

Internal Equilibria and Partial Vapor Pressures of Mixtures of Primary Normal Alcohols with Normal Paraffin Hydrocarbons

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Internal Equilibria and Partial Vapor Pressures of Mixtures of Primary Normal Alcohols with Normal Paraffin Hydrocarbons

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1. Heats of mixing for mixtures of primary n -alcohols and n -hydrocarbons have been determined down to practically infinite alcohol dilution over a temperature range from 10°C to 45°C. It has been found that (1) the heat of mixing is always negative and that the heat absorption, per mol of alcohol, increases with increasing dilution of the alcohols to a limit of 5800 cal. per mol; that the curves of the molar heat absorption against molar alcohol concentration are identical for all investigated systems—the first four primary n -alcohols in n -hexane and n -heptane. Furthermore, reports in the literature that n -hydrocarbons may be mixed with each other without any heat effect were confirmed.

2. The present experiments and evidence gathered from the literature indicate that (1) primary n -alcohols, in the pure liquid state, are completely associated to double molecules and that when mixed with a hydrocarbon they dissociate into single molecules; (2) that the association takes place between the two hydroxyl groups of two single molecules on account of their electrostatic dipole forces; (3) that the observed heat absorption is entirely due to the dissociation of double molecules, i.e., breaking up of the (electrostatic) hydroxyl bond and that there is no thermal effect of the aliphatic groups in the alcohol molecules upon the hydrocarbon solvent; and (4) that the equilibria

between single and double molecules are identical at equal molar concentrations for all primary n -alcohols in all n -hydrocarbons.

3. This theory leads to an equation for the partial vapor pressures of n -alcohols in n -hydrocarbons:

$$\log p = \log f - (\lambda - Q)/RT + B - b,$$

where p = the partial vapor pressure at the mol fraction f , λ = the heat of vaporization of pure alcohol, Q = heat of mixing at mol fraction f and temperature T , and b = a universal function of Q . B is determined by the ordinary (simplified) vapor pressure equation

$$\log P = -\lambda/RT + B$$

and is constant over the whole temperature range investigated. λ and B depend upon the nature of the alcohol, while Q and b depend upon molar concentration and temperature.

4. It is shown that after b has been determined once as a function of Q in a specific case, one can calculate partial vapor pressure curves of other systems.

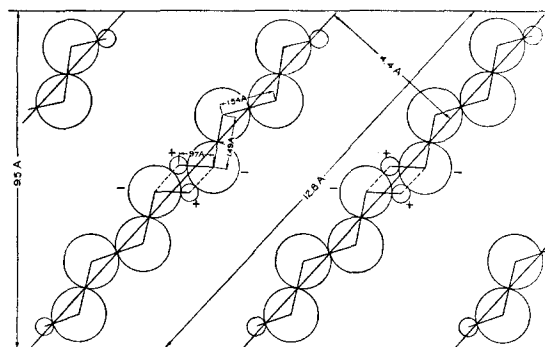
5. An equation has been developed which permits the calculation of the degree of dissociation and therefore Q , for any temperature and concentration.

WHILE extensive experimental material is available on the physical properties of liquid mixtures, it usually appears impossible to obtain an accurate idea of the changes which the components undergo during the process of mixing. Attempts to introduce chemical conceptions, such as the formation of double, triple, etc., molecules, have frequently been made in the past but usually have met with failure; on the other hand, no other general method of treatment has been offered thus far. However, consideration of the experimental data presented in this paper on mixtures of primary normal alcohols with normal paraffin hydrocarbons appears to justify the adoption of a specific and simple picture in this particular case. It may be assumed that similar simple conditions may be found in other systems

and further, that the simplicity of the present case may allow an approach to the fundamental laws governing equilibria in liquid systems.

Primary normal alcohols, in the liquid state, show x-ray diagrams which indicate the existence of cybotactic groups containing two sets of planes:¹ one set of planes is produced by the arrangement of the molecules as double molecules, two OH groups being together and the two molecules forming a straight chain, the other by the arrangement of two such double molecules lying side by side with the two pairs of OH groups not directly adjacent but slipped by one another so that the set of planes containing them is not normal to the length of the chain. In Fig. 1, the

¹ Stewart, Chem. Rev. 6, 483 (1929). Compare also further references there.

