MONTHLY REPORT

Physical-Chemical and Chemical Engineering Problems
Summary of Progress - March 15 to April 15, 1942

Subsection B-7-B - Oxygen Problems - E. P. Stevenson, Chairman
Problem NL-B 42 - Development of Chemicals and Apparatus for Regenerative Production of O_2.
Problem AC-12 - Manufacture of O_2 while in Flight for use of the Combat Crew.

SALCOMINE

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Preparation and Equivalents

A search for new materials and improvements on the material Salcomine for the absorption of oxygen has continued, and also a study of the behavior of the material Salcomine has received considerable attention in the past month. Several new compounds have been found that show some absorption for oxygen, but in most cases the amount of oxygen absorbed is small or the rate is very slow. The most promising new compound is one prepared from salicyl aldehyde and bistrimethylenetriamine which will absorb at least 8% of oxygen reversibly, although apparently there is considerable decomposition or repetitions of the cycle. Work is being pushed on this and related compounds with all possible speed.

Dr. Gilliland's life cycle tests on an original sample of Salcomine have ended. The material has now been analyzed and found peculiarly to have an increased nitrogen-cobalt ratio which would seem to indicate that some nitrogen has been fixed in the compound. In addition to an increase in the nitrogen-cobalt ratio there is a decrease in the amount of nitrogen and cobalt which would indicate an absorption of some foreign matter which so far has not been identified. Also the magnetic susceptibility has increased very greatly which would indicate that the compound has been changed in some manner other than the mere oxidation of the cobalt ion. It is felt that the deteriorated material is not a definite compound, but no decision has yet been reached upon this score, and the work will continue to analyze the change in the material on successive repetitions of the absorption cycle.

Large quantities of the 3-nitro compound of the cobalt chelate has been prepared and studied. The temperature required to effect the deoxygenation of this material at atmospheric pressure is about 90°C, which is somewhat higher than that required to deoxygenate the parent chelate compound. Also it has been observed that the humidity of the gas used to effect the oxygenation plays an important role in the reaction, the presence of moisture materially speeding the oxidation reaction up to a relative humidity of 5%, beyond which there is no increase in the rate. The 3-nitro compound is hygroscopic and absorbs water from the gas stream even though the relative humidity of the gas is as low as 5%. The amount of oxygen absorbed by the nitro compound varies markedly with the partial

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pressure of the oxygen above it. The nitro compound is believed to be somewhat less explosive than the parent oxygen-carrying compound as evidenced by the ignition of a fine suspension of the material in air by a spark.

An apparatus has now been constructed for determining the life of oxygen-carrying compounds that can be used in connection with the preparation and testing of new materials. This should greatly speed the evaluation of these materials.

The subject of deterioration of the chelate compound or other equivalents which may be used is extremely important from the point of view of operation of units employing these materials, and a very considerable effort is now being made to arrive at a satisfactory explanation of the deterioration of the compound by a study of the characteristics of operation which leads to the deterioration. It is believed in general that the high temperatures of desorption greatly aggravate the difficulty and recently attention is being given to operating cycles in which somewhat lower temperature is used.

Life Tests

The activity life tests on the Salcomine have been continued and the latest results indicate that the absorption efficiency decreases about 2% per 100 cycles for an absorption carried out with air at 80 lbs. per sq. in. gauge, and a deoxygenation temperature of 100°C. Also it has been observed that the decrease in activity is roughly proportional to the air flow, indicating that the loss in activity is possibly due to something stripped out of the air, a conclusion which is checked by the analysis given above.

Further life activity tests are being carried out under a variety of conditions in an attempt to definitely evaluate the controlling factors. Chief among these is operating at somewhat lower temperatures of desorption. Among the proposed tests is one in which two absorption units are operated in series to determine whether or not both beds are deactivated at the same rate or whether one is more rapid than the other, thus giving a further check upon the stripping of poisons from the air.

Work is continuing at the Rumford Chemical Company on the examination of reactivity and life of Salcomine materials as a function of its physical form. Tests are being made with various pellet shapes and densities.

