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REPORT ON DISTRIBUTION STUDIES BETWEEN MELTS AND SOLID PHASES USING RADIOACTIVE TRACERS

by

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ABSTRACT

The distribution of Ce(III) between molten $BaCl_2$ and solid $BaZrO_3$ in vacuo at 1000°C has been studied. Radiotracer experiments in which cerium ranged in concentration from 10^{-13} to 18.7 atom per cent of the cerium-zirconium content showed that essentially none of the cerium remained in the molten phase.

X-ray examination of the insoluble residue from the experiments showed the presence of monoclinic and tetragonal zirconia and a third phase identified as $Ce_2O_3.2ZrO_2$. The major reaction occuring in the system was concluded to be $3BaZrO_3+2CeCl_3 \rightarrow Ce_2O_3.2ZrO_2+3BaCl_2+ZrO_2$.

A new ternary oxide of yttrium and chromium was prepared and its formula and density determined. Its x-ray powder pattern can be indexed on the basis of a monoclinic cell. This compound and $LaCrO_3$ were used as solid phases in preliminary work on the investigation of common ion and foreign ion exchange phenomena. Radioyttrium 90 was separated from its parent radiostrontium 90 by ion exchange for use in these studies.

From a thermodynamic point of view, the problem of predicting the distribution of trace ion between solids and melts is one of evaluating $\Delta F°$ for the exchange reaction by which equilibrium is attained. A summary of the literature has been made with this in mind, and several methods for resolving and evaluating $\Delta F°$ are proposed.

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REPORT ON DISTRIBUTION STUDIES BETWEEN MELTS AND SOLID PHASES USING RADIOACTIVE TRACERS.

I. Introduction

The broad aims of the present research are, briefly: (a) to study the distribution of trace elements between a solid and a molten salt, including the effects of oxidation state of the trace element, temperature, and composition of the melt, (b) to measure exchange rates of common, as well as foreign, ions between a melt and solid, and (c) to investigate the factors that influence the tolerance of a solid phase toward foreign ions whose charges differ from those of the ions of the solid.

The work previously reported was directed primarily toward finding systems in which these aims could be pursued effectively. The results reported in Section 1, below, refer specifically to the system $BaZrO_3$-$BaCl_2$-$CeCl_3$ to which considerable interest was attached during the earlier work. The continuing study of this system has served to clarify most of the uncertainties raised at the time of the last report, and at the same time to point the way to a promising line of further investigation in harmony with the research aims stated above. Most of the work on this system has been incorporated in the thesis submitted by one of us (J.J.Casey) in partial fulfillment of the requirements for the doctor's degree granted at the University of Connecticut in June 1954. For a more detailed discussion of the material reported in sections 1.1, 1.2, and 1.3, reference may be made to this thesis. A paper based on this material is now in preparation, and will shortly be submitted for publication.

Section 2 presents the results of work on systems involving ternary oxides of yttrium or lanthanum with chromium or cobalt. The results obtained are promising.

In Section 3 are outlined current efforts to develop a useful thermodynamic approach to some of the problems encountered in this research.

Section 4 provides a summary of the proposals advanced in each of the first three sections for future work under an extension of the contract.

1. THE SYSTEM $BaZrO_3$-$CeCl_3$-$BaCl_2$

1.1 The nature of the high temperature reaction

Evidence presented in the last annual report indicated that in the neighborhood of 1000°C a reaction takes place between solid barium zirconium oxide and cerium(III) chloride in a flux of molten barium chloride. This reaction has been further studied, the uncertainties evident at the time of the last report have been largely resolved, and the essential nature of the product phase is believed to be understood.

The techniques found necessary for working with this system have been described. The desired amount of cerium chloride solution was added to barium chloride and evaporated in an atmosphere of hydrogen chloride, then dried under vacuum for an hour at 125°C. After mixing with the required amount of barium zirconium oxide, the sample was placed in a covered platinum test tube and sealed into a fused silica capsule.

The capsule was placed in a furnace at 1000°C and reaction was allowed to take place for a minimum of eighteen hours. The product was removed from the test tube and finely ground in a cool agate mortar. It was then leached free of barium chloride with cold water. The residue was freed of water by washing several times with acetone and was dried in a vacuum desiccator. X-ray data were obtained for the residues so prepared and also for residues after oxidation for several hours at 1000°C.

X-ray powder photographs were taken with Picker cameras of radius 35 mm. and 107 mm. Copper K-α radiation was used. The films used for calculations were from the large camera and were corrected for shrinkage.

With increasing value of the ratio Ce:Zr, gradual disappearance of the cubic perowskite pattern of barium zirconium oxide was noted. At the same time there appeared the lines of a face-centered cubic phase, a tetragonal phase, and a phase characterized as monoclinic through the close resemblance of its X-ray pattern to that of monoclinic zirconia. Table 1 shows this gradual change.

Table 1

Variation in X-ray patterns with increasing cerium

Sample No.	Atom Ratio Ce:Zr	Intensities of Patterns $BaZrO_3$	F. C. C.	Tetrag.	Mono.
1	0.026	vs	none	none	none
2	0.064	vs	vvw	none	vvw
3	0.122	vs	m	vw	vw
4	0.202	s	m	w	w
5	0.430	m	s	w	w
6	0.501	w	s	w	m
7	0.636	vw	vs	w^+	m
8	0.667	none	vs	w^+	m

Only after the Ce:Zr atom ratio had surpassed 0.667 was any Ce(III) ion found in the solidified molten phase. This fact, and the X-ray data, indicated that the reaction was essentially:

$$2CeCl_3 + 3BaZrO_3 \longrightarrow 3BaCl_2 + 3ZrO_2 + Ce_2O_3,$$

but that the oxide products were present in more than one phase.

1.2 Characterization of the product phases

Lattice parameters for the face-centered cubic phase were calculated from the X-ray data for several of the residues obtained from samples of different Ce:Zr ratios. They were the same within the limits of experimental error. The lattice parameter was originally determined to be about 5.35 Å., but the presence of certain weak lines required a doubling of the cell edge, which was calculated to be 10.699 Å. with an estimated error of ± 0.005 Å. The low precision was the result of the very diffuse character of the lines in the back reflection region, where there was no resolution into doublets, even in the case of annealed samples. The data for the face-centered cubic phase from a typical residue are presented in Table 2.

