. Menter, and M. J. Pryor (Univ., Cambridge, England)
J. Chem. Soc. 1950, 3229-36

When Fe, freed from its original air-formed oxide film, is immersed in 0.1 N NaOH contg. dissolved O, it becomes covered as shown by electron diffraction with a thin film of $\gamma$-$Fe_2O_3$. The view is put forward that this film is responsible for passivity and results from a heterogeneous reaction between O dissolved in the solution and the Fe. A de-aerated solution of 0.1 N NaOH attacks Fe very slowly. The reaction is controlled mainly by high polarization of the cathodic discharge of $H^+$ ions. The potential of an Fe specimen in 0.1 N $K_2CrO_4$ is unaffected by dissolved O. It appears that $K_2CrO_4$ can oxidize the surface of film-free Fe to $\gamma$-$Fe_2O_3$ in the absence of dissolved O by the heterogeneous mechanism previously suggested (CA 43 9015 c).

CA 45, 3133 d

Removal of Chlorates from Alkali Hydroxides
Tom S. Perrin and Roger L. Annis (to Diamond Alkali Co.)
Brit., 642,946, Sept. 13, 1950

Caustic soda solutions are freed of contaminating $ClO_3$ by bringing the solutions into contact with H at elevated temperature and pressure in the presence of a dispersed Ni catalyst. The rayon industry consumes large quantities of NaOH which must be free of chlorates, a normal contamination in electrolytically prepared NaOH solution. The described process provides a means for quantitative removal of $ClO_3$ at relatively low cost. Caustic liquor contg. 50% NaOH and 0.10% $NaClO_3$ can be entirely freed of the latter within 1 hour by dispersing 0.18% of Raney Ni in the solution and heating to 165° under an H pressure of 165 pounds per square inch. The Al contained in the Raney Ni can be removed by leaching out with NaOH prior to the use of the Ni in the preparation of high-purity NaOH. The NaCl formed in the reduction is virtually insoluble in the concentrated NaOH and can be removed with the catalyst by filtration or decantation. By repeated use 0.5 g of Ni will destroy approximately 16 g. of $NaClO_3$ and purify 11 l. of a 36% NaOH solution, without causing a Ni contamination of the latter.

CA 45, 3133 h

Shipping Caustic Soda Liquors
Otto Kay (to Allied Chem. and Dye Corp.)
U. S., 2,526,878, October 24, 1950

Hot, concentrated (over 60%) NaOH solutions are kept from contamination during shipment in Ni-lined tank cars by inserting a C or Ni anode in the solution, with the tank lining as cathode, and maintaining a cathode c.d. of 0.0003 to 0.001 amp./sq.ft. No H is evolved, and practically no Ni is dissolved. A good Pb-plate storage battery will supply sufficient current for a 5-day period.

CA 45, 3693 a

Applications of the Eastman Thermocell Equation. I. Certain Absolute Ionic Entropies and Entropies of Transfer of Alkali Metal and Tetraalkylammonium Bromides and Hydroxides
J. C. Goodrich, et.al. (U. of Calif., San Francisco)
J. Am. Chem. Soc. 72, 4411-18 (1950)

The usefulness and validity of the Eastman (CA 22, 1089) thermocell equation were demonstrated by calculations based on thermocell e.m.f. measurements on thermocells using Ag-AgBr electrodes and thermocells using Hg-HgO electrodes and on cond. measurements. Entropies of transfer for $Li^+$, $Na^+$, $K^+$, $NH_4^+$, $Br^-$, $OH^-$, $Me_4N^+$, $Et_4N^+$, $Pr_4N^+$, and $Bu_4N^+$ were presented. The abs. partial molal entropy of H ions was calculated from the data and given as -2.1 + 0.4 e.u., based on the abs. partial molal entropy of $Br^-$ detd. by the Eastman equation with the assumption of zero entropy of transfer for large tetraalkylammonium ions. The tabulated ionic entropies of transfer are valid on a relative basis regardless of this assumption.