FIG. 1. Cybotactic group of *n*-propyl alcohol.

cybotactic group of *n*-propyl alcohol is shown, from Stewart's data on the distance of the planes. The value of 12.8 Å for the length of the double molecule is estimated from his formula for the length of *n*-paraffin molecules and additional information on the dimensions of the OH group.² The distance between the two adjacent OH groups is assumed arbitrarily to be that of the closest possible approach.

The head-to-head association is certainly caused by the strong electrostatic forces arising from the polar OH groups. The dipole moment of the OH group itself amounts to about 1.6×10^{-18} e.s.u.,³ which is rather large compared to other groups. On the other hand, the separation of the poles must be rather small, since the distance of the nuclei of the atoms amounts to only 0.97 Å.² It follows that the poles themselves are extraordinarily strong and that two molecules are linked together with considerable force. Information on the strength of this electrostatic bond may be obtained from a paper by M. Dunkel,⁴ who shows that the increase of the heat of evaporation of an alcohol over that of the corresponding paraffin is fairly constant throughout the homologous series and amounts, on the average, to 7250 cal. per mol. Since there is no association of alcohol molecules in the gas phase, this value may be interpreted to represent the heat of formation of double molecules. The large value of 7250 cal. per mol—comparable to a chemical bond—suggests that association in the liquid state is practically complete.

² Hengstenberg and Mark, *Naturwiss.* **20**, 539 (1932).

³ Eucken and Meyer, *Phys. Zeits.* **30**, 397 (1929).

⁴ M. Dunkel, *Zeits. f. physik. Chemie* **138**, 42 (1928).

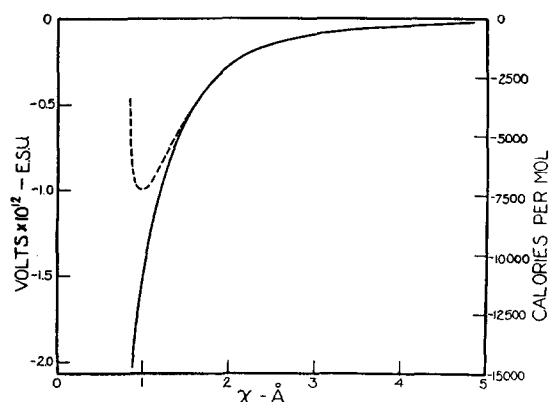


FIG. 2. Estimated curve of the potential energy between two hydroxyl groups.

Coulomb's law for the potential energy of two dipoles, placed parallel with opposite poles adjacent, is

$$V = -2e^2(1/x - 1/(x^2 + y^2)^{1/2}),$$

where e is the pole strength, y the diameter of the polar group and x the interpolar distance. If one identifies y with 0.97 Å, which is probably too large a value, one may calculate e from the above dipole moment and, correspondingly, the potential energy as a function of x , as shown in Fig. 2. At very close approach, repelling forces will appear. If one places the minimum of potential energy at $X=1$ Å and $-V=7250$ cal. per mol, the dotted curve may represent approximately the combined influence of attraction and repulsion.

Normal hydrocarbons tend to arrange themselves parallel to each other at a distance of 4.6 Å. There is practically no heat effect if one mixes two different *n*-hydrocarbons with each other, and the partial vapor pressures (p) above the mixture follow Raoult's law:

$$p = fP, \quad (1)$$

where f = the mol fraction and P the vapor pressure of the pure substance. As shown by thermodynamics, Raoult's law can hold only in the absence of any heat of mixing.

Dunkel⁴ has shown that chemical groups, like $-\text{CH}_2$, $-\text{CH}_3$, preserve their contributions to the intra-molecular force in equal strength in different compounds. The aliphatic radical of an alcohol molecule, therefore, has the same effect upon a

neighboring molecule as if it were a part of a hydrocarbon molecule instead. Therefore, it contributes nothing to the heat of mixing of n -alcohols and n -hydrocarbons, which appears to be entirely due to the dissociation of the hydroxyl groups.

In view of the above considerations certain predictions can be made about the effects to be observed in the mixing process. At very low alcohol concentrations, the hydroxyl dissociation should be complete. Hence, if association of all alcohols in the pure state is complete, the heat absorbed during mixing should approach a final value identical for all n -alcohols in all n -hydrocarbons. The present experiments show this to be the case and the value found is 5800 cal. per mol, which is lower than the value of 7250 cal. quoted above because of the higher dielectric constant of the liquid medium. At higher concentrations, equilibria between double and single molecules are established. The degree of dissociation determines the molar heat effect. For equal molar concentrations, this should also be identical for all n -alcohols in all n -hydrocarbons, since the concentrations of OH groups are identical and the hydrocarbon groups do not influence each other.