Toxicity Tests

Inasmuch as a large number of uses of oxygen are directly connected with the supply of human needs for breathing, the toxicity of oxygen produced by the Salcomine absorption method is important. It is known that small traces of carbon monoxide occur in the gas produced by this method which, while in general are small under contitions obtaining on the surface of the earth, become vastly greater at high altitudes. A small Salcomine unit has been built and delivered to the University of Chicago for a study of toxicity of the gas produced in such equipment. Methods of eliminating this hazard are also being studied. In addition, toxicity of Salcomine itself with respect to handling, dust carry-over, etc. is being examined.

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Reaction Cycles

The methods of operating with Salcomine originally proposed included absorption of gas at relatively low temperatures and desorption of oxygen at steam temperatures. There were two inherent drawbacks to this method of operating: (1) transporation of the whole absorption unit over a large range of temperature from absorption to desorption and back again, which was wasteful of energy and introduced numerous problems of heat and refrigeration and (2) deterioration of the Salcomine at the high temperatures of desorption. It was later proposed to investigate a relatively adiabatic system in which the absorption and desorption were carried on at relatively equivalent temperatures through large changes of pressure. Tests of the latter system indicate that it should be possible to operate such a unit in which sufficient heat capacity is included to give relatively isothermal operation at a temperature of around 60-65°C with an absorption pressure of about 600 lbs./sq.in.. An adiabatic unit has been constructed in which Salcomine powder is mixed with 7 or 8 times its mass of copper chips to serve as a heat reservoir.

The Du Pont Company has continued its exploration of a system wherein Salcomine is suspended in a liquid and believes that it has found a combination of materials and conditions giving promise of satisfactory operation. The Salcomine is suspended in a hydrocarbon oil and exhibits therein fair yields of oxygen and not too great deterioration with repetitions of the absorption-desorption cycle. A principle drawback at present is a rather high solubility of nitrogen in the oil. The system shows sufficient promise to warrant its further evaluation and steps are being taken to carry this out under the auspices of the Du Pont Company.

Oxygen Producing Units

The unit for the Naval Research Laboratory is still under construction, but should be completed and ready for testing before the end of April. It is planned to test this unit at Cambridge before disassembling and shipping to Washington. This unit, it will be remembered, is to produce 5 cu.ft. of oxygen per minute when operated upon laboratory facilities of compressed air of 80 lbs./sq.in., or the output may be considerably stepped up with operation with compressed air at 250 lbs./sq.in. for which the unit is designed.

The construction of mobile units for operation upon trucks designed by the Kellogg Company has been deferred, pending the construction and testing of a shipboard unit designed to meet the requirements of destroyer tenders and airplane tenders for machine shop operation and the charging of gas cylinders. The requirements of these shipboard units are somewhat less than that of the mobile unit and much can be learned of the operating cycle which will be similar in both units. The four reactors of the shipboard unit will be similar to four reactors planned for the mobile unit, and are to be of the pancake type, that is a large cylinder packed with the Salcomine will have distributed through the bed of Salcomine layers of spiral coils through which heating and cooling fluids will be circulated.

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These reactors are now being built by the American Machine and Foundry Company, who at present have the complete engineering details worked out in cooperation with the Kellogg Company. It is understood that the fabrication of these units is now in progress.

Several small units of the type employed by Dr. Gilliland in his life cycle tests have been completed and sent to various experimental points for use in tests on the operation of new compounds, toxicity, etc.

OXYGEN PRODUCTION BY MECHANICAL METHODS

Problem AC-12 - The Manufacture of O_2 while in Flight, for Use of the Combat Crew.

Problem NL-B6(d) - Equipment for Manufacture of Liquid O_2 (Submarine Plant)

Progress Reports, S.N. 201, 3/7/42, "Cascade O_2 System"
S.N. 206, 3/16/42, "Tests on O_2 Rectification Equipment."