Table 2

X-ray data for the face-centered cubic phase in the unoxidized residue.

d/n	N	hkl	Intensity	a (Å)
3.217	11	311	vvw	10.6695
3.078	12	222	vs	10.6628
2.665	16	400	s	10.6600
2.451	19	331	vw	10.6837
2.375	20	420	vvw	10.622
2.186	24	422	vvw	10.710
2.054	27	511 333	vw	10.6730
1.8888	32	440	vs	10.6846
1.8022	35	531	vvw	10.6621
1.6949	40	620	vvw	10.7196
1.6113	44	622	vs	10.6880
1.5422	48	444	m	10.6846
1.4978	51	711 551	vvw	10.6964
1.4790	52	640	vvw	10.6652
1.4237	56	642	w	10.6540
1.3894	59	731 553	w	10.6721
1.3363	64	800	w	10.6904
1.3028	67	733	vvw	10.6634
1.2262	76	662	m	10.6896
1.1955	80	840	m	10.6928
1.0914	96	844	m	10.6936
1.0281	108	10,2,2 666	m	10.6844
0.9453	128	880	vvw	10.6950

Table 2. (continued)

d/n	N	hkl	Intensity	a (Å)
0.9320	132	10,4,4 882	vw	10.708
0.9037	140	10,6,2	m	10.6928
0.8913	144	12,00 884	m	10.6956
0.8457	160	12,4,0	m	10.6974
0.8160	172	10,6,6	m	10.7016
0.8043	176	12,4,4	m	10.6702

When the residues were oxidized, a change in the face-centered cubic phase resulted. Certain weak lines disappeared, allowing indexing on the basis of a small cell, whose lattice parameter was calculated to be 5.272 ± 0.002Å. Refer to Table 3.

Table 3

X-ray data for the face-centered cubic (fluorite) phase in the oxidized residue.

N	d/n	θ(radians)	a (Å)
3	3.037	0.25671	5.2604
4	2.2630	0.29756	5.2600
8	1.8631	0.42661	5.2696
11	1.5886	0.50669	5.2686
12	1.5210	0.53152	5.2689
16	1.3154	0.62622	5.2616
19	1.2093	0.69121	5.2712
20	1.1788	0.71280	5.2717
24	1.0758	0.79891	5.2703
27	1.0135	0.86436	5.2663
32	0.9319	0.97415	5.2717
35	0.8910	1.04564	5.2712
36	0.8787	1.07024	5.2722
40	0.8327	1.18328	5.2665
43	0.8031	1.28761	5.2669
44	0.7941	1.32834	5.2675

By comparison with the work of Duwez and Odell(1) it was concluded that the face-centered cubic phase in the oxidized residue was a solid solution of cerium(IV) oxide-zirconium(IV)oxide of approximately fifty mol per cent composition. This means that the face-centered cubic phase in the unoxidized residue must have the approximate composition $Ce_2O_3.2ZrO_2$. The X-ray data for this phase are compatible with a fluorite structure having ordered oxygen vacancies, which would indicate an ordered arrangement of metal atoms. The X-ray data may also be compatible with a structure of the pyrochlorite type(2).

Attempts were made to vary the composition of the phase but these were unsuccessful, as indicated by the constancy of the lattice parameter. It therefore appeared likely that the phase represented a preferred structure. This is in harmony with the results of Trombe and Foex(3) on the zirconia-lanthanum oxide system. These authors found a preferred structure at the composition represented by $La_2O_3.2ZrO_2$, for which they reported a lattice parameter of 5.39Å. In the present work this phase was reproduced using the same method as for $Ce_2O_3.2ZrO_2$ and a lattice parameter of 10.8022±0.0005Å. was found. The doubling of the cell edge was again made necessary because of the presence of a few very weak lines.

It is interesting that the oxidized phase ($CeO_2.ZrO_2$) was produced at a temperature at which Duwez and Odell found instability for these solid solutions with less than ninety mol per cent cerium(IV)oxide, their preparations having been carried out at 2000°C with subsequent aging at lower temperatures.

The tetragonal and monoclinic phases underwent no detectable contraction on oxidation, and it was therefore concluded that these phases contained little cerium. Both would be explainable on the basis of zirconia alone which had only incompletely reverted to the monoclinic form.

1.3 Entry of cerium(III) into the lattice of $BaZrO_3$

It has been demonstrated that a reaction occurs in the system under study in the course of which barium zirconium oxide is converted into other products. This suggests that barium zirconium oxide is unsuitable as a solid phase in which to study the distribution of cerium, one of the original objectives of this research. Whereas this conclusion is certainly justified for high concentrations, it does not necessarily apply to low or trace concentrations. Preliminary evidence for the entry of small amounts of cerium(III) into the lattice of $BaZrO_3$ has been obtained in the experiment to be described, and is of particular interest in view of the studies that have preceded it and the possibilities that are suggested.

A reaction mixture containing 17.4 atom per cent cerium with respect to zirconium was equilibrated for 40 hours at 1000°C. About 0.06 microcurie of radiocerium was present in the mixture. The product was extracted with hot water to remove barium chloride. The extract was made basic with ammonia, but no precipitate was obtained. Carrier cerium was added to the solution, and the resulting precipitate was centrifuged, washed, and mounted for counting. After the removal of barium chloride, the residue from the experiment contained product phases and unreacted barium zirconium oxide. The barium zirconium oxide was removed by treatment with hot concentrated hydrochloric acid, in which the product phases are insoluble. The acid solution was made ammoniacal, and the hydrous oxide precipitate of zirconia and any cerium(III)oxide was washed and mounted for counting. The remaining undissolved residue from the experiment was washed and mounted. The counts per minute obtained from the three mounted samples are presented in Table 4.