EXPERIMENTAL PROCEDURE AND RESULTS

The hydrocarbons used were Eastman "practical" hexane and heptane. They were redistilled, especially to insure complete elimination of moisture. The n -alcohols used were anhydrous methyl-, ethyl-, n -propyl- and n -butyl alcohol.

The liquids were mixed in a Dewar flask, constantly stirred, and temperature readings were taken with a Beckmann thermometer. The alcohol sample was contained in a special pipette which was completely immersed in a weighed amount of liquid hydrocarbon and which could be opened from the outside. Figs. 3a and 3b show two different constructions of such pipettes. In Fig. 3a, the alcohol sample is enclosed by mercury and may be pushed out by turning the threaded shaft with the piston on the end. In the construction shown in Fig. 3b, two valves, one on the top, the other on the bottom, may be opened simultaneously, thus releasing the enclosed liquid. The amount of alcohol was determined by weighing the pipettes before and after filling. The

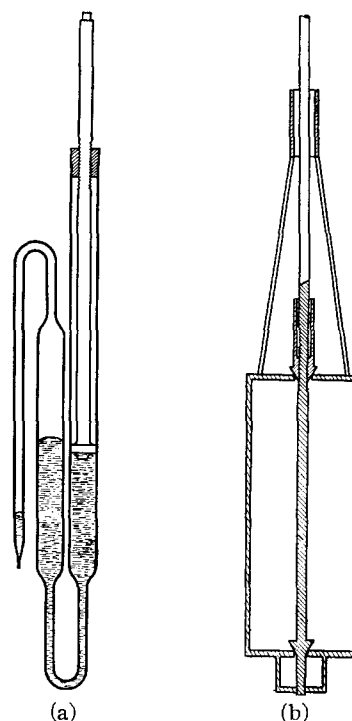


FIG. 3. Sample containers (pipettes) for measuring heats of mixing.

measurements were made by determining the temperature drift before and after mixing. Care was taken to eliminate heat effects due to evaporation by keeping the gas space above the liquid sufficiently small. The heat capacity of vessel and liquid was determined by passing a known current through an immersed resistance wire and determining the temperature change and heating time.

In Fig. 4, the molar heats of mixing the above-named alcohols in heptane and hexane at 29°C are plotted against the concentration (mol per cc). The results of experiments with all the materials fall on one curve, as expected, and approach at infinite dilution a value of $Q_{\infty} = 5800$ cal. This holds for other temperatures as well, the only difference being a change in the slope of the curves, corresponding to more dissociation at higher temperature and *vice versa*, for any given concentration.

THE DISSOCIATION EQUILIBRIUM IN THE LIQUID PHASE

The equilibrium between double and single molecules, at any temperature T and mol frac-

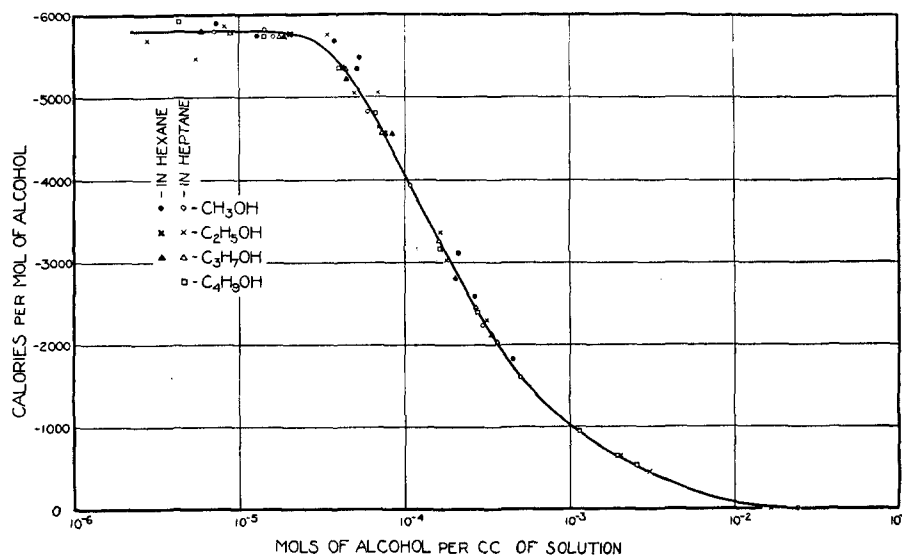


FIG. 4. Heats of mixing of primary normal alcohols in hexane and heptane.

