THE SEPARATION OF ISOTOPES BY DISTILLATION AND ANALOGOUS PROCESSES

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Separation by Distillation

Results of an investigation on the effect of pressure and other conditions on the efficiency of separation of isotopes by the process of distillation are described below.[2] The element used was mercury. By "efficiency" is meant the ratio of the actual separation obtained in a given operation to that obtainable under ideal, that is completely irreversible, conditions. The methods of determining experimentally the actual changes of atomic weight of the separated fractions, and of calculating the theoretical changes, are as previously described.[3] Briefly, the increase of atomic weight of the *residue* in a partially reversible distillation is given by $\Delta A = EB \ln C$, where E is the efficiency, B the separation coefficient, and C the cut, the latter two quantities as previously defined.[3] For the corresponding total *distillate*, the decrease of atomic weight is $-\Delta A = EB \ln C/(C - 1)$. The value of B is taken,[4] on the basis of recent work to be described in a later paper, as 0.0063. Out of a series of runs in which mercury vapor was diffused molecularly, a number made under the most favorable conditions, and probably nearly 100% efficient, agreed closely in giving this value.[5]

The conclusion previously reached[3] that a slight separation of isotopes occurs in the distillation of mercury (first wholly treated with nitric acid) at 2 cm. pressure was wholly confirmed by a detailed study of the densities of the fractions obtained in 8 successive redistillations. Experimental data are omitted because of lack of space. Dense im-

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[2] This investigation was made in connection with the development of a rapid and efficient combined process of evaporation and molecular diffusion, which is now being operated with the object of obtaining an extensive separation of the isotopes of mercury. Previous work with the evaporation method (see Refs. 3 and 4) has dealt only with a few special conditions.

[3] Mulliken and Harkins, THIS JOURNAL, 44, 37–65 (1922).

[4] The value 0.0057 previously given by Mulliken and Harkins was obtained by assuming their best run 100% efficient. Calculation from the best runs of Brönsted and von Hevesy [*Phil. Mag.*, 43, 31 (1922)] gives the same figure. On the new basis, these runs were about 90% efficient. Laby and Mepham [*Nature*, 109, 206 (1922)] report a result for the distillation of mercury in a high vacuum, which corresponds to an efficiency of 49%.

[5] The use of a value obtained by experiments on molecular diffusion is legitimate, because the mathematical formulation and constants of the theory are identically the same as for irreversible distillation.

purities (platinum, gold, etc.?) were found to be present[6] in the residue from the first, and to a slight extent from the second, distillation. No further changes as great as 1 part per million in the density occurred in further distillations, except such as could be shown to be due to an inefficient separation of isotopes. No evidence of light impurities was found.

Perhaps the most striking result of the investigation is the ease with which a fairly high separation efficiency can be obtained. Thus by distillation at a rate of 15 cc. per hour (3.5 gm./cm.^{2}/hr.) from a 300cc. flask with neck bent over and sealed to a water-jacketed condenser, an efficiency of about 50% is obtained, if the air pressure in the apparatus does not exceed 0.1 or 0.2 mm. (of mercury). The best efficiencies so far obtained in more ideal types of apparatus[3,4] in which the evaporating and condensing surfaces are close together, have been about 90%, and this only with a pressure of 0.001 mm. or less, and a low evaporation rate. Another result of the present work is the confirmation it gives of the kinetic theory picture[7] of the mechanism of distillation, decreasing gradually in irreversibility with increasing pressure.[8]

The efficiency of separation falls with increasing evaporation rate, more rapidly in the *flask* type of apparatus than in the *direct-condensation* type. Thus in the *former* type, as the rate of evaporation rose from 1.5 to 24 g./cm.^{2}/hr., the efficiency fell, with a clean evaporating surface, from 54% to 24%, and with a dirty surface, from about 57% to about 43%. With the small apparatus of the *latter* type used by Mulliken and Harkins,[3] a range of efficiency from 84% to 64% was obtained for a range of evaporation rate from 0.9 to 13 gm.[9] The efficiency in the flask type, to which the following discussion will refer exclusively, seems to be determined largely by the pressure, whether of air or of mercury vapor, prevailing in the flask. The initial mass motion of the molecules escaping from the liquid is greatly reduced by this pressure, with the result that many, especially the lighter ones, return to the evaporating surface. Thus the evaporation becomes partly reversible, with corresponding decrease of separation efficiency. The effect of a given air pressure is the more marked, the lower the evaporation rate, but for moderate rates, the air pressure has practically no effect on efficiency until it ex-

[6] The mercury used lost 4 parts per million in density by the first distillation, a corresponding density *increase* being concentrated in the residue, this increase being found to be inversely proportional to the volume of the latter, as would be expected.

[7] See in particular Langmuir, *Phys. Rev.*, [2] **2**, 329 (1913).