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Table 4

Activities of samples in counts per minute

1.	Precipitate from $BaCl_2$ leachings	12 c/m
2.	Precipitate from $BaZrO_3$ leachings	2200 c/m
3.	Undissolved residue	5210 c/m

These results show that a maximum of about thirty per cent of the cerium was associated with the barium zirconium oxide phase. If this quantity were serving solely to replace barium (in the ratio of 2 Ce^{+3}:Ba^{+2}), then twelve per cent of the original barium ions would have been replaced in the solid.

The results of this one experiment cannot be taken as more than a strong indication that entry of cerium(III) into the lattice of barium zirconium oxide is possible in the range of low concentrations. The possibility is of such interest, however, as to invite further investigation. With the nature of the high temperature reaction clarified, and with suitable handling techniques established, it is proposed to resume the study of the distribution of tracer cerium in this system, after first verifying the results of the experiment just described.

1.4 Scattering and self-absorption corrections in the radiochemical determination of barium-140.

Reference was made in the previous report to the need for an experimental determination of the effects of sample thickness on the counting rate of samples of radiobarium. Such a study is now in progress.

A large number of barium chromate samples of different thickness have been prepared containing known amounts of barium-140. The growth of the 40-hr. daughter, lanthanum-140, and the decay of the equilibrium mixture (13-day half-life) are being followed. The results of this work will permit a quantitatively correct interpretation of the complex decay curves to be made. Such interpretation is not possible at present for thick samples, primarily because the less energetic beta radiation of barium-140 is more subject to thickness effects than is the lanthanum-140 radiation. Therefore the ratio of counting efficiencies for the two varies from sample to sample, and an experimentally determined correction must be applied.

1.5 A simple method of separating barium-140 from its daughter lanthanum-140.

During the course of the tracer work, it has been found that carrier-free traces of lanthanum in neutral aqueous solution adhere sufficiently well to the surface of pyrex glass to permit basing a practical separation procedure on this phenomenon. If dilute solutions of radiobarium nitrate are kept in flasks packed with glass wool, the lanthanum daughter is almost quantitatively retained on the glass. It is therefore possible to withdraw an aliquot of active barium nearly free of lanthanum at any time it is desired.

2. SYSTEMS CONTAINING TERNARY OXIDES OF YTTRIUM OR LANTHANUM WITH CHROMIUM OR COBALT.

The search for suitable systems in which to study the distribution of trace ions between a molten salt and a solid led us to consider the possibility of replacing lanthanum in $LaCrO_3$ or $LaCoO_3$ with yttrium, using sodium chloride as the liquid phase. This appeared to be a convenient system since suitable radioactive isotopes of both yttrium and lanthanum are available, and since $LaCrO_3$, recently prepared in these laboratories, has also been found to have the perowskite structure.

2.1 The $LaCoO_3$ System

Lanthanum cobalt oxide was found to be unsatisfactory for use as a solid phase in the study of distribution between the solid and liquid phase because of its solubility in aqueous solutions of ammonium chloride. Insolubility is desired because the flux and yttrium (as the oxide or chloride) must be leached from the solid phase by a slightly acid solution. This solid phase was originally thought to be insoluble in slightly acid solution, but the colored solution resulting from boiling lanthanum cobalt oxide in concentrated ammonium chloride solution could only be due to the cobalt chloride complex ion. Further work on the $LaCoO_3$ system has been deferred for the present.

2.2 Preparation of $LaCrO_3$ and $YCrO_3$

Lanthanum chromium oxide was prepared by two methods. The first was a solid phase method whereby quantities of lanthanum nitrate and chromic oxide were intimately mixed in proportions which conformed to the stoichiometry of $LaCrO_3$. The mixture was heated in a hydrogen atmosphere at 900°C for twenty-four hours. The second method involved the same conditions except that the mixture was reacted in a sodium chloride flux. The latter preparation, after leaching in water and drying gave the clearer X-ray pattern, which was probably due to better crystal formation from the melt.

In order to obtain prior evidence of what might be expected from the distribution experiments, the preparation of a compound of the lanthanum chromium oxide type with yttrium replacing lanthanum was attempted.

Chromic oxide was prepared by ignition of reagent grade chromic nitrate until there was no further loss of weight. Yttrium oxide, reported to be 99% pure, was used without further purification. Intimately ground mixtures of the two oxides, with the yttrium oxide to chromic oxide molar ratio always greater than one, were heated in a sodium chloride flux at 900°C in a hydrogen atmosphere. The flux was removed from the water-insoluble product by leaching with water; excess yttrium oxide was removed by leaching with very dilute hydrochloric acid.

In order to establish that the yttrium oxide-chromic oxide reaction product was a pure compound and to determine its formula weight, samples were prepared with the reactants mixed in various proportions. X-ray powder patterns of these products were always the same except for the additional lines of the excess reagent. On leaching the product with very dilute hydrochloric acid, washing, and drying, excess yttrium oxide was removed from the product, and X-ray patterns of these samples were taken. The data obtained from one of these photographs were used in the structure investigation. The same sample was subjected to a chemical analysis. Chromium was determined by dissolving the sample in boiling, concentrated perchloric acid, adding potassium iodide, and titrating the resulting iodine with sodium thiosulfate. Yttrium was determined as the oxalate. A sample analysis showed: chromium, 28.75±0.05 per cent; yttrium, 46.1±0.1 per cent. The theoretical percentages for $YCrO_3$ are: chromium, 27.54 per cent; yttrium 47.06 per cent. On the basis of the formula $YCrO_3$ for the reaction product, the above figures would indicate an excess of about 2.5 per cent chromic oxide.

The density of yttrium chromium oxide was determined pycnometrically by water displacement and an average value of 5.78±0.05 g/cc. was obtained. Using this value and that of the volume of the unit cell as determined by X-ray methods, a value of 190 ± 2 molecular weight units was obtained, as compared to the formula weight for $YCrO_3$ of 188.9. The molecular weight is not a sensitive test of formula, but when the X-ray and chemical evidence are considered together, the simple formula seems well established.