CA 45, 3701 f

Low-Temperature Heat Capacities of Inorganic Solids. I. The Heat Capacity of Boric Acid from 16 to 296°K. Description of the Ohio State University Solid Calorimeters
H. L. Johnston and Eugene C. Kerr (Ohio State U., Columbus)
J. Am. Chem. Soc. 72, 4733-8 (1950)

The heat capacities of boric acid, contg. less than 0.05% impurities, were measured between 16 and 296°K. The data yielded a value of 21.21 ± 0.1 cal. per mole per degree for the entropy at 298.16°K. A table of thermodynamic functions was prepared for boric acid at smoothed values of the temperature. Disorder due to H bonding in the layer lattice of boric acid was discussed. This disorder, which makes an entropy contribution of 0.69 e.u., may be responsible for a spread or hump that appears to exist in the heat-capacity curve between 20 and 160°K. If this is true, the disorder entropy is contained in the tabulated values derived from the heat capacities.

II. The Heat Capacity of Crystalline Boric Oxide from 17 to 300°K
E. C. Kerr, H. N. Hersh and H. L. Johnston
Ibid. 4738-40

The heat capacities of cryst. $B_2O_3$ were measured from 17 to 300°K. The entropy at 298.16°K. derived from the heat-capacity data is 12.87 ± 0.1 e.u. Values of $S^\circ$, $(H^\circ - H_0^\circ)$, $(H^\circ - H_0^\circ)/T$, $-(F^\circ - H_0^\circ)/T$ were computed for integral values of temperature.

IV. Heat capacities and entropies of lithium hydroxide and of lithium hydroxide monohydrate from 15 to 300°K. Third-law check on the entropies through the reaction $LiOH + H_2O$ (gas) = $LiOH \cdot H_2O$. T. W. Bauer, H. L. Johnston, and E. C. Kerr. Ibid. 5174-6.

Heat capacities of LiOH and $LiOH \cdot H_2O$ were measured from 15 to 300°K. Integration of the heat-capacity curves yielded molal entropy values at 298.16 K. of 10.23 ± 0.05 e.u. for LiOH and 17.07 ± 0.05 e.u. for $LiOH \cdot H_2O$. The change in entropy at 25° for the reaction $LiOH \cdot H_2O$ (cryst.) = LiOH (cryst.) + $H_2O$ (gas) obtained from Ueda's (CA 26, 4998; 27, 5627) data for dissocn. pressures of the hydrate and for heats of solution of the 2 crystals, combined with the value 10,520 ± 3 calories for the molal heat of vaporization of $H_2O$ is in good agreement with $\Delta S^\circ_{25}$ for the same reaction computed from the author's exptl. entropies for the crystals and with the spectroscopic value for the crystals and with the spectroscopic value for the entropy of steam (Gordon, CA 28, 2256-5) the application of the 3rd law to the calorimetric entropies of both LiOH and $LiOH \cdot H_2O$ was thus confirmed.

CA 45, 3703 d

The Heat of Solution of Halides, Sulfuric Acid, Oxalic Acid, Sodium Hydroxide, and Urea in Ethyl Alcohol-Water Mixtures
M. Bobtelsky and R. D. Larisch (Hebrew Univ., Jerusalem)
J. Chem. Soc. 1950, 3612-15

The detn. of the heat of solution was based on 2 measurements: (1) the change of temperature on dissolving the substance in alc.-$H_2O$ mixtures, and (2) the specific heat of the resulting solution. Halides studied included hydrated chlorides of Al, Cu, Ni, Co, K, and Fe, and anhyd. $FeCl_3$. Electrically heated twin calorimeters of special design were used. S-shaped curves were obtained when heat of solution was plotted vs. alc. content, with a pronounced min. at about 30% (wt.) of alc. In most cases a max. was observed at about 75% (wt). of alc. A const. difference of 26.2 kcal. between the curves for anhyd. and hydrated $FeCl_3$, up to the highest alc. concn., is equal to the mol. heat of formation of the hexohydrate at 23°. If the hydrate is dissolved in a mixt. contg. 83% alc., no heat effect is observed. At higher alc. concns. heat is absorbed.

CA 45, 4415 c

Caustic Soda Purification by Liquid-Liquid Extraction
H. C. Twiehaus and N. J. Ehlers
Chem. Ind. 63, 230-3 (1948)

NaOH produced by electrolysis of NaCl in diaphragm cells contains NaCl 0.9-1.1% and $NaClO_3$ 0.05-0.10% and is purified by countercurrent flow of 49-51% aq. NaOH and liquid $NH_3$, at a concentration of 70-95%, in an extn. column under pressure, which is controlled by continuous withdrawal of the upper liquid $NH_3$ phase, through a valve at the top of the column, to a still for recovery. In plant practice, the purified NaOH (95% of the feed) contains NaCl approximately 0.08 and $NaClO_3$ 0.0002%. The concentration of the liquid $NH_3$ determines the concentration of the purified NaOH which may be much higher than that of the feed. Residual $NH_3$ is removed from the NaOH by flashing at reduced pressure followed by treatment in a steam evaporator. Heavy metals are removed by absorptive agents. Comparative analyses are given and the costs of purifying the NaOH are discussed.