Cycle Analysis

The Keyes cycle employing helium as an auxiliary refrigerant has been evaluated independently by Dr. Babcock and Professor Dodge with respect to the proposed submarine plant. The analyses concur in somewhat smaller heat exchanger requirements for the Keyes cycle compared to the low pressure system proposed by Kellogg, operating on air alone, but the saving in heat exchanger equipment appears to be entirely offset by increased power consumption of the Keyes exchanger (1.1 H.P. per pound of liquid oxygen as against 0.79 H.P.), which on the basis of producing 4000 pounds of liquid oxygen per hour will be an increment of 1400 H.P. or 7000 pounds gross weight of equipment. Furthermore, this increased horse power when translated into weight of fuel oil consumed in 30 days (at 6 hours per day) would be 126,000 pounds.

The Keyes cycle and the equipment being developed by Dr. Keyes has been placed in the hands of the Linde Company for evaluation. The initial part of this program will involve a theoretical study of the cycle.

Apparatus Study

Air Reduction Company has proceeded further with its tests for rectification tubes for the lower boiler of a double rectification column, the work to date indicating that the best system is one employing a series of disk shaped baffles in these columns; such a system will yield a nitrogen of 92.5% purity, somewhat better than obtained with the Podbielniak construction.

Small scale preliminary tests are being made on Stedman packings for rectification columns with results that are sufficiently promising to warrent refining the apparatus to minimize heat leaks. It is planned that full size columns employing different types of packing will be fabricated and sent to the University of California for testing, inasmuch as this laboratory has sufficient refrigerating

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equipment to conduct such large scale tests. CONFIDENTIAL

American Machine and Foundry Company has been fabricating units of the Keyes-Collins type interchanger which are on test at the Yale laboratory, using air to air heat exchange and also steam to air over a range of flow rates.

A system for studying regenerators in heat transfer and air purification has been designed, and most of the necessary materials have already been obtained. As soon as assembled, test work will proceed at the Yale laboratory.

A system is being set up at Yale for producing purified air at any pressure up to 500 lbs./sq.in., and at any temperature down to 80° K. This system will include a number of items of equipment such as a two-stage compressor, air receiver, pressure regulating valve, air filter, carbon dioxide scrubber, air drier, Freon precooler and air to air exchanger, some of which material is difficult of procurement.

A laboratory program is being conducted both at Yale and the University of California on the drying of air by solid absorbents. At Yale a system is being set up employing alumina or other gels, and the main variables of absorption and reaction and their influence on the degree of moisture removal is being studied.

The University of California is proceeding with a study of the removal of water from high pressure air by refrigeration. Simultaneously, data are being obtained on the removal of carbon dioxide with potassium hydroxide solutions. The studies of the purification of air are extremely important for further design work on any of the various oxygen units.

Dr. Keyes is postponing further work upon his oscillating type of compressor because other methods of handling this problem were of more immediate solution. The oscillating air-refrigerated expansion engine is being modified to make it single acting, piston-rod connected.

Dr. Keyes is continuing work with his rotating rectification column, and has introduced a modification in which studs or projections are supplied on shell as well as on the rotating element. The engineering of large scale models and their testing is contemplated.

Oxygen Producing Units

For the time being truck units employing the cascade process advocated by Professor Giauque are in abeyance because of the press of other work. Although it was admitted that the power factor on such cascade systems is advantageous as compared with other cycles, the use of combustible auxiliary refrigerants is considered to be a very great disadvantage and the substitution of other refrigerants brings this system very close to one or two others now being developed elsewhere.

A contract is being set up with the Independent Engineering Company of O'Fallen, Illinois to expedite the development of two mobile units desired by the Army Air Corps. The first of these is a low pressure cycle (5 atmospheres) involving the use of an expansion engine and an air refrigeration system; the second is a 500 to 600

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lbs./sq.in. Linde type system with Freon forecooling and no expansion engine.

The Air Reduction Company is going ahead with the design and construction of a somewhat smaller unit for production of 360 cu. ft. of oxygen per hour as a gas, this unit employing a Linde type system with precooling by an ammonia refrigerant to -40°C. It is contemplated that this truck unit will weigh approximately 5000 pounds (with truck).