2.3 Structure of $LaCrO_3$ and $YCrO_3$

In the work on the systems Y-$LaCrO_3$ and La-$YCrO_3$ valuable information relative to phase changes can be obtained from X-ray diffraction data. However, prior knowledge of the structure and diffraction patterns of the pure compounds - lanthanum chromium oxide and yttrium chromium oxide - is necessary. Lanthanum chromium oxide is known (4) to be a simple cubic perowskite type with lattice parameter a = 3.88Å. Yttrium chromium oxide, a new compound prepared in this laboratory, yields an X-ray diffraction pattern which bears a resemblance to that of the cubic perowskite. This pattern is, however, much more complex in that several of the strong lines characteristic of the cubic pattern appear as multiplets. It was soon noticed that there were relationships among the $\sin^2\theta$ values (where θ is the Bragg angle) which would normally be taken to be characteristic of the tetragonal system. By applying analytical methods (5) based on these relationships and also graphical methods (Hull Davy charts and Bunn charts) several possible tetragonal cells were investigated. None of these proved satisfactory either because some lines were unaccounted for or the agreement between observed and calculated $\sin^2\theta$ values, was, in many cases, poor. That these apparently tetragonal relationships among $\sin^2\theta$ values did not lead to a tetragonal unit cell was taken to mean that the squares of the lengths of at least two cell edges were very close to being equal and the cell angles close to 90°.

In view of the fact that the tolerance factor, t, in the Goldschmidt relationship, $R_A + R_O = t\sqrt{2}\,(R_B + R_O)$, has the value of 0.86, there is considerable precedent from which to expect a monoclinic or orthorhombic distortion of the perowskite structure for this compound(6). Attempts to index the powder pattern on the basis of a monoclinic cell were successful. The dimensions which give the best fit between observed and calculated $\sin^2\theta$ values were $a = c = 7.61 \pm 0.01$ Å, $b = 7.54 \pm 0.01$ Å and $\beta = 92°56' \pm 6'$. All but two lines of the X-ray powder pattern were indexed on the basis of this cell. (Table 5). One of the two very weak lines which could not be indexed, matched a moderate reflection of the chromic oxide pattern. The remaining strong and moderate lines of chromic oxide were effectively covered by the yttrium chromium oxide pattern. Thus the small excess of chromic oxide indicated by chemical analysis could also be implied from X-ray evidence.

Table 5

COMPARISON OF OBSERVED AND CALCULATED INTERPLANAR SPACINGS

I	$d_{obs.}$	$d_{calc.}$	hkl
vvw	5.59	5.52	$\bar{1}01$
vvw	5.21	5.24	101
w	4.31	4.29	111
m	3.775	3.770 3.801	020 200
vw	3.624	(3.62)	Cr_2O_3
s	3.387	3.393 3.377	210 120
vw	3.054	3.059 3.047	121 211
vw	2.972	2.961	220 β
s	2.756	2.759	$\bar{2}02$
vvs	2.674	2.677	220

(continued - 2)

s	2.621	2.619	202
m	2.587	2.591	$\bar{2}12$
w	2.472	2.474	212
vw	2.365	2.368	301
vw	2.312	2.323	$\bar{3}11$
m	2.263	2.259 2.266	311 131
m^-	2.223	2.227	$\bar{2}22$
m	2.152	2.152	222
m	2.095	2.097	230
w^+	2.049	2.050	$\bar{3}21$
w	2.005	2.005 2.007	321 231

(continued - 3)

I	$d_{obs.}$	$d_{calc.}$	hkl
s	1.902	1.901	400
m^+	1.883	1.885	040
m^-	1.858	1.859	$\bar{2}32$
m	1.842	1.843 1.839	410 $\bar{3}03$
vw	1.815	1.813 1.812	232 $\bar{4}11$
vvw	1.737	1.736	$\bar{4}02$
vvw	1.722	1.723	331
s	1.690	1.689 1.692	240 $\bar{4}12$
w	1.670	1.672 1.666	$\bar{4}21$ 402
w^+	1.626	1.627	412
vvw	1.607	?	?
vw	1.593	1.594	332
m^+	1.577	1.577	$\bar{4}22$
m^+	1.555	1.557	$\bar{2}42$
s	1.525	1.524 1.527	422 $\bar{4}13$
m^+	1.428	1.429	$\bar{4}32$
vw	1.404	1.402	250
vw	1.380	1.380 1.382	$\bar{4}04$ 423
w^+	1.357	1.357	$\bar{4}14$
m^+	1.339	1.339	440
vvw	1.325	1.325 1.326 1.324	$\bar{4}33$ $\bar{4}41$ 252
w	1.310	1.310 1.311	441 404

(continued - 4)

w	1.293	1.292 1.292	414 531
vw	1.273	1.272 1.273	351 $\bar{5}31$
w	1.249	1.249 1.248 1.250	442 $\bar{5}32$ 610
w	1.206	1.205	$\bar{6}12$
w^+	1.193	1.193	260
w	1.183	1.183 1.182 1.184	540 $\bar{2}61$ 602
vw	1.171	1.170	612
vw	1.159	1.159 1.159	$\bar{5}24$ 504
w	1.137	1.137 1.139	533 $\bar{4}52$
w	1.132	1.132	630
vw	1.117	1.117 1.118 1.118	542 $\bar{3}61$ 452
w	1.098	1.098 1.099	$\bar{6}32$ 613
w	1.077	1.076 1.077	444 070
w	1.070	1.069	$\bar{6}14$
w	1.018	1.018 1.018 1.017	$\bar{4}62$ $\bar{4}54$ 703
m^-	1.002	1.003	642
m^-	0.9936	0.9938 0.9940	624 722

All linear dimensions of this cell are roughly twice those to be expected for the primitive perowskite unit and thus it corresponds to eight molecules.

2.4 $YCrO_3 - \overset{*}{Y}^{+3}$; $LaCrO_3 - \overset{*}{La}^{+3}$ Exchange Systems

Exchange studies on the systems yttrium chromium oxide-radioyttrium^{+3} ion, and lanthanum chromium oxide - radiolanthanum^{+3} ion in molten sodium chloride to determine the rate and extent of exchange are now in progress. The same procedure was followed in preparing samples of radiolanthanum and radioyttrium in sodium chloride flux as was employed in the radiocerium-barium chloride system with the same precautions to prevent hydrolysis of the tripositive ion. Equilibration of the liquid phase with yttrium or lanthanum chromium oxides was then allowed to take place at the desired temperature. If a temperature below 900°C was desired the sodium chloride flux was replaced by a mixture of sodium and potassium chlorides so that the flux would melt at a lower temperature.

