[Contribution from the Chemical Institute of the Science College,
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ON THE SYSTEM ACETONE–ETHYL ETHER.

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Received April 9, 1918.

I. Introduction.

The theory of concentrated solutions is evidently one of the most important problems in physical chemistry as yet unsolved. The molecular theory of binary mixtures of van der Waals is indeed a preëminent one, but it requires complicated mathematical apparatus in solving even apparently simple problems, and for a system in which chemical reactions take place, it presents difficulties so great that no noteworthy progress has yet been achieved.

In the case of an ideal solution, nevertheless, the problem is comparatively simple. By the expression "ideal solution," for the present purpose, is meant a homogenous liquid mixture in which the following two conditions are fulfilled: (1) The volume of the solution is the sum of the volumes of the components (in the liquid state) under the same pressure and at the same temperature. (2) The total energy of the solution is the sum of the total energies of the components (in the liquid state) under the same pressure and at the same temperature.

There are many examples which approximately fulfil the above conditions. In most cases, however, the situation is complicated by unknown causes, one of which may be the attraction between different species of molecules, as is described by van der Waals. Among these non-ideal solutions, there are, nevertheless, numerous examples, in which reversible chemical reactions take place, but whose volumes and total energies are equal to the sums of the respective quantities of the components, called quasi-ideal solutions. I have studied the system acetone–ethyl ether as an example of quasi-ideal solution. The molecular condition of an associated liquid can be inferred from the study of the vapor pressures of the mixtures of that liquid and another normal liquid when they form quasi-ideal solution. The method of investigation was already worked out by Professor K. Ikeda,[1] to whom the theory is due.

As is well known, ethyl ether is a substance very nearly normal, while acetone is probably somewhat associated, the temperature coefficient of molecular surface energy of acetone being about 1.8, while in a normal liquid it should be 2.1.[2]

The system acetone–ethyl ether has been studied by Professor Ikeda,

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[1] Ikeda, *J. Coll. Sci. Imp. Univ. Tokyo*, **25**, Art. 10 (1908).

[2] Ramsay and Shields, *Z. physik. Chem.*, **12**, 433 (1893). The method of calculation is somewhat doubtful. See Ramsay, *Ibid.*, 15, 106 (1894); see also Nernst, "Theoretische Chemie," 6th Ed., p. 281.

using the data obtained by Cunaeus.[1] The latter author determined the composition of the gas phase by measuring the index of refraction. Unfortunately, the method is not an exact one for gaseous mixtures so readily condensable. Therefore, in the calculations, Cunaeus employed the values calculated by the following equation given by van der Waals,

$$\frac{1}{P}\,\frac{dP}{d(1-x')} = \frac{x-x'}{x'(1-x')},$$

where x, x' and P denote the empirical molar fractions of acetone in the liquid phase, in the gas phase, and the pressure, respectively. Accordingly, the data employed are less reliable than those obtained by direct observations. In order to secure more trustworthy data I attempted to determine the total and partial-vapor pressures of the system by a more direct method. The densities of the gaseous as well as the liquid phases were also measured. The results of all these observations and deductions therefrom are given in the following pages.

II. Experimental Part.

Materials.

Acetone.—Pure material obtained from Merck was crystallized with sodium bisulfite and then distilled from a solution of sodium carbonate. The distillate was dehydrated over calcium chloride and fractionated. The portion having the boiling point 56.13–56.18° under 760 mm. pressure was collected.

Ethyl Ether.—Ordinary material was washed with water and dehydrated over calcium chloride and then boiled with metallic sodium for several hours and fractionated. The portion boiling at 34.51–34.57°, under 760 mm. pressure, was taken.

Molecular Weights in Vapor Phases.

In the first place it was necessary to determine the molecular weight of acetone in the vapor state, in order to see how much of the vapor pressure is due to the simple molecules and how much to the associated. The molecular weight of acetone vapor at temperatures higher than the boiling point corresponds to the simple molecule C_3H_6O. Nevertheless, in the present study observations of the vapor pressures were carried out at ordinary temperatures, and therefore the determination of molecular weight of acetone vapor at these temperatures was necessary.

There are several well-known methods employed for the determination of vapor density of volatile liquids at comparatively low temperatures. In the present study, however, I used the ordinary method devised by Menzies,[2] but somewhat modified, so as to give more accurate results.

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[1] Cunaeus, *Z. phys. Chem.*, **36**, 232 (1901).

[2] Menzies, *Ibid.*, **76**, 355 (1911).