tion f , can be measured by the heat of mixing. The degree of dissociation may be given by

$$\alpha = Q/Q_{\infty}, \quad Q_{\infty} = 5800 \text{ cal.} \quad (2)$$

if the assumption is made that no heat is required to separate double molecules one from another. Since a double molecule resembles a normal hydrocarbon and these show no evidence of a heat of mixing, this assumption is probably justified.

The results of investigations on the dielectric properties of mixtures of alcohols and hydrocarbons⁵ may be interpreted from the viewpoint developed thus far. The molar polarization P of a substance in which the molecules are free to assume a perfectly random orientation is represented by the Debye equation, written in the following form:

$$P = \frac{E-1}{E+2} \frac{M}{d} = \frac{4\pi}{3} N + \frac{4\pi N \mu^2}{9k T}. \quad (3)$$

Furthermore,

$$[(n^2-1)/(n^2+2)](M/d) = (4\pi/3)N, \quad (4)$$

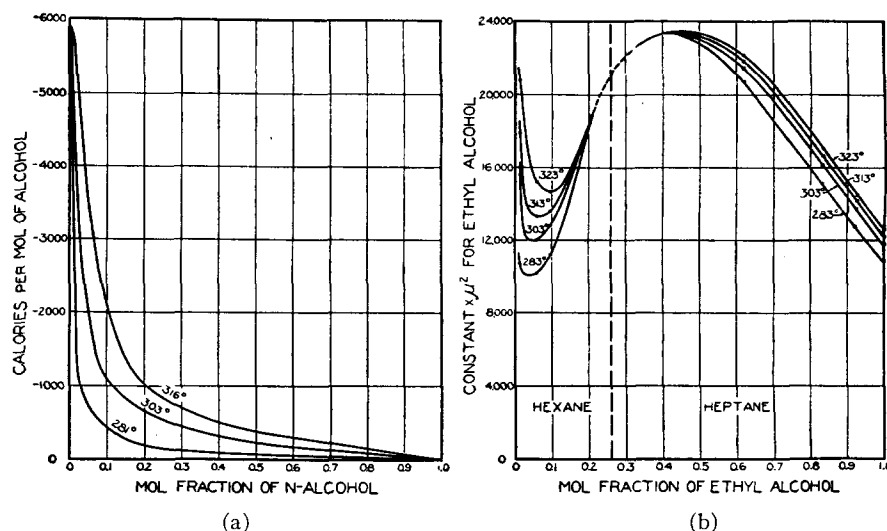
where n = the index of refraction for light of infinite wave-length, E = the dielectric constant, M = the molecular weight, d = the density, N = Avogadro's number and μ = the dipole mo-

ment. The index of refraction should remain about the same for dissociated and undissociated alcohol, as the electronic structure does not change (no "sharing" of electrons). One may, therefore, calculate the factor $(4\pi/9k)N\mu^2$ in (3) from Smyth and Stoops' data. Values thus obtained for ethyl alcohol in hexane at high dilutions and ethyl alcohol in heptane at higher concentrations are plotted as isotherms against the mol fraction f in Fig. 5b. In Fig. 5a, corresponding heats of mixing curves are shown. Both types of curves, from zero concentration upward, drop rapidly in the first part. The reason is the same in both cases: the degree of dissociation rapidly diminishes. A single alcohol molecule possesses a strong dipole moment, while double molecules are only slightly polar, because of their symmetry. The subsequent slope of the curves in Fig. 5b has been discussed by Malsch.⁶ It may be pointed out that alcohol double molecules may be deformed by transverse vibrations which bulge the central OH groups out and cause slight polarity. The effect upon an electric field will be increased at higher concentrations when several double molecules are coupled together in the same cybotactic group.

In order to investigate the quantitative connection between degree of dissociation, concen-

⁵ Smyth and Stoops, J. Am. Chem. Soc. **51**, 3312 (1929).