CA 45, 5004 a

Dissociation Constant of Calcium Hydroxide
C. W. Davies and Bernard E. Hoyle (Edward Davies Chem. Labs., Aberystwyth, Wales)
J. Chem. Soc. 1951, 233-4; cf. CA 32, 4052-4

Prior detns. by different methods (Kilde, CA 28, 4650-4; Bell and Prue, CA 43, 6055 a) do not agree. Redetn. of the soly. of $Ca(IO_3)_2$ in $Ca(OH)_2$ gives 0.050 for the dissocn. const. of $Ca(OH)_2$, in good agreement with the value of B. and P. This value falls off as the ionic strength increases, which may explain K's low value. At 25° 1/4 of the Ca in a satd. $Ca(OH)_2$ solution is present as $CaOH^+$.

CA 45, 5888 c

Barium Hydroxide from Barium Sulfide
Mikiyoski Ohshima, H. Arita and M. Sasaki
Japan, 177,553, Jan. 31, 1949

Fe oxide prepared by heating pyrite is used for treating aq. BaS for prepg. $Ba(OH)_2$.

CA 45, 6515 b

Electrolytic Cleaning of Metals
Hugh G. Webster (to J. H. Shoemaker)
U. S., 2,547,510, April 3, 1951

A bath for the electrolytic cleaning of oxide and scale from ferrous metals consists of NaOH 85, NaCl 10, Na aluminate 1, NaCN 2, and NaF 4 parts.

CA 45, 6896 e

Production of Sodium Hydroxide Solution by Ion Exchange
Harry Stern (Iowa State Coll., Ames)
Iowa State Coll. J. Sci. 25, 358-60 (1951)

When the exchange resin, Dow HCR, satd. with Na ions is brought into contact with a soln. of $Sr(OH)_2$, equil. is reached in a few min. The resulting soln. may contain as much as 3.5% NaOH. The optimum conditions are: 1.3N $Sr(OH)_2$, and $Sr(OH)_2$ equiv. to 2.8 times the $Na^+$ on the resin. The resin can be recharged by the use of NaCl. The $Sr^{++}$ can be sepd. from the soln. by pptn. as the basic chloride. The basic chloride can be converted to $Sr(OH)_2$ and HCl at 1700°F. in the presence of steam and $SiO_2$ and the HCl collected. Other bases could not be substituted for $Sr(OH)_2$. $Ca(OH)_2$ was not sol. enough. $NH_4OH$ was too little ionized. $Ba(OH)_2$ was molecularly adsorbed on the resin and formed a ppt. of $Ba(OH)_2 \cdot NaOH$ which removed NaOH from the soln. Other resins were not satisfactory.

CA 45, 6914 h

Melting Points of Mixtures of Sodium Formate and Sodium Hydroxide
G. D. Sirotkin
J. Applied Chem. U.S.S.R. 23, 285-7 (1950)(Engl. translation); Zhur. Priklad. Khim. 23, 275-7 (1950)

Tabulated data give the m.ps. of several mixts. of NaOH and Na formate, detd. by fusion in a capillary tube. A compd., $HCOONa \cdot NaOH$, is found which forms two eutectic points on the fusibility diagram, (a) corresponding to 2 mols. of HCOONa per mol. of NaOH with m.p. of 150°, and (b) corresponding to a compn. of 2 mols. of NaOH per mol. of HCOONa with m.p. of 170°.

CA 45, 6940 b

The Electrolytic Caustic Soda Industry
Wen-Siao Chang (Taiwan Alkali Co., Formosa)
J. Taiwan Pharm. Assoc. 1, 107-13 (1949); 2, 40-7 (1950)

A review.