The apparatus employed consisted of a vaporizing vessel, a thermostat and a manometer as shown in Fig. 1. The vessel A had a capacity of about 300 cc. The lower part of this vessel was connected to a tube which was marked at its neck with a circle, D, which served to define the height of the mercury head. B was a glass stopper, provided at the lower side with a glass rod to which a loop, C, was attached. This loop served to support a thin glass bulb containing a weighed quantity of the liquid. Just under the loop was another glass rod attached horizontally to the side wall of the vessel which served to break the bulb projected below the loop. The volume of the vessel was determined by measuring the weight of mercury just sufficient to fill it. This vessel was connected with a manometer: a glass tube furnished with a scale and a mercury reservoir.

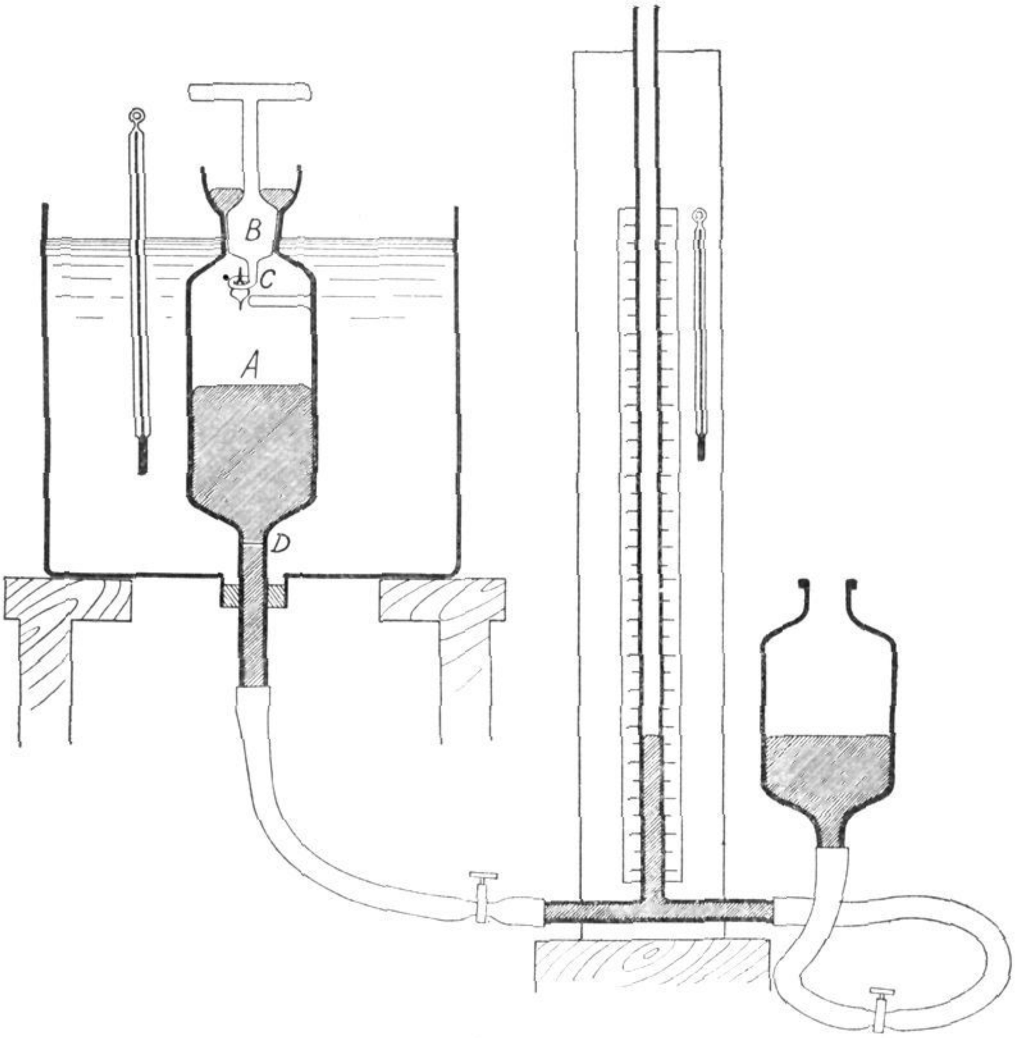

Fig. 1.