⁶ Malsch, Phys. Zeits. **33**, 383 (1932).

FIG. 5. (a) Heats of mixing; (b) Polarization.⁵

tration and temperature, the application of the law of mass action may be attempted:

$$(\alpha^2/(1-\alpha))c = \text{const.} = K, \quad (5)$$

where c = number of mols per cc. As is shown by Table I, the mass law itself does not hold for any isotherm. Surprisingly, however, van't Hoff's equation

$$\ln K_1/K_2 = (2Q_\infty/R)((T_2 - T_1)/T_2 T_1) \quad (6)$$

holds between the K values for equal α 's at

TABLE I. Application of van't Hoff's equation to the temperature dependency of the dissociation equilibrium.

$T^{\circ}\text{C}$	30	44.4	30	44.4	30	42.4	30	42.4
mol per cc $\times 10^4$.68	1.7	1.0	2.5	2.0	5.1	5.0	10.7
α	.863	.863	.755	.755	.517	.517	.293	.293
$\alpha^2 c / (1 - \alpha) \times 10^6 = K$	36.8	91	22.8	57.5	11.0	23	6.0	12.9
$\left(\ln \frac{K_1}{K_2} \right) \frac{T_1 T_2}{T_1 - T_2} R$	11700		12200		11300		11800	
	<i>Mean value</i> = 11750 cal.							

$T^{\circ}\text{C}$	9.1	30	8.3	42.4	9.2	42.3
mol per cc $\times 10^4$.212	1.01	.578	5.6	2.0	13.5
α	.733	.733	.495	.495	.245	.245
$\alpha^2 c / (1 - \alpha) \times 10^5 = K$	4.24	20.3	2.81	27.1	1.59	10.75
$\left(\ln \frac{K_1}{K_2} \right) \frac{T_1 T_2}{T_1 - T_2} R$	12300		11900		10400	
	<i>Mean value</i> = 11500 cal.					

TABLE II. Comparison between mass action law Eq. (5) and new Eq. (7).

α	0.863	0.755	0.517	0.293
$K \times 10^5$	36.8	22.8	11.0	6.0
$K^* \times 10^5$	14.1	15.8	13.5	14.8

different temperatures and concentrations, where $2Q_\infty = 11,600$ cal. represents the heat of formation of one mol of double molecules from 2 mols of single molecules. This fact permits the calculation of values of the heat of mixing for any temperature and concentration from one experimental isotherm of the heat of mixing.

Since the mass law as expressed by Eq. (5) does not hold, one may adjust it empirically by adding an "activity coefficient." Introducing the factor $(1.492)^{(1-\alpha)/\alpha}/(1.084)^{2\alpha/(1-\alpha)}$ in (5), one obtains

$$\frac{\alpha^2}{1-\alpha} c \times \frac{(1.492)^{(1-\alpha)/\alpha}}{(1.084)^{2\alpha/(1-\alpha)}} = \text{const.} = K^*, \quad (7)$$

and

$$\ln K_1^*/K_2^* = \ln K_1/K_2 = (2Q_\infty/R)(T_2 - T_1)/T_1 T_2. \quad (8)$$

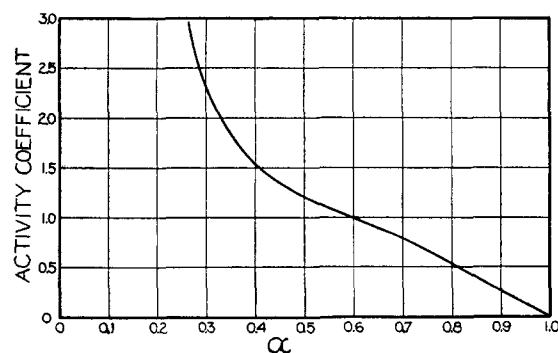


FIG. 6.

In Table II, the K values of Table I, for 30°C, are compared with K^* values. The comparison extends over a wide range of dissociation and shows that Eq. (7) holds satisfactorily. The constancy of K^* obtained here holds for other isotherms as well, of course, because of Eq. (8). In Fig. 6 the activity coefficient is plotted against α . For $\alpha=1$ it becomes zero, for $\alpha=0$ it becomes infinitely large.