CA 45, 6988 e

Alkali Metal Alloy Coatings
Harvey N. Gilbert (to E. I. duPont)
U. S. Pat. Appl. 748,353
Official Gaz. 634, 985-6 (1950)

A molten alkali metal hydroxide contg. an alkali metal hydride 0.5-5.0% by wt. of hydroxide (preferably the same metal from group of Na, K, Li, Rb, and Cs) brought in contact with the surface of a base metal (from group of Zn, Cd, Pb, Sn, and Au, or alloys thereof, or another metal with coatings thereof, e.g., galvanized iron) forms alkali metal alloys of any thickness integral with the base metal. Zn elements treated with molten NaOH-$Na_2H_2$ produce superior dry cells.

CA 45, 7414 b

Electrolytic Dissociation of Metal Hydroxides
C. W. Davies (Edward Davies Chem. Labs., Aberystwyth, Wales)
J. Chem. Soc. 1951, 1256-8

The hydroxides of most metals are much weaker electrolytes than are their other compds. It is suggested that for the hydroxides, but not for other ion pairs, the configuration $M^+$, $H_2O$, $OH^-$ tends to pass over into $M^+$, $OH^-$, $H_2O$, and so the protective effect of ionic hydration is lost. Both for the alkali and alk.-earth metals, the strength of the hydroxide increases with the interionic distance, in agreement with the idea that the radius r of the bare cation is the governing factor. When $z^2/r$, where z is the valency of the cation, is plotted against pK, a straight line is obtained for the alkali and alk.-earth metals. This relation is a criterion of ion-pair formation due wholly to electrostatic forces. The pK values of Zn, Cu, Tl, and Ag are greater than are those predicted by the linear relation; the size of the deviation should indicate the amt. of covalent bond character.

CA 45, 7452 e

Electrolytic Concentration of Caustic Soda
C. R. V. Linden (Iowa State Coll., Ames)
Iowa State Coll. J. Sci. 25, 376-7 (1951)

The effluent from a $Cl_2$-NaOH electrolytic cell contains 11% NaOH, 14-18% NaCl, and water. It must be concd. to 50% NaOH and the NaCl removed. If concd. electrolytically, evolution of Cl corrodes the electrodes. Preliminary expts. showed that low c.d., close spacing of electrodes, high temp. and smooth surfaces lower the tendency for evolution of Cl.

CA 45, 7512 e

Inhibiting the Corrosion of Ferrous Equipment Used in the Regeneration and Boiling of Alkali Metal Solutions
G. W. Ayers, E. E. Harton, and L. R. Mazurk (to Pure Oil Co.)
U. S., 2,556,387, June 12, 1951

The corrosion of Fe metals in a soln. of boiling 5-50% caustic alkali is prevented by adding from about 0.01 to 5.0% (preferably about 1%) $NaNO_3$. This inhibitor is especially useful in preventing corrosion during the regeneration of strong alkali sweetening solns. for hydrocarbon oils. These solns. contain large amts. of alkali, soly. promoters, and oxidation catalysts, as well as impurities from the oils.

CA 45, 7851 c

Solubility of Calcium Hydroxide in Presence of Potassium and Sodium Hydroxides
Nicola Fratini (Facolta ingegneria, Rome)
Ann. Chim. Applicata 39, 616-20 (1949)

The soly. of $Ca(OH)_2$ was detd. at 20 and 40° in the presence of NaOH and KOH. Both alkalies exert the same effect on the soly., which decreases from 0.02 mols. CaO per *l*. with no alkali present to 0.003 mols. CaO per *l*. with 0.2 mols. per *l*. of either NaOH or KOH.

CA 45, 7898 b

Alkali Metals
Paul F. Bente
U. S. Pat. Appl. 643,002
Official Gaz. 638, 288 (1950)

In the production of Li, Na, or K by electrolysis of the fused hydroxide with an insol. anode, water liberated at the anode is sol. in the fused hydroxide and reduced the current efficiency to about 50%; addn. of a bromide or iodide (or mixt. of the two) of the same alkali metal in range of from 15 to 42 mole % decreases the soly. of the water. In all cases, the m.p. of the electrolyte should not exceed 450°.

CA 45, 8385 d

New Investigations on Metal Hydroxides and Hydrated Oxides
Oskar Glemser
Fortschr. Chem. Forsch. 2, 273-310 (1951)

A review with emphasis on work in the past 15 years. A distinction is made between metal hydroxides, hydrated hydroxides (as $LiOH \cdot H_2O$), aquated oxides (as $TiO_2 + xH_2O$), and hydrated oxides. 114 references.