To carry out the experiment, a thin glass bulb containing the liquid was tied with a thin iron wire to the loop of the stopper. After the air in the vessel had been quite expelled by repeatedly raising and lowering the reservoir, the mercury head was exactly adjusted to the mark, and the height of the mercury column in the manometer tube was read. The reservoir was then raised a little, and the stopper of the vessel was rotated until the bulb was broken. The vaporization of the substance depressed the mercury column, and after a short time the vapor acquired the temperature of the thermostat. The mercury head having been brought exactly to the mark, the manometer height was read. The difference between these two readings corresponds to the pressure of the vapor at that temperature. From the data thus obtained, we can easily calculate the molecular weight in the usual way. In the present experiments the volume of vaporizing vessel was determined to be 267.91 cc., and the temperature of the thermostat was fixed at 25.00°.

The molecular weight of pure ethyl ether was first determined and the following data obtained:

TABLE I.

Weight of ether. Gr.	Vapor pressure. Mm.	Molecular weight. Uncorr.	Molecular weight. Corr. for v. d. W.[1]
0.1368	127.9	74.36	74.08
0.2259	209.6	74.94	74.48
0.3098	286.2	75.26	74.63
0.3140	289.9	75.26	74.62
0.4082	377.4	75.14	74.31

It is assumed in these calculations that the vapor obeys the simple gas laws, therefore, the resulting value of the molecular weight is by no means exact. Evidently it is not quite constant, but increases with the quantity of substance taken. To the values might be added an approximate correction, calculated by means of the van der Waals equation; but even then the observed molecular weights are, in most cases, larger than the calculated value, $C_4H_{10}O = 74.08$, the maximum deviation amounting to 0.7%. A probable explanation of at least a part of the deviations is the adsorption of the vapor on the glass wall and the mercury surface, since the vapor pressure is relatively high while the temperature is relatively low.

For acetone the data and results are shown in Table II.

Evidently here also the apparent molecular weight increases with the vapor pressure, even when the correction based upon van der Waals' equation has been taken into account. This comes, doubtless, partly from the above-mentioned adsorption, but in addition to this, probably, molecular association occurs in acetone vapor to a slight extent. Yet the deviations from the calculated value, $C_3H_6O = 58.048$, are not so large as to affect the calculation of the degree of association in the liquid phase. Therefore I have assumed in the later calculations that the acetone vapor has normal molecular weight at ordinary temperatures.

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[1] The values of constants a and b in van der Waals' equation determined by Young (1910) as: $a = 0.0346$, $b = 0.00600$. These values were used in the calculation.

TABLE II.

Weight of acetone.	Vapor pressure.	Molecular weight. Uncorr.	Molecular weight. Corr. for v. d. W.[1]
0.0473	56.7	57.99	57.92
0.0493	58.6	58.47	58.39
0.0536	63.7	58.48	58.39
0.0934	110.7	58.64	58.49
0.0959	114.2	58.37	58.22
0.09835	116.7	58.58	58.42
0.10445	124.2	58.45	58.29
0.1379	163.4	58.66	58.44
0.1412	166.1	59.08	58.86
0.1481	174.3	59.06	58.82

For the mixture of acetone and ethyl ether the following data were obtained:

TABLE III.

Weight of acetone.	Weight of ether.	Vapor pressure.	Mean molecular weight. Observed.	Mean molecular weight. Calculated.
0.0388	0.06145	103.4	67.41	66.93
0.05015	0.0584	114.4	65.96	65.70

From this table it is evident that there is no reaction between these two substances in the gaseous state.

Measurements of Vapor Pressures.

Apparatus.—Several forms of apparatus have been used in the determination of the vapor pressure of binary mixtures. Among those, those used by Zawidzki[2] and by Rosanoff and others[3] are preëminent. In the present study I have employed a new apparatus somewhat similar to that used by Y. Yamaguchi[4] in the study of the ethyl ether-chloroform system.

My apparatus is shown in Fig. 2. A represents a vessel of about 200 cc. capacity, to the stopper of which a coil of thin platinum wire and a thermometer were attached. The side tube B was wound with manganin wire and was thereby warmed electrically to prevent the condensation of vapor. C represents a receiver having a capacity of about 10 cc., and D and E were condensers cooled by a freezing mixture. This apparatus was placed in a thermostat, being covered with water to the neck of the vessel A. The upper mouths of the condensers D and E were connected to a manometer, a manostat, and finally to a water pump.

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[1] The values of a and b obtained by Sajotschewsky (1878) (Landolt-Börnstein-Roth, *Tabellen*, 4th Ed.) are:

$$a = 0.02774 \text{ and } a = 0.02459$$
$$b = 0.004437 \text{ and } b = 0.003896$$

Hence I assumed in calculations $a = 0.026$ and $b = 0.0042$.

