

The Separation of Liquid Mixtures by Centrifuging.—In a previous paper¹ by the author it was shown thermodynamically that the same separation of isotopes should be obtainable by centrifuging a liquid as a gaseous mixture, at a given speed. The same result was stated to be true of ideal solutions in general, but this is incorrect. The result depends not only on the ideality of the solution, but also on equality of the vapor pressures and of the atomic or molecular volumes of the components. These conditions are fulfilled in few cases except that of a mixture of isotopes. The type of proof used can, however, serve as a basis for the calculation of the changes of composition of *any* solution when subjected to centrifugal force. Thus, suppose a liquid and its saturated vapor are centrifuged side by side, separated by a membrane permeable only to the vapor. Assuming, as we may for the purpose, that condensation of the vapor due to its supersaturation is inhibited, a state of equilibrium must finally be reached between liquid and vapor at every point. In so far as the ideal gas law holds for the vapor, the following equation must be true for the relative value, at the peripheral and central ends of the centrifuge tube, of the ratio of the vapor pressures (p_1 and p_2) of two components,

$$r_p = \frac{p_2/p_1}{(p_2)_0/(p_1)_0} = e^{(v^2v_0 - 2)(M_2 - M_1)/2RT} \quad (1)$$

similar to Equation 23 of the previous paper.² In order to get the

composition ratio, $r_x = \frac{x_2/x_1}{(x_2)_0/(x_1)_0}$, one must know how the mol-fractions (x) depend on the vapor pressures, taking into account the effect of the external pressure (P) due to the centrifugal force. For an ideal solution under *any* external pressure, we have $p_1 = p_1'x_1$ and $p_2 = p_2'x_2$. By integrating approximately the thermodynamic equation $vdp = VdP$, using a suitable average value for the molecular volume V , we obtain $p' = (p')_0 e^{PV/RT}$. Then

$$r_p = \frac{p_2'x_2/p_1'x_1}{(p_2')_0(x_2)_0/(p_1')_0(x_1)_0} = r_x r_{p'} = r_x e^{P(V_2 - V_1)/RT}$$

Making use of Equation 1, $r_x = e^{[(v^2 - v_0^2)(M_2 - M_1) - 2P(V_2 - V_1)]/2RT}$. Since $P = \rho(v^2 - v_0^2)/2$, approximately (see Ref. 24 of paper referred to; ρ is the average density of the liquid), this becomes

$$r_x = e^{(v^2 - v_0^2)[(M_2 - M_1) - \rho(V_2 - V_1)]/2RT} \quad (2)$$

This reduces, in the case of a mixture of isotopes, where $V_2 = V_1$, to Equation 23 of the paper referred to. For ideal solutions in general, however, the molal volumes or densities of the components may often be more im-

¹ Mulliken, THIS JOURNAL, 44, 1033 (1922).

² In Equation 1, v and v_0 refer, respectively, to the peripheral and central values of the *speed*, M_1 and M_2 to the atomic or molecular weights of the components.

portant than the molecular weights. For *non-ideal* solutions, Equation 1 holds, and by the general methods of development above used, equations analogous to 2 could be obtained, although they would be much more complicated in general.³ The separation of solutions (other than colloidal) by centrifuging has been little studied. Vibration was shown in the previous paper to be an important cause of difficulty in obtaining separations by an ordinary centrifuge.

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THE OXIDATION OF ACETOL WITH POTASSIUM PERMANGANATE¹

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The work presented in this paper is a continuation of a series of similar studies being made in this laboratory on the oxidation of organic compounds.³ The main purposes of our investigation were the following: (1) to determine the influence of the initial concentration of the alkali upon the character and amounts of the reaction products formed; (2) to ascertain the influence of temperature on the character and the amounts of these products; (3) to learn, if possible, by means of exact quantitative data the course followed by the reactions involved in the oxidation of acetol by means of neutral and alkaline solutions of potassium permanganate. Previous investigations⁴ on acetol have not been carried out under carefully controlled conditions and as a consequence the various results are not comparable, nor do they shed much light on the mechanism of the oxidation.

³ Miller, *Trans. Am. Electrochem. Soc.*, **21**, 209 (1912), gives equations for the concentration distribution of a solute in a dilute solution under centrifugal force.

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¹ This paper was read at the New York meeting of the American Chemical Society in September, 1921.

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³ THIS JOURNAL, (a) **34**, 1087 (1912); (b) **35**, 54 (1913); (c) **38**, 375 (1916); (d) **41**, 1267, 1386 (1919).

⁴ Linneman, *Ann.*, **134**, 174 (1865). Emmerling and Wagner, *ibid.*, **204**, 40 (1880). Perkin, *J. Chem. Soc.*, **59**, 793 (1891). Nef, *Ann.*, **335**, 269 (1904). Denis, *Am. Chem. J.*, **38**, 561 (1907).