CA 45, 8728 g

Sodium Hydroxide and Sodium Carbonate From P-Fe-Al Ore and Sodium Sulfate
Yoshihiko Okae
Japan, 178,423, Apr. 7, 1949

The ore contg. $Fe_3(PO_4)_2 \cdot 8H_2O$ and $2AlPO_4 \cdot 4Al(OH)_3 \cdot 12\ H_2O$ is heated to 800° for 2 hrs. with C and $Na_2SO_4$, then treated in boiling water to form $Na_3PO_4$, FeS and $Al(OH)_3$. $Na_3PO_4$ is dissolved in boiling water and treated with $Ca(OH)_2$ to give NaOH. The residue is treated with NaOH to give $NaAlO_2$, which is sepd. from the FeS. By passing $CO_2$ over $NaAlO_2$ or treating it with $Ca(OH)_2$, $Na_2CO_3$ or NaOH is formed.

CA 45, 8920 i

Electrolytic Alkali Industry
Shinzo Okada (Kyoto Univ.)
J. Electrochem. Soc. Japan 19, 3-9 (1951)

Review.

CA 45, 8958 g

Stress Corrosion Cracking in Alkaline Solutions. Report of Technical Practices Committee 5C-Subsurface Corrosion by Alkaline Solutions.
H. W. Schmidt, et.al.
Corrosion 7, 295-302 (1951)

The results are presented of an industrial survey on the failure of materials in alk. solutions, largely dealing with NaOH. The relationship of temp. and concn. to failure can be expressed only in an approx. manner. To prevent stress corrosion cracking, the following recommendations were made, based on actual plant practice; decrease residual and applied stress, decrease temp., change materials of construction, and apply protective coatings. Points requiring further attention are outlined.

CA 45, 9199 a

How to Handle Liquid Caustic
R. A. Springer (to Diamond Alkali Co., Painesville, O.)
Chem. Eng. 58, No. 8, 112-13, 282 (1951)

Procedures are given for handling and diln. of 50 and 73% aq. NaOH. Costs of these two com. concns. are compared.

CA 45, 9231 f

Potassium Hydroxide
E. R. Saxena, D. S. Datar, and S. H. Zaheer
Indian, 43,437, May 30, 1951

KOH is obtained from feldspar by heating a mixt. of feldspar, $CaSO_4$ and $CaCO_3$ in the proportion of 1:1:4 at 800 to 900° for 4-6 hrs. and then leaching the product with water and evapg. the soln.

CA 45, 9354 d

Low-Temperature Thermodynamic Properties of Sodium Hydroxide
John C. R. Kelly and Paul E. Snyder (Carnegie Inst. of Technol., Pittsburgh, Pa.)
J. Am. Chem. Soc. 73, 4114-15 (1951)

The heat capacity of pure cryst. NaOH was detd. from 60 to 300°K. by use of a low-temp. adiabatic calorimeter. The NaOH used was purified by mono-alcoholate formation. From the exptl. data, smoothed values of $(H_T - H_0^\circ)$, $-(F_T^\circ - H_0^\circ)$, and $S_T$ were calcd. at several temps. These calcns. yield the value of 15.34 ± 0.1 entropy units for the entropy of this compd. at 298.16°K.

CA 45, 9818 e

Anhydrous Caustic Soda
Francis M. Joscelyne (to Imperial Chemical Industries Ltd.)
U. S., 2,556,185, June 12, 1951

A 90% NaOH soln. is heated to about 280°, subjected to a partial water-vapor pressure of less than 600 mm. of Hg, and sprayed down an empty tower. NaOH is thus deposited as a granular, dry anhyd. solid.

CA 45, 10104 f

Caustic Alkali by Electrolysis
Shinzo Okada and Shiro Yoshizawa
Japan, 180,004, Aug. 23, 1949

Instead of using a pure Hg electrode, a Hg-Cu (Cu 0.001-2.0%) or Hg-Ag (Ag 0.01-1.0%) electrode is used to prevent H formation due to Mg, Ca, or Fe impurities which cause an explosion when mixed with the Cl given off at the anode.

CA 45, 10517 d

New Methods in the Production of Anhydrous Sodium Hydroxide I, II.
Milan Belsky
Chem. Prumysl 1 (26), 51-3, 89-91 (1951)

A review.

CA 45, 10519 a

Dehydration of Caustic Alkali
Richard E. Hulme (to Diamond Alkali Co.)
U. S., 2,562,495, July 31, 1951

Caustic soda with less than 1% water is obtained by passing a preheated soln. in a thin film against a surface held at a temp. above the m.p. of NaOH and in vacuo, and then sepg. the two-phase system of water vapor and NaOH by impingement against a second hot surface.