[2] Zawidzki, *Z. phys. Chem.*, **35**, 129 (1900).

[3] Rosanoff, THIS JOURNAL, **31**, 448 and 953 (1909).

[4] Yamaguchi, *J. Tokyo Chem. Soc.*, **34**, 691 (1913).

To carry out the measurement, about 100 cc. of solution was introduced into the vessel A and then electricity of suitable current strength was passed through the coils attached to A and B. The pump was then started, and when the pressure was reduced to the amount corresponding to the vapor pressure of the solution at the temperature of thermostat, the solution began to boil. The boiling temperature of the liquid was continually observed, and was held at an exactly constant temperature, say 20 or 30° in my experiment, by regulating the pressure. At every instant, the vapor must have been in equilibrium with the solution from which it has just been evolved, although condensing continually in the receiver C. After some minutes the condensed liquid filled C, and flowed back to A. In the present experiments the receiver C filled in 8–10 minutes, and in each observation the boiling was continued more than one hour in order to reach a state of equilibrium between the liquids in A and C. The pressure was now read and air introduced into the boiling vessel through the 3-way cock F communicating with the atmosphere. The mouths of vessels A and C were opened and about 10 cc. of solution taken from each. The solution from C corresponds to the vapor which is in equilibrium with the solution from A. Hence the composition of vapor and liquid can be found by determining the composition of these solutions.

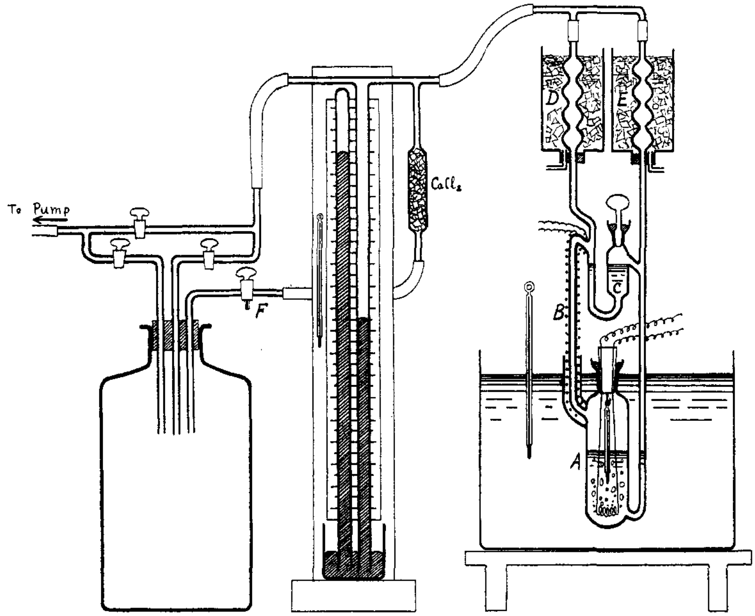

Fig. 2.

A density-composition curve had been previously obtained by density measurements of known mixtures of the liquids; this curve served to determine the compositions of the unknown mixtures of these liquids as soon as their densities are known. The result of density measurements of known mixtures are as follows:

TABLE IV.

Specific Gravities of Acetone-Ether Mixtures.

Molar fraction of acetone.	Specific gravity (25.04°/4°).
0	0.70760
0.10764	0.71418
0.20752	0.72052
0.31186	0.72766
0.41842	0.73524
0.45646	0.73806
0.54939	0.74515
0.56104	0.74608
0.63691	0.75227
0.72850	0.76005
0.77158	0.76380
0.85858	0.77182
0.93418	0.77903
1.0	0.78567

Also, the vapor pressures of pure acetone at various temperatures were measured. The data thus obtained are given in the following table compared with those of Regnault (1862)[1] and Taylor:[2]

TABLE V.

Vapor Pressures of Acetone.

Temp.	Author. Mm.	Regnault.	Taylor.
5.0°	89.2	...	...
10.0	115.6	...	...
15.0	147.1	...	...
20.0	184.8	179.6	182.5
25.0	229.2	...	229.0
30.0	282.7	281.0	281.0
35.0	346.4	...	343.0
40.0	421.5	420.2	416.0
45.0	510.5	...	505.0
50.0	612.5	620.9	607.0

The total- and partial-vapor pressures of acetone-ether mixtures at 30.00° and 20.00° are shown in the following tables and in Figs. 3 and 4. The values in the first and third columns were determined by interpolation from the densities of the respective solutions and Table IV.