[8] The *efficiency* tells directly what fraction of the evaporating molecules escapes permanently from the liquid in a single attempt,—at least when the mercury surface is clean, and except in so far as some part of the inefficiency may be due to imperfect mixing between the surface and body of the liquid.

[9] The examples given in this paper are taken from or based on more extensive data, obtained with several forms of apparatus and under varied conditions.

ceeds 0.1 mm. The following efficiencies, obtained with a 300cc. flask at evaporation rates near 15 cc. per hour, may be cited: 58% at 10^{-5} mm. air pressure,[10] 54% at 0.02 mm., 46% at 0.8 mm., 20% at 10 mm., 9% at 30 mm. A high pressure of mercury vapor, due to high evaporation rate or high outlet resistance, produces similar results.[11] A film of dirt on the evaporating surface, although it greatly reduces the rate of evaporation at a given temperature, was found to increase the efficiency markedly at moderate rates.[12] Probably evaporation here gives place partly or wholly to molecular diffusion of vapor, saturated at the temperature of the liquid, through the film, into the region of lower pressure in the flask. The following examples will illustrate the effect of a film at various rates: (1) without film, efficiency 54% at 1.5 g./cm.²/hr., 27% at 8 g., and 24% at 24 g.; (2) with film of soot, 58% at 3 g., 49% at 14 g., and 37% at 36 g.

In view of the ease with which a very considerable degree of irreversibility can be secured, as shown by the above work on isotopes, it may be worth while to call attention to the possibility of obtaining, in the distillation of mixtures of *non-isotopic* liquids differing in molecular weight, distillates differing in favor of the lighter components from those obtainable by the substantially completely reversible conditions of ordinary distillation. Thus a constant-boiling mixture, quite aside from the well-known usual change of the constant-boiling composition with pressure, could, if its components differed considerably in molecular weight, be separated quite rapidly by a series of irreversible distillations. Laboratory or industrial applications of this method are possibilities. A mixture of isotopes has the characteristics of a constant-boiling mixture at all compositions and all pressures, and so can be separated *only* by resorting to irreversible conditions.

Attempted Separation by Electrolytic Solution and by Heterogeneous Reaction

With the idea that the mechanism of electrolytic solution should be analogous to that of distillation, an attempt was made to separate the isotopes of mercury by dissolving the metal electrolytically in potassium

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[10] These results were obtained with a dirt film on the surface.

[11] Condensation on the walls, with reflux, was found not to affect appreciably the efficiency, presumably because it takes place under substantially equilibrium conditions. The result is the same as if the condensed material merely had not evaporated, except for a small secondary effect due to the increase in the *gross* evaporation rate for a given *net* rate. Direct return of molecules from vapor to evaporation surface, on the contrary, is directly injurious to efficiency.

[12] At very *low* rates, such a film has little effect on efficiency, though it does on rate; (as compared with the maximum theoretical rate for a perfectly clean surface); at very *high* rates, the effect on rate is less marked than at moderate rates, although the effect on efficiency is still considerable.

cyanide solution. It was hoped that the immediate formation of stable complex ions, which could diffuse away at leisure, would permit the maintenance of the necessary non-equilibrium conditions at the phase boundary. A close approach to equilibrium could otherwise hardly be avoided, due to the slowness of liquid diffusion. The results, however, were completely negative, probably because of instability of the complex ions close to the electrode, or to delay in their formation,[13] or to the intermediation of Hg_2^{++} ions, or to all these factors. A positive result would be of great interest because of its bearing on the mechanism of the electrode process; but the possibility of attaining such a result seems remote. An analogous experiment which should have a similar bearing on the mechanism of heterogeneous reactions between condensed phases, namely, the reaction of mercury with powdered sulfur, also failed to yield a separation of isotopes. It is probable that all attempts to separate isotopes by solution or precipitation processes, whether physical or chemical, involving the transfer of molecules or ions across the boundary between two *condensed phases*, are doomed to fail, although theoretically feasible, because of the difficulty of obtaining irreversible conditions at such a boundary.

Summary

1. A new experimental value, 0.0063, of the separation coefficient of mercury, is reported in place of the previous value, 0.0057.

2. The process of purification of mercury has been studied by means of density determinations.

3. The effect of various factors on the efficiency of separation of isotopes by the method of non-equilibrium distillation has been studied. An efficiency of 50% is very easily obtained. A film of dirt increases efficiency at the higher rates.

4. The possibility of applying irreversible distillation as a new factor in the separation of *non-isotopic* liquid mixtures is pointed out.

5. The failure of attempts to secure a separation of the isotopes of mercury by electrolytic solution or by reaction with sulfur is reported. This is ascribed to the great difficulty of obtaining non-equilibrium conditions at the boundary between two condensed phases.

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[13] Compare Leblanc and Schick, *Z. physik. Chem.*, **8**, 697 (1902).