CA 46, 9 i

Periodicity in the Group of Alkali Metals
G. G. Diogenov
Doklady Akad. Nauk S.S.S.R. 78, 899-900 (1951)

A new periodicity phenomenon is found if the thermal effects of reciprocal systems formed by hydroxides and nitrates of alkali metals are listed in 4 groups: (I) systems formed by neighboring elements, Li, Na//OH, $NO_3$ 11.2 kcal., Na, K//OH, $NO_3$ 6.1, K, Rb//OH, $NO_3$ 2.0, Rb, Cs//OH, $NO_3$ 3.0 kcal.; (II) systems formed by skipping 1 element, Li, K//OH, $NO_3$ 17.3, Na, Rb//OH, $NO_3$ 7.9, K, Cs//OH, $NO_3$ 4.7; (III) systems formed by skipping 2 elements, Li, Rb//OH, $NO_3$ 19.1, Na, Cs//OH, $NO_3$ 10.8; (IV) system formed by the 1st and the last element, Li, Cs//OH, $NO_3$, 22.0 kcal. A plot of the heat effects in that order is periodic. The systems Li, Na//OH, $NO_3$ and Li, K//OH, $NO_3$ were investigated for the 1st time. The 1st system proved to be irreversibly reciprocal, the 2nd singular. From the table, the singularity can be expected to increase from Li, K to Li, Rb to Li, Cs. Within one group, whereas Li, Na is irreversibly reciprocal close to singular, Na, K can be expected to be irreversibly reciprocal with a slight shift of equil., and K, Rb and Rb, Cs typically reversible-reciprocal.

CA 46, 223 b

The Development of the Methods of Production of Caustic Alkali Liquors
H. Ehlers (Elektrochem. Kombinat, Bitterfeld, Ger.)
Chem. Tech. (Berlin) 3, 226-30 (1951)

A review.

CA 46, 223 e

Purifying Alkali Metal Hydroxides
Chester C. Brumbaugh (to Diamond Alkali Co.)
U. S., 2,562,169, July 31, 1951

Alkali metal hydroxide solns. contg. undesirable amts. of chlorate ion are treated with alkali metal sulfites. The sulfite is suitably added in an excess, e.g., about 20% excess, of the stoichiometric amt. necessary to destroy the known amt. of chlorate ion present. Elevated temps. are used, e.g., temps. from 100° to the m.p. of the anhyd. alkali metal hydroxide. Thus the sulfite is preferably incorporated as an incident of concn. procedure. The sulfite may be added either as solid salt or as satd. or dil. aq. soln. A particular advantage of this method is that is reduces the chlorate-ion content to a tolerable limit without adding any other difficulties. The method is particularly applicable in the reduction of caustic soda to relatively anhyd. condition by heat-exchange evaporator systems of water removal or by the falling-film evaporator and separator system. The sulfite may be added to the feed to such a concn. system at any suitable time continuously or intermittently. In a caustic soda soln. contg. 0.166% chlorate, based on the content in anhyd. caustic soda, treatment with $Na_2SO_3$ added in the ratio of 14.1 lb. per ton of evaporator product, yielded a caustic soda having a chlorate content of the order of 0.002%. Cf. CA 45, 3133 d.

CA 46, 332 i

Heat Capacities of Inorganic Substances at High Temperatures. II. Heat Capacity of Calcium Hydroxide
Koichi Kobayashi
Science Repts. Tohoku Univ., First Ser., 34, 153-9 (1950)

The heat capacity of $Ca(OH)_2$ was measured between 310 and 670°K. with a heat-conduction calorimeter. $C_p = 14.18 + 3.202 \times 10^{-2}T - 2.17 \times 10^{-5}T^2$ cal./mole ($360 < T < 670$°K.). From this equation, the values $H_T^\circ - E_0^\circ$, $S_T^\circ - S_0^\circ$, and $-((F^\circ - E_0^\circ)/T)$ are calcd. $\Delta E_0^\circ$ is calcd. for the reaction $Ca(OH)_2 = CaO + H_2O$ (g) and found to be 25,790 ± 23 cal./mole using values of $-((F^\circ - E_0^\circ)/T)$ and the equil. const. $K_p$. $\Delta H^\circ_{291.1}$ is calcd. to be 26,099 cal./mole. By comparing the observed value of $\Delta H^\circ$ for the reaction $Ca(OH)_2 = CaO + H_2O$ (e) with the calcd. value above the $\Delta H^\circ$ for the reaction, CaO (cryst.) = CaO (finely divided) is found to be about 470 cal./mole.