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[1] Landolt-Börnstein-Roth, *Tabellen*, 4th Ed., p. 385.

[2] Taylor, *J. Phys. Chem.*, 4, 336 (1900).

TABLE VI.

Vapor Pressures of Acetone-Ether Mixtures at 30°.

Empirical molar fraction of acetone in solution. x.	Total pressure. P. Mm.	Empirical molar fraction of acetone in vapor.	Partial pressure. Acetone. P_α. Mm.	Partial pressure. Ether. p. Mm.
0	646.0	0	0	646.0
0.03867	645.3	0.03375	21.8	632.5
0.1327	637.0	0.1040	66.2	570.8
0.2509	616.9	0.1730	106.7	510.2
0.3454	597.0	0.2218	132.4	464.6
0.4958	557.8	0.3004	167.5	390.3
0.6507	502.7	0.4003	201.2	301.5
0.7047	479.7	0.4455	213.7	266.0
0.8381	409.6	0.5934	243.1	166.5
0.9337	337.8	0.7899	266.8	71.0
0.9528	326.0	0.8304	270.7	55.3
0.9799	297.4	0.9302	276.6	20.8
1.0	282.7	1.0	282.7	0

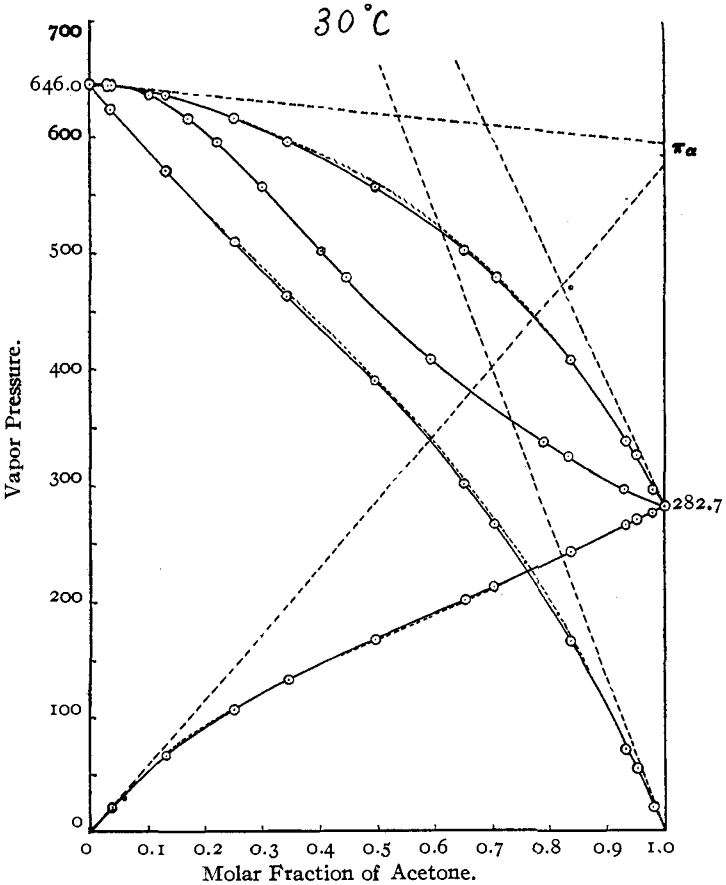

Fig. 3.

TABLE VII.

Vapor Pressures of Acetone-Ether Mixtures at 20°.

Empirical molar fraction of acetone in solution. x.	Total pressure. P. Mm.	Empirical molar fraction of acetone in vapor.	Partial pressure. Acetone. P_α. Mm.	Partial pressure. Ether. p. Mm.
0	443.5	0	0	443.5
0.05198	441.8	0.04429	19.6	422.2
0.1271	435.9	0.09585	41.8	394.1
0.2490	420.7	0.1668	70.2	350.5
0.4570	387.0	0.2717	105.2	281.8
0.6121	351.2	0.3611	126.8	224.4
0.6662	334.0	0.4049	135.2	198.8
0.8416	271.6	0.5911	160.5	111.1
0.8883	247.6	0.6781	167.9	79.7
0.9317	222.8	0.7832	174.5	48.3
0.9358	221.3	0.7910	175.0	46.3
0.9790	196.8	0.9216	181.4	15.4
0.9959	185.9	0.9902	184.1	1.8
1.0	185.2	1.0	185.2	0