THEORETICAL DISCUSSION

A general theory on equilibria in liquid phases does not exist, except for ionic solutions. The use of the simple mass action law has frequently met with failure in the past and it is not applicable in the present case, even if more than one equilibrium is assumed. In order to account for any of the measured isotherms by assuming triple-, quadruple-, etc., molecules it would be necessary to consider a very large number of such additional equilibria and it would be impossible to account for the simple relationship (8) between the isotherms themselves.

Furthermore, it appears doubtful whether a successful theory may be built upon the assumption of electrostatic forces between the solute molecules, as in the case of ionic solutions. In the first place, deviations from the mass action law are observed even at high dilution, while, on the other hand, the electrostatic dipole potential rapidly diminishes with increasing distance. Second, one will probably find it difficult to fulfill the relationship (8).

Eq. (7) may be formally derived if one is allowed to assume that the osmotic pressures of double and single molecules in separate solutions are proportional to their concentrations and that, if both kinds of molecules are in the same solution together, their respective osmotic pressures are increased for an amount proportional to the concentration of the other component. Thus, if a_1 and a_2 are proportionality factors and c_1 and c_2 the concentrations of single and double molecules, respectively, the increase in the osmotic pressure of the single molecules due to the presence of double molecules amounts to a_1c_2 and the corresponding increase for the double molecules, as compared with their osmotic pressure in a solution which is free of single molecules, amounts to a_2c_1 .

With these assumptions, one may now calculate the free energy of transforming 2 mols of single molecules into 1 mol of double molecules. Consider three solutions: one containing single molecules at the standard concentration C_{1s} , another containing double molecules at the standard concentration C_{2s} , and the third containing single and double molecules together at equilibrium concentrations c_1 and c_2 . By means of semi-permeable pistons we first compress 2 mols of single molecules from C_{1s} to c_1 ; second, transfer them into the equilibrium solution; third, remove 1 mol of double molecules from the equilibrium solution and fourth, expand the latter from equilibrium concentration c_2 to standard concentration C_{2s} . In steps one and four the free energy change equals simply $2 RT \ln C_{1s}/c_1$ and $RT \ln c_2/C_{2s}$, respectively. In steps two and three, work is done because of the increased osmotic pressure of each participant. The work which is done in step two equals $2 a_1 v_1 c_2$, where v_1 is the volume which contains one mol of single molecules. Correspondingly in step three, the work done equals $-a_2 v_2 c_1$, where v_2 is the volume containing one mol of double molecules. The free energy of transforming two mols of single into one mol of double molecules is, therefore, given by

$$\Delta F = 2RT \ln C_{1s}/c_1 - 2a_1 v_1 c_2 - RT \ln C_{2s}/c_2 + a_2 v_2 c_1.$$

Introducing $v_1 = 1/c_1$ and $v_2 = 1/c_2$ and transposing,

$$\Delta F = RT \ln C_{1s}^2/C_{2s} - RT \ln c_1^2/c_1 - 2(c_2/c_1)a_1 + (c_1/c_2)a_2. \quad (9)$$

Since ΔF , at the temperature T_1 , must be independent of any specific equilibrium concentrations c_1 and c_2 , one obtains, for constant temperature

$$\ln c_1^2/c_2 + (2c_2/c_1)(a_1/RT) - (c_1/c_2)(a_2/RT) = \text{const.} \quad (10)$$

Introducing the degree of dissociation, α , by means of

$$\alpha = c_1/c \quad (11)$$

and

$$1 - \alpha = 2c_2/c, \quad (12)$$

where c is the number of mols $C_nH_{2n-1}OH$ per unit volume, one obtains

$$\ln (2\alpha^2/(1-\alpha))c + ((1-\alpha)/\alpha)(a_1/RT) - (2\alpha/(1-\alpha))(a_2/RT) = \text{const.} \quad (13)$$

Since the energy of a fully excited degree of freedom increases in proportion to the temperature and a_1 and a_2 possess the dimensions of an energy, it is plausible to assume that for different temperatures the quotient a_1/RT and a_2/RT remains constant:

$$a_1/RT = \text{const.} = \ln A_1, \quad \text{and} \quad a_2/RT = \text{const.} = \ln A_2. \quad (14)$$

Hence

$$\frac{\alpha^2}{1-\alpha} c \times \frac{A_1^{(1-\alpha)/\alpha}}{A_2^{2\alpha/(1-\alpha)}} = \text{const.} = K^*. \quad (15)$$

Introduction of the numerical value 1.492 for A_1 and 1.084 for A_2 leads to Eq. (7) which is in numerical agreement with the experimental data.