After the reaction had taken place the capsule was broken open and the material in the test tube was leached out. The insoluble solid phase was mounted and counted in a G.M. counter. The activity in the solid phase is a measure of the amount of exchange of the yttrium (or lanthanum) between the liquid and solid phase.

To determine the distribution of yttrium between the solid phase, lanthanum chromium oxide, and the liquid phase, molten sodium chloride, a similar procedure will be used.

2.5 Source of Radioactive Tracers

In order to apply X-ray diffraction to elucidate some of the problems involved in this research problem, either isotopes of very short half life must be used, or duplicate samples with non-radioactive elements must be prepared. Since isotopes with very short half-lives of both yttrium and lanthanum are available, namely Y^{90} (61 hours) and La^{140}(41.4 hours), the former method was adopted. The short half-lives are, however, detrimental in that the daughter isotopes must be separated from their respective parents, Sr^{90} and Ba^{140}, immediately before use.

A method for the rapid and complete separation of Y^{90} from its parent Sr^{90} is being investigated. It employs an ion exchange column 10 cm long and 0.6 cm in diameter packed with Nalcite HCR. The equilibrium mixture of Sr^{90} - Y^{90} is placed on the column and eluted at one drop per minute with 5% lactic acid buffered at a pH of 4.5 with ammonium lactate. The yttrium is eluted first. In an experimental run under these conditions, five drop samples were taken of the eluted material and dried and counted. A curve of the type shown in Figure 1 was obtained.

After waiting about 84 hours for transient equilibrium to be established, the column was monitored and nearly all of the activity was found to be concentrated near the top of the column. This indicates that although the yttrium is eluted quite readily, the strontium moves down the column only very slowly under the conditions used. A second elution was performed under conditions identical to the first. It can be seen in the figure that the amount of activity was nearly the same in both cases. Monitoring the column again showed nearly no movement in the strontium band. The decay curves of the eluted material are perfectly straight on a semi-logarithmic plot, indicating a high degree of radiochemical purity.

It is proposed to use the same method for the separation of lanthanum-140 from its barium parent.

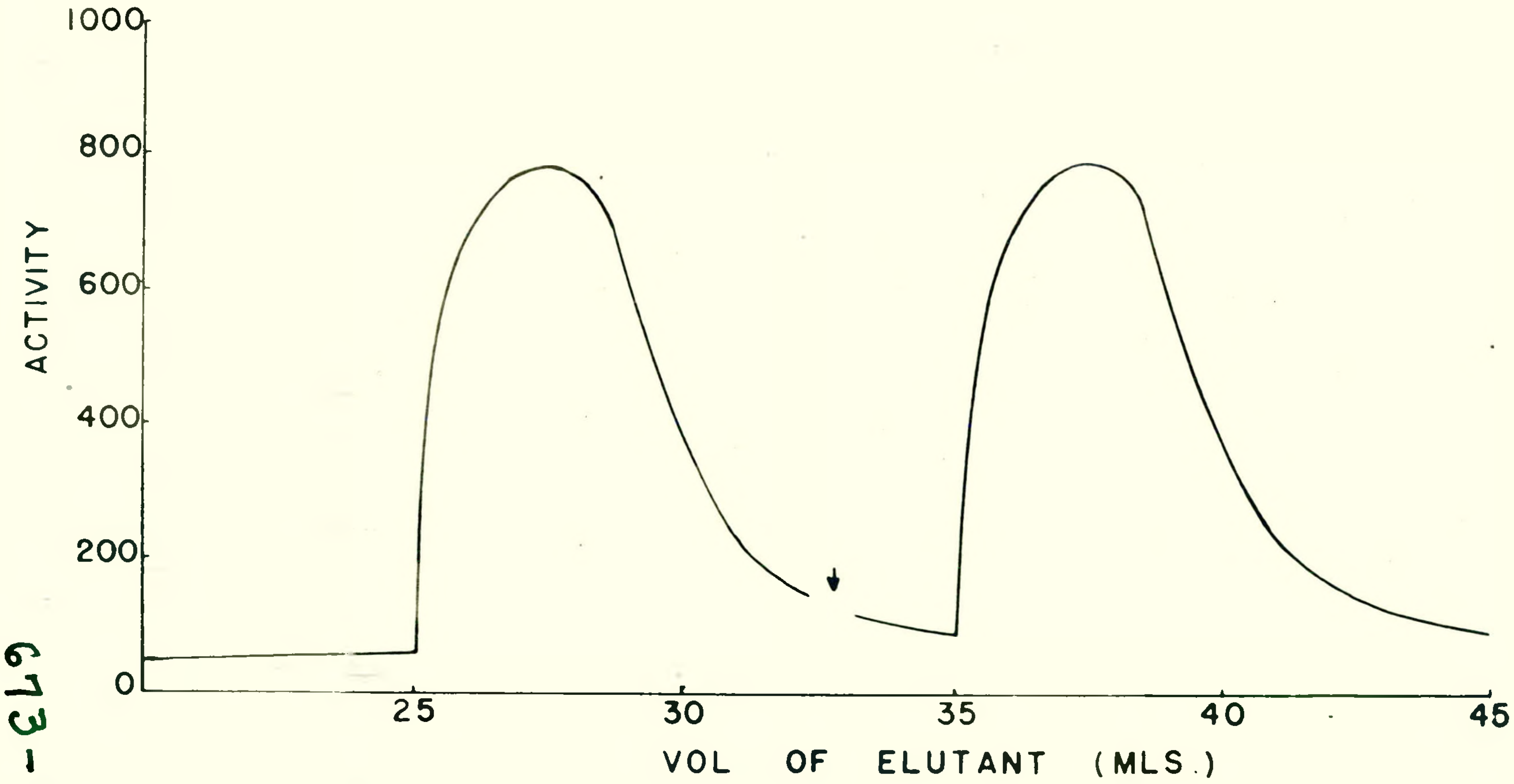

FIG. 1 ACTIVITY OF 5 ML SAMPLES VS TOTAL VOL ELUTED
A TIME LAPSE OF 84 HRS. OCCURRED AT ARROW

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3. THERMODYNAMIC INVESTIGATION OF EQUILIBRIUM IONIC DISTRIBUTION RATIOS IN INORGANIC SYSTEMS AT ELEVATED TEMPERATURES.