The Air Reduction Company is giving further attention to the design of a pilot plant for the submarine job (about one-tenth the size of the proposed submarine plant). It is believed by them to be next to impossible to design a double rectification column within the confines of the submarine and their design is therefore based upon a single column with suitable packing, for example Berle saddles. With promised compressor efficiencies of 80-85% Air Reduction is optimistic about producing a unit having a power consumption of 0.5 H.P. per pound of liquid oxygen. In connection with tests of the Kleinschmidt turbine at Annapolis, it has been proposed that we supply a full scale oxygen plant, delivering approximately 4000 pounds of oxygen per hour, this plant to be designed and built for tests in the early fall. This is a man-sized job which will require great activity in all quarters.

CENTRAL ENGINEERING WORK

Problem AC-12; NL-B-60; NL-b-42

Engineering development work on the production of oxygen.

The Kellogg Company is continuing in its capacity of evaluating equipment with respect to oxygen-producing units and in furthering the design of these units.

Operating in close cooperation with the Kellogg Company the Clark Brothers Company, Inc. is working upon engines and compressors; various companies including the Air Cooled Motors Corporation of Syracuse, N. Y., The Chrysler Corporation, the Davey Compressor Company, and the Elliott Company are acting as consultants for Clark Brothers Company. Work is being continued towards developing, building and testing the following equipment: a 600 lbs./sq.in., 60 H.P. air compressor; a 100 lbs./sq.in., 50 H.P. air compressor; 20 cu. ft./min., 2000 lbs./sq.in. oxygen compressor; a 70 cu. ft./min., 75 lbs./sq.in. to 14.7 lbs./sq.in. expansion engine; and a 5 H.P. Freon refrigerating compressor. It is understood that work is progressing on the development of these units, although the completion by July 1st of all units is doubtful. The oxygen compressors will include carbon sleeves or carbon rings. All of the the design work has been done upon these units and their construction is authorized.

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UNDERWATER PROPULSION

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Problem NL-B6 - Operation of Submarine Engines While Submerged
b) Engine tests on O_2 - supplying chemicals, O_2, and O_2-containing fuels
c) Absorption of Exhaust gases

Efforts have been centered on the study of engine flexibility and operating characteristics at power outputs below full load under oxygen recycle operation. From the data at hand it would appear that for part load operation, it would be more desirable to run below maximum speed rather than attempt to stay atmaximum speed and reduce the fuel flow to meet the desired operation.

Tests are continuing, aimed at the dispersion of exhaust gases from a submarine under such conditions that visibility from above the surface of the water is completely absent. It is felt that the dispersion of the gas completely while hidden below the hull of the submarine is a practical impossibility and that therefore consideration should be given to the visibility of clouds of bubbles, as viewed from an airplane under various conditions of depth and surface.

Inasmuch as some concern is felt for the length of time that a submarine can remain on the surface for the operation of an oxygen plant, some further consideration and interest is being shown in storage of large amounts of liquid oxygen upon submarines, such oxygen to be supplied from a base of operations.

MISCELLANEOUS

Problem NL-B1-(Item f) Development of an instrument for the measurement of O_2 Partial Pressure.
New Problem NA-106 "Development of Oxygen Breathing Equipment and Associated Apparatus".
Item 1, "Development of Oxygen Breathing Apparatus for Use with liquid O_2".
Item 4, "Development of Means for Automatically Eliminating Nitrogen in Oxygen Rebreathing Equipment."

Work has been done in the past month to increase the sensitivity of the Pauling oxygen indicating instrument by increasing the strength of the magnets.

Work is continuing on the methods of handling liquid oxygen supplies on board planes as a source of oxygen for the crew. This has included development of vaporizing units that will operate under all conditions of altitude and plane attitude and also control methods for supplying oxygen to the breathing masks. This work is proceeding at the University of Minnesota, the Mayo Clinic and under the auspices of Dr. J. A. Mathis. It is understood that the Linde Company is also working directly with the Bureau of Aeronautics of the Navy Department on this same subject.

The job of selectively eliminating nitrogen from the breathing atmosphere re-circulated through K_2O_4 regenerating material has been accepted, although it appears at the present to be extremely difficult

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of solution. The problem is of considerable importance because the K_2O_4 "Re-breathing" system now employed is quickly made inoperative, except by frequent freezings with pure O_2 are employed, by an accumulation of nitrogen from the blood stream.

S. S. Prentiss
Technical Aide
Section B-7

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