From Eq. (14) one obtains

$$a_1/T = 0.7 \text{ cal./deg. per mol} \quad \text{and} \quad a_2/T = 0.184 \text{ cal./deg. per mol.}$$

These values may possess a physical meaning in connection with the above assumptions. The writer believes, however, that further discussion of these assumptions would be premature.

PARTIAL VAPOR PRESSURES

A knowledge of the heat of mixing makes it possible to deduce an equation for the partial vapor pressures of n -alcohols in the n -hydrocarbons. For this purpose the validity of Raoult's law may be assumed in a modified form:

$$p = f \times P', \quad (16)$$

where P' is a hypothetical vapor pressure which would be established if pure alcohol were in the same state of dissociation as it is in the solution, at the concentration (mol fraction) f . The energy difference between dissociated and undissociated alcohol may be denoted by \bar{L}_1 ; and one may write⁷

$$Q = -\bar{L}_1 - (n_{\text{hydr.}}/n_{\text{alc.}})\bar{L}_2. \quad (17)$$

The second term represents the change in the heat content of the hydrocarbon solvent. The hydroxyl group of every dissociated alcohol molecule induces a momentum in neighboring hydrocarbon molecules, with the effect that the heat content of the solvent increases in proportion to the alcohol dissociation, while that of the alcohol solute decreases. Substituting, therefore,

$$-\bar{L}_1 = \alpha q_1 \quad \text{and} \quad -(n_{\text{hydr.}}/n_{\text{alc.}})\bar{L}_2 = -\alpha q_2,$$

one obtains

$$-\bar{L}_1 = \alpha q_1 = Q + \alpha q_2. \quad (18)$$

Since the specific heats of dissociated and undissociated alcohol are different because of the creation of new degrees of freedom in the dissociated state, there is an entropy difference ΔS . The free energy of changing the alcohol modification characterized by the vapor pressure P' to the normal state characterized by the vapor pressure P is equal to

$$F = RT \ln \frac{P'}{P} = \bar{L}_1 - T\Delta S = Q - (T\Delta S - \alpha q_2). \quad (19)$$

It seems again plausible, from the physical picture developed above, that ΔS is determined by the degree of dissociation, i.e., Q , alone, and that both ΔS and q_2 are independent of the nature of either the primary n -alcohol or the paraffin hydrocarbon. Combining (19) and (16) and transposing

$$\ln p = \ln f + \ln P + Q/RT - (1/R)(\Delta S - \alpha q_2/T). \quad (20)$$

For the present limited temperature range, ΔS and q_2/T are fairly constant with temperature. Introducing, therefore,

$$(1/R)(\Delta S - \alpha q_2/T) = b, \quad (21)$$

the term b appears to be essentially a function of Q .

The vapor pressure P is given by the simplified vapor pressure equation, which is very satisfactory over a limited temperature range (ca. 100°),

$$\ln P = -\lambda/RT + B, \quad (22)$$

where the constant B may be determined from

⁷ Compare Lewis-Randall, *Thermodynamics*, p. 90 (1923).

the boiling point, and data for λ , in the present case, may be found in the literature.

Combining (20), (21) and (22) one obtains finally

$$\ln p = \ln f - (\lambda - Q)/RT + B - b, \quad (23)$$

where λ and B depend upon the nature of the alcohol while Q and b depend essentially upon the degree of dissociation, i.e., concentration and temperature.

Measurements are available of the partial vapor pressure curves of methyl alcohol in hexane at 45°C and of ethyl alcohol in heptane at 30°C.⁸ Knowing the values of Q and the corresponding values of λ and B for both systems, one may determine b as a function of Q independently for both systems. Fig. 7, which is plotted from the

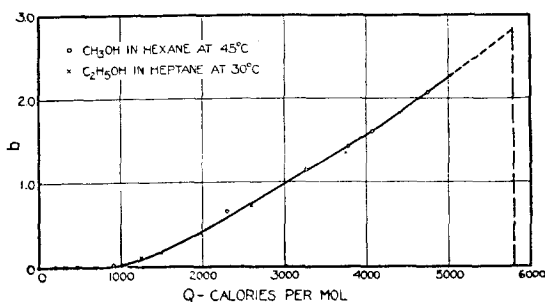


FIG. 7. Identity of Q , b curves (Eq. (20)) for two different alcohol-hydrocarbon systems.

numerical data given in Table III, shows that these functions are indeed identical, as anticipated.