3.1 The Problem

If the cation A^{+++} in an AY-rich liquid flux can exchange with the cation B^{+++} in a BX-rich solid,

$$(1) \qquad A^{+++}_{AY(l)} + B^{+++}_{BX(s)} = A^{+++}_{BX(s)} + B^{+++}_{AY(l)},$$

then

$$(2) \qquad \frac{[A^{+++}_{BX(s)}]\,[B^{+++}_{AY(l)}]}{[A^{+++}_{AY(l)}]\,[B^{+++}_{BX(s)}]} = \left[\frac{A^{+++}}{B^{+++}}\right]_{BX(s)} \Big/ \left[\frac{A^{+++}}{B^{+++}}\right]_{AY(l)}$$

$$= K_D = \exp(-\Delta F^\circ_D/RT)$$

when the system AY(l)-BX(s) is in equilibrium with respect to this particular ion exchange. ΔF°_D refers to the exchange or distribution reaction (1).

Thus from the thermodynamic point of view the problem of predicting the selectivity coefficient K_D is one of evaluating ΔF°_D.

We note here that both the flux AY and the exchanger BX may contain additional components. The cations have been triply charged merely to emphasize the ionic character of the exchangeable species.

3.2 A Note on the Ionic Hypothesis.

It has been assumed above that the system AY(l)-BX(s) is completely ionic. This is an important assumption. We give two examples which emphasize the thermodynamic role of this ionic hypothesis.

3.21 If the system AY(l)-BX(s) were supposed by us to be non-ionic, yet analysis showed some AX and BX in the AY-rich phase at equilibrium and also AX in the BX-rich phase, we might legitimately postulate two independent equilibria

$$(3a) \qquad BX_{BX(s)} = BX_{AY(l)} \qquad \text{and}$$

$$(3b) \qquad AX_{BX(s)} = AX_{AY(l)}$$

with distribution coefficients

(4a) $$\frac{(BX_{AY(l)})}{(BX_{BX(s)})} = K_D^{BX} \quad \text{and}$$

(4b) $$\frac{(AX_{AY(l)})}{(AX_{BX(s)})} = K_D^{AX}$$

This procedure is thermodynamically correct, and the second relation involving K_D is recovered once it is assumed that both the liquid flux and solid exchanger are strong electrolytes. For then the activity of BX is known to be proportional to the product (B^{+++}) (X^{---}) and likewise for AX. Thus

(4a)' $$\frac{(B^{+++}_{AY(l)}) \quad (X^{---}_{AY(l)})}{(B^{+++}_{BX(s)}) \quad (X^{---}_{BX(s)})} = K^{BK}_{D'} \quad \text{and}$$

(4b)' $$\frac{(A^{+++}_{AY(l)}) \quad (X^{---}_{AY(l)})}{(A^{+++}_{BX(s)}) \quad (X^{---}_{BX(s)})} = K^{AX}_{D'},$$

and $K_D = K^{BX}_{D'}/K^{AX}_{D'}$.

Note that the distribution ratio $(A^{+++}_{BX(s)})/(A^{+++}_{AY(l)})$ is dependent upon the ratio of the B^{+++} concentrations:

(2)' $$\left(\frac{(A^{+++}_{BX(s)})}{(A^{+++}_{AY(l)})}\right) = \left(K_D \frac{(B^{+++}_{BX(s)})}{(B^{+++}_{AY(l)})}\right)$$

This feature of the exchange equilibrium is examined further in our second example.

3.22 Whenever the exchange is slight, the concentrations of B^{+++} and X^{---} in the nearly pure exchanger phase remain essentially constant, and equation (4a)' can be put into the simple form

(4a)'' $$(B^{+++}_{AY(l)}) \ (X^{---}_{AY(l)}) = K^{BX}_{sp} \quad \text{or}$$

$$(B^{+++}_{(AY(l)}) = K^{BX}_{sp}/(X^{---}_{AY(l)}),$$

which in (2)' reveals the interesting fact that the A^{+++} distribution ratio is directly proportional to the concentration of the X^{---} ion in the flux:

(2)"
$$\frac{(A^{+++}_{BX(s)})}{(A^{+++}_{AY(l)})} = K'(X^{---}_{AY(l)}).$$

By increasing the X^{---} concentration in the flux through the addition of soluble CX, one represses the solution of BX in AY, $(B^{+++}_{AY(l)})$ does not build up, and the exchange reaction (1) is favored as written. The effect may be enormous if BX is only slightly soluble in the flux. Suppose, for example, that $K^{BX}_{sp} = 10^{-20}$. Then normally $(X^{---}_{AY(l)}) = 10^{-10}$, and CX would not have to be very soluble in order to cause the observed A^{+++} distribution ratio to increase by a factor of several million.

3.3 Evaluation of ΔF°_{D}.

The procedure in this section will be to resolve ΔF°_{D} into a sum, each term of which is a ΔF° corresponding to an equilibrium that either has already been studied or is chemically simpler than the exchange reaction (1). This procedure is classical in many applications of chemical thermodynamics; our point of view, however, is more that suggested recently by Gurney (Ionic Processes in Solution, McGraw-Hill, 1953, Chapter 6). Several resolutions of ΔF°_{D} are given below.