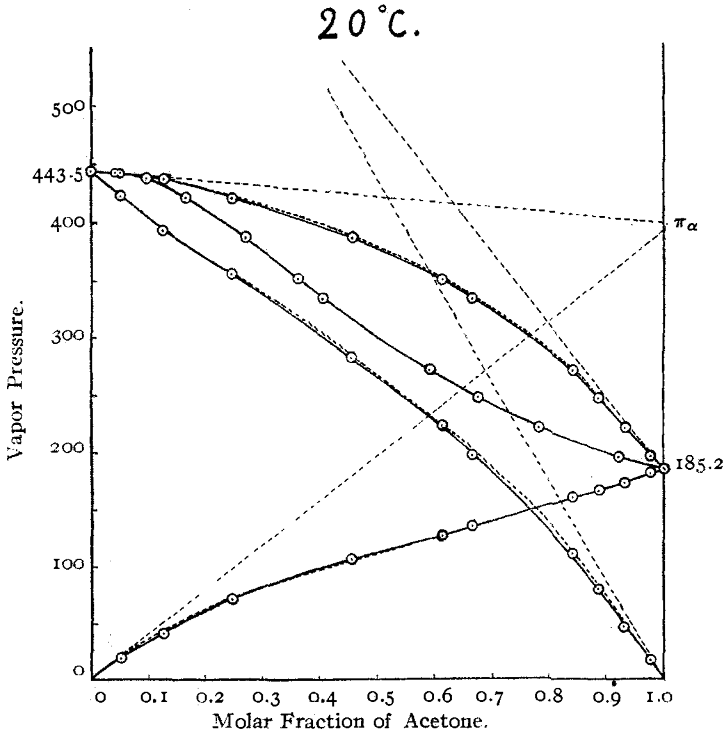

Fig. 4.

III. Theoretical Discussion.

Molar Fractions and Vapor Pressures.

The following two assumptions are made in the discussion which follows:

1. The system acetone-ethyl ether is a quasi-ideal solution, *i. e.*, a solution in which reversible chemical reactions take place, but whose volume and energy are equal to the sum of the respective values of the component chemical species. Most of the pairs which are considered to form ideal solutions consist of components of allied chemical nature, as, for instance, in the case where both components are hydrocarbons of the same homologous series, or halogen substituted hydrocarbons of the same type, etc. If such a system had components of the same type of constitution, and in addition to this, one of the components was associated while the other was normal, then it would be one of the most favorable examples for applying the theory of quasi-ideal solutions suggested by Ikeda. Unfortunately, however, we cannot find such an example. In the acetone-ether system, nevertheless, the constitutions of the components are not altogether dissimilar; hence, to consider the system as a quasi-ideal solution is not very unreasonable.

2. The polymer of acetone has only one type, $(C_3H_6O)_\nu$, and a reaction,

$$\nu C_3H_6O \rightleftarrows (C_3H_6O)_\nu,$$

takes place in the system. Organic compounds of the aldehyde or ketone type are readily polymerizable. For example, the system acetaldehyde-paraldehyde was studied by Hollmann[1] and it has been established beyond doubt that there takes place only a reaction represented by

$$\underset{\text{Acetaldehyde.}}{3C_2H_4O} \rightleftarrows \underset{\text{Paraldehyde.}}{C_6H_{12}O_3}.$$

Therefore, in acetone it is not improbable that there is only one chief chemical reaction which we have to consider in the study of this system.

According to these two assumptions, we have the following relations:

$$K = C_\alpha^\nu / C_\beta \tag{1}$$

and

$$C_\alpha + C_\beta + C = 1 \tag{2}$$

where K = the equilibrium coefficient of the reaction

$$\nu C_3H_6O \rightleftarrows (C_3H_6O)_\nu,$$

C_α = actual molar fraction of C_3H_6O.
C_β = actual molar fraction of $(C_3H_6O)_\nu$.
C = actual molar fraction of ether.

Now let x be the empirical molar fraction of acetone, then $1 - x$ is the empirical molar fraction of ether. The relation between these two sorts of molar fractions is expressed by the following equation:

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[1] Hollmann, *Z. phys. Chem.*, 43, 129 (1903).

$$x = \frac{C_\alpha + \nu C_\beta}{C_\alpha + \nu C_\beta + C} = \frac{C_\alpha + \nu C_\beta}{1 + (\nu - 1)C_\beta} \tag{3}$$

At a constant temperature K is constant and we have

$$x = \frac{C_\alpha + \nu C_\alpha^\nu / K}{1 + (\nu - 