This means, of course, that having once determined $b=f(Q)$ for one system, Eq. (23) will allow one to calculate the partial vapor pressure also for other systems of this type. This generalization seems to be justified despite the fact that the comparison is limited to only two cases because of scarcity of experimental data. It may be pointed out that the two systems under consideration consist of different alcohols in different hydrocarbons at different temperatures and, therefore, provide a very severe test.

Fig. 7 shows that ΔS is not linear in Q , i.e., α . This seems to indicate that the specific heat of the solute alcohol does not increase in proportion to the dissociation. No suggestion can be made,

⁸ Ferguson, J. Phys. Chem. **36**, 1123 (1932); Ferguson, Freed and Morris, J. Phys. Chem. **37**, 87 (1933).

TABLE III. Application of Eq. (23) to mixtures of ethyl alcohol-heptane at 30°C and methyl alcohol-hexane at 45°C.

	λ	B for $\log_{10} p$ in mm Hg				
Methyl Alcohol	9180	8.83				
Ethyl Alcohol	10000	9.16				
<i>Ethyl Alcohol-Heptane, $t=30^{\circ}\text{C}$</i>						
f	0.009	0.020	0.038	0.059	0.100	0.200
p (mm Hg)	17.5*	40	50	55	59.5	63.7
Q	5030	3750	2640	1970	1300	770
b	2.28	1.35	0.73	0.39	0.11	0.00
<i>Methyl Alcohol-Hexane, $t=45^{\circ}\text{C}$</i>						
f	0.030	0.045	0.053	0.070	0.114	0.300
p (mm Hg)	150	229	260	282	300	312
Q	4750	4080	3780	3280	2270	729
b	2.09	1.62	1.43	1.17	0.66	0.00

* Approximate.

at present, to account for this except, perhaps that it may be connected with the peculiar activity coefficient in Eq. (7).

Eq. (23), however, not only allows one to calculate partial vapor pressure curves from calorimetrically measured heats of mixing but to predict, from the slope of these curves, whether the components are miscible in all proportions or separate into two liquid phases. This is demonstrated in Fig. 8. If supersaturation would prevent the separation into two phases, the partial vapor pressure, in the range of supersaturation, would go through a maximum and a minimum. Methyl alcohol and hexane, below 45°C, are no longer miscible in all proportions. The partial vapor pressure curve of methyl alcohol calculated

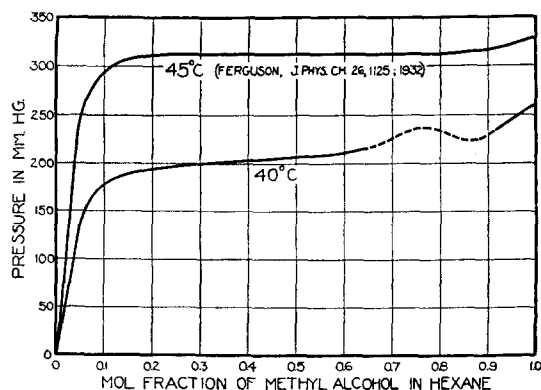


FIG. 8. Formation of two liquid phases in the system methyl alcohol-hexane, indicated by calculated vapor pressure curve.

from (23) for 40°C indeed goes through a maximum and minimum, as shown by the dotted part. The actual extension of the range of immiscibility differs somewhat from the range over which the dotted part in Fig. 8 extends. These limits are very sensitive to the Q values used and the lack of coincidence of the theoretical and experimental range may be accounted for by changes in Q within the limit of error in the heats of mixing data.

The partial vapor pressure curve of the hydrocarbon may, in principle, be determined from the alcohol curve by means of the Duhem-Margules equation

$$-(1-f)d \ln p_{\text{hydr.}}/df = f d \ln p_{\text{alcohol}}/df, \quad (24)$$

which, by combining with Eq. (23), becomes

$$-(1-f) \frac{d \ln p_{\text{hydr.}}}{df} = 1 + f \left(\frac{1}{RT} \frac{dQ}{df} - \frac{db}{df} \right). \quad (25)$$