3.31 The transfer of A from flux AY to exchanger BX can be carried out (somewhat loosely) as follows: transfer of A from AY to metal A (reaction a), from metal A to salt AX (reaction c), and finally from salt AX to salt BX (reaction f). Add to this a similar sequence for B (reactions b, d and e below), and the exchange (1) is effected.

$$\begin{array}{llclclcl}
\text{(a)} & A^{+++}_{AY(l)} & + & Y^{---}_{AY(l)} & = & A_{A(l)} & + & Y^{\circ} \\
\text{(b)} & B_{B(l)} & + & Y^{\circ} & = & B^{+++}_{BY(l)} & + & Y^{---}_{BY(l)} \\
\text{(c)} & A_{A(l)} & + & X^{\circ} & = & A^{+++}_{AX(s)} & + & X^{---}_{AX(s)} \\
\text{(d)} & B^{+++}_{BX(s)} & + & X^{---}_{BX(s)} & = & B_{B(l)} & + & X^{\circ} \\
\text{(e)} & B^{+++}_{BY(l)} & + & Y^{---}_{BY(l)} & = & B^{+++}_{AY(l)} & + & Y^{---}_{AY(l)} \\
\text{(f)} & A^{+++}_{AX(s)} & + & X^{---}_{AX(s)} & = & A^{+++}_{BX(s)} & + & X^{---}_{BX(s)} \\
\hline
\text{(1)} & A^{+++}_{AY(l)} & + & B^{+++}_{BX(s)} & = & A^{+++}_{BX(s)} & + & B^{+++}_{AY(l)}
\end{array}$$

The standard free energy changes corresponding to reactions (a) through (d) are directly related to the free energies of formation of the salts AY, BY, AX and BX which can be estimated quickly, easily and often quite accurately by means of the simple approximation: $\Delta F^{\circ}(T) = \Delta H^{\circ}(298) - T\Delta S^{\circ}(298)$. Unknown standard enthalpies and entropies of formation at 298°K can be estimated from group trends in the periodic table, sometimes with considerable confidence.

The standard free energy change corresponding to reaction (e) should generally be relatively small and, in fact, vanishes whenever the liquids BY and AY are just miscible in all proportions.

This pretty much places the full burden of predicting ΔF°_{D} or ΔF°_{1} upon equilibrium (f) and the corresponding standard free energy change ΔF°_{f}. The remainder of this section is concerned with this term.

If the solids AX and BX are just miscible in all proportions (such is the case with UO_2 and ThO_2), $\Delta F^{\circ}_{f} = 0$, and ΔF°_{D} can be obtained immediately from the standard free energies of formation of the four salts AY, BY, AX and BX. Even if AX and BX are not completely miscible, ΔF°_{f} may be negligible compared to the sum $(\Delta F^{\circ}_{a} + \Delta F^{\circ}_{b} + \Delta F^{\circ}_{c} + \Delta F^{\circ}_{d})$ when the terminal solid solutions are somewhat removed from pure AX and pure BX. In other cases it may be necessary to examine ΔF°_{f} more carefully.

3.32 The procedure here is similar to the one used on ΔF°_D itself: Resolve ΔF°_f into a sum of F°'s that can individually be evaluated. Two such resolutions are discussed below.

3.321 The transfer of AX from AX(s) to BX(s) can be carried out as follows: transfer of AX from AX(s) to AX(l), from AX(l) to BX(l), and finally from BX(l) to BX(s).

$$\begin{array}{llcllcllcl}
\text{(a1)} & A^{+++}_{AX}(s) & + & X^{---}_{AX}(s) & = & A^{+++}_{AX}(l) & + & X^{---}_{AX}(l) \\
\text{(a2)} & A^{+++}_{AX}(l) & + & X^{---}_{AX}(l) & = & A^{+++}_{BX}(l) & + & X^{---}_{BX}(l) \\
\text{(a3)} & \underline{A^{+++}_{BX}(l)} & \underline{+} & \underline{X^{---}_{BX}(l)} & \underline{=} & \underline{A^{+++}_{BX}(s)} & \underline{+} & \underline{X^{---}_{BX}(s)} \\
\text{(f)} & A^{+++}_{AX}(s) & + & X^{---}_{AX}(s) & = & A^{+++}_{BX}(s) & + & X^{---}_{BX}(s)
\end{array}$$

Again, much as before, ΔF°_{a2} may be small and negligible whenever the terminal liquid solutions in the system AX(l)-BX(l) are somewhat removed from the pure components and, in any event, can be estimated from phase diagrams for the molten salts.

The free energies of fusion, ΔF°_{a1} and ΔF°_{a3}, can be calculated from liquidus temperatures and heats of fusion. The principal problem here will probably be the heats of fusion. Certain phase diagrams can yield this information, and a survey of the data on entropies of fusion in inorganic systems might suggest some useful rules.

3.322 The transfer of AX from AX(s) to BX(s) can also be carried out as follows: rather than melt the solids, sublime them; i. e., transfer AX from AX(s) to AX(g), from AX(g) to BX(g), and finally from BX(g) to BX(s). The corresponding equations are nearly those in (3.321) with the subscript (l) replaced by (g). ΔF°_{b1} is the standard free energy of sublimation of AX, ΔF°_{b2} is for all practical purposes identically zero, and ΔF°_{b3} is the standard free energy of sublimation of AX from an infinitely dilute solution in BX.

These free energies of sublimation, ΔF°_{b1} and ΔF°_{b3}, can be calculated from vapor pressure data. Two reliable points are sufficient, or one point (say the boiling point) and the heat of vaporization, or the boiling point and the normal entropy of vaporization. A survey of the entropies of vaporization (or sublimation) in inorganic systems might, therefore, suggest some useful rules when only one point on the vapor pressure curve is known. Heats of vaporization, which are related to the lattice energies, would be just as useful.

The principal problem here is probably the evaluation of Henry's Law constant (or its equivalent) for the system AX dissolved in BX.

3.4 A Note on the Lattice Energy Problem.

Traditionally the lattice energy problem has been taken to be the calculation of the energy of the reaction:

$$AX(s) = A^{+++}_{(g)} + X^{---}_{(g)}$$

for ionic crystals at absolute zero. Most of the calculations have been carried out on the alkali halides (Seitz, Modern Theory of Solids, p88). To the approximation that $\Delta C_p = 0$, such calculations give the energy of sublimation when combined with dissociation energies.