CA 46, 1318 g

Study of Gas Evolution by Means of Automatic Recording of the Volume with a Kurnakov Pyrometer
L. G. Berg and B. Ya. Teitel'baum (A. E. Arbuzov Chem. Inst., Kazan)
Doklady Akad. Nauk S.S.S.R. 79, 791-4 (1951)

The vol. of gas evolved on heating a solid under conditions of uniform rise of the temp. is recorded by measuring the elec. resistance of a high-resistance Pt or nichrome wire stretched in the axis of a Hg-filled gas buret. As the gas displaced the Hg, an increasing length of the wire is bared, and its elec. resistance corresponds to the vol. of gas collected. The temp. t and the temp. difference $\Delta t$ are recorded simultaneously. With an equimol. mixt. $MgCO_3$ + $CaCO_3$, gas evolution ($CO_2$) begins at about 650° and reaches a max. at about 750°, where the t curve has a horizontal portion and the $\Delta t$ dips to a min.; the end of that gas evolution, corresponding to the dissocn. $MgCO_3 = MgO + CO_2$, is marked by the beginning of a horizontal portion of the vol. curve. Dissocn. of $CaCO_3$ begins at about 900°, and is again marked by the beginning of a horizontal portion of the t curve. The $\Delta t$ curve again dips to a min., and at the end of the gas evolution, the vol. curve levels off. Thermograms of $Ca(OH)_2$ + $Mg(OH)_2$ show arrests at about 400 and 525°, with minima of the $\Delta t$ curve. In contrast to the dolomite curve, the corresponding portions of the gas-vol. ($H_2O$) curve are not rigorously horizontal, but slowly slope downward. This is taken to indicate that slow dehydration sets in long before the dissocn. pressure has reached the external pressure, apparently owing to the drying effect of CaO which creates an environment of dry air around the sample.

CA 46, 1375 a

Sodium Hydroxide from Electrolysis of Sodium Sulfate by Use of Cation-Absorbing Resin
Senman Uezuki
Japan, 173,586, Sept. 2, 1946

A satd. soln. of $Na_2SO_4$ is electrolyzed to obtain NaOH in cathode chamber. $H_2SO_4$ in an anodic chamber is treated with $H_2SO_4$-absorbing resin (I) and it is returned to electrolytic bath with added $Na_2SO_4$. I is regenerated by treating it with aq. $NH_4OH$. $(NH_4)_2SO_4$ soln. is used for regeneration with an addn. of $NH_4OH$ until $(NH_4)_2SO_4$ (II) crystallizes out. II is treated with FeO and heated to 150-250° to give off $NH_3$ and $FeSO_4$ in residue. $NH_3$ is recovered and is used for the regeneration of resin. $FeSO_4$ is heated to 700°, and $SO_3$ gas is absorbed in concd. $H_2SO_4$. FeO is used repeatedly.

CA 46, 1428 h

Anticorrosive, Dark Film on Steel
Taizo Kobana (to Fuji Communications Instruments Manufg. Co.)
Japan, 172,871, June 10, 1946

One liter of soln. contg. NaOH 700, $NaNO_3$ 20, $NaNO_2$ 20, and $Na_2HPO_4$ 15 g. is heated to 140°. Steel is immersed in this soln., washed with water, and dried.

CA 46, 1725 f

Kurrelmeyer, Louis H.
The Potash Industry
Albuquerque: Univ. New Mexico, 1951, 83 pp. $1.50

Reviewed in Soil Sci. 71, 473 (1951)

CA 46, 1726 e

Sodium Hydroxide from Sodium Sulfate by Using Iron Oxide or Hydroxide Catalyst
Yoshihiko Okae
Japan, 180,137, Sept. 6, 1949

An equiv. amt. of C to reduce $Na_2SO_4$ to $Na_2S$ is heated with FeO or $Fe(OH)_2$ while superheated steam is passed thru for the reaction $Na_2S + FeO + H_2O \longrightarrow FeS + 2NaOH$.

# GENERAL INFORMATION CONCERNING HYDROXIDES

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