Owing to the exponential distance dependence of the repulsive forces between ions, the repulsive part of the lattice energy amounts to only about 10% - 20% of the Madelung term at equilibrium. In view of this, one is tempted to consider a direct frontal attack on the problem of evaluating ΔF°_D: Ignore second and higher order electrical interactions (dipole-dipole and dipole-quadripole, etc.) and zero point energy differences, assume $\Delta C_p = 0$, and evaluate the Madelung and repulsive terms using the ionic-radius, hard-sphere approximation, which replaces the quantum mechanically derived exponential repulsive term by a step potential of infinite height.

At best, this calculation only gives ΔH°_D; i.e., K_D at absolute zero. At higher temperatures ΔS°_D plays an increasingly important role ($\Delta F^\circ_D = \Delta H^\circ_D - T\Delta S^\circ_D$). Until the lattice entropy problem has been simply solved, we can suggest only that ΔS°_D may perhaps be approximately a linear function of ΔH°_D; empirical correlations such as this have been observed in many diverse systems.

3.5 The Use of Data on Metal-Salt Systems.

ΔF°_D may be resolved according to the following scheme,

$$\begin{array}{llllllllll}
(5) & A_{A(l)} & + & B^{+++}_{BX(s)} & = & A^{+++}_{BX(s)} & + & B_{A(l)} \\
(6) & & & B_{A(l)} & = & B_{B(l)} & & \\
(a) & A^{+++}_{AY(l)} & + & Y^{---}_{AY(l)} & = & A_{A(l)} & + & Y^\circ \\
(b) & B_{B(l)} & + & Y^\circ & = & B^{+++}_{BY(l)} & + & Y^{---}_{BY(l)} \\
(e) & B^{+++}_{BY(l)} & + & Y^{---}_{BY(l)} & = & B^{+++}_{AY(l)} & + & Y^{---}_{AY(l)} \\
\hline
(1) & A^{+++}_{AY(l)} & + & B^{+++}_{BX(s)} & = & A^{+++}_{BX(s)} & + & B^{+++}_{AY(l)},
\end{array}$$

which takes advantage of the fairly extensive data on metal-salt systems (reaction 5).

ΔF°_5 may represent an important part of ΔF°_D. Indeed, if the liquid pairs A-B and AY-BY are just miscible in all proportions and the standard free energies of formation of AY and BY are equal, $\Delta F^\circ_1 = \Delta F^\circ_D = \Delta F^\circ_5$.

This resolution of ΔF°_D is being studied.

3.6 Summary.

The following methods have been proposed for evaluating ΔF°_D.

1. Resolution according to scheme (a) through (f) (Section 3.31). This method is best when solids AX and BX are fairly miscilbe in each other.

2. Resolution according to scheme (a) through (f) plus the fusion steps in (a1) through (a3) (Section 3.321). Perhaps the most generally applicable method of all.

3. Resolution according to scheme (a) through (f) plus sublimation steps (Section 3.322). Useful when the salts are relatively volatile.

4. Direct frontal attack: the Madelung calculation (Section 3.4). Intriguing, but requires additional information on ΔS°_{D}.

5. Resolution according to scheme (5) + (6) + (a) + (b) + (e) (Section 3.5). Probably the most accurate method when good equilibrium data on metal-salt systems are available.

3.7 Literature Survey.

A survey was made of the literature to find what information of thermodynamic value is available on hetergeneous equilibrium in multi-component anhydrous inorganic systems of the type studied in Reports 1 and 2.

Exchange reactions of liquid alloys and melts of oxides, silicates, sulfides and halides (7) have been studied and equilibrium constants determined. Phase diagrams are also available for certain of these systems.

Wasastjerna(8), Hovi(9) and Wallace(10) have studied the alkali halide exchange reactions from the classical and statistical thermodynamic viewpoint and obtained some agreement with experimental data.

While K for exchange reactions of the type $A^{+++}_{AY(l)} + B^{+++}_{BX(s)} = A^{+++}_{BX(s)} + B^{+++}_{AY(l)}$ focuses attention on the exchanging ions, Rinck(7d) has provided data for K on sodium halide fluxes suggestive of a possible role of flux anion on the mass action constant.

Richardson(11) suggests that the nature of the species in the solid and liquid state are the same in cases where there are low entropies of fusion, Koch and Wagner(12) indicate that at the temperatures employed it may be necessary to consider the mixed crystal as a "defect solid state". In this connection the monograph of Ress(13) may prove useful. The requirements of random mixing may be met by ions of same charge and comparable ionic radius, but probably not by ions of different valency as Wagner(14) points out in his discussion of the solution laws of molten salts.

Any application of a Born-Haber cycle requires knowledge of lattice energies and thus an evaluation of the Madelung constant. Two methods are suggested, that of Wheeler(15) or Templeton(16), depending on the complexity of the structure.

Roy and Osborn(17) have applied Goldsmidt's theory of isomorphism to phase diagrams. For systems having similar ionic radii and coordination number similar phase diagrams result. It seems that slags, ceramic systems and petrology will be sources of available data.

4. SUMMARY OF PROPOSED RESEARCH

The present section serves to summarize the proposals for further work which were presented in somewhat greater detail in earlier sections of the report.

4.1 The System $BaZrO_3$ - $CeCl_3$ - $BaCl_2$

The nature of the barium zirconium oxide system is now reasonably well understood, and it is proposed to return to the problem of the distribution of cerium ion between this solid and a barium chloride flux. The results of the preliminary experiments discussed in section 1.3 indicate that cerium enters the lattice of barium zirconium oxide in low concentration, and tracer studies of the distribution should prove of direct value in advancing the principal aims of this research.

4.2 Systems containing $LaCrO_3$ and $YCrO_3$

For reasons previously discussed, the ternary oxides, $LaCrO_3$ and $YCrO_3$, appear to be particularly attractive as solid phases for exchange and distribution studies. It is proposed to investigate the exchange of lanthanum and yttrium between these solids and melts containing either the same or the other of the two ions. Radioactive tracers prepared by the technique described in section 2.5 will be used.

4.3 Thermodynamic investigations

The problem of predicting the distribution coefficient in melt-solid systems is essentially that of predicting the value of ΔF for the exchange reaction. It is proposed to investigate five possible approaches by which this prediction might be made. These are summarized in section 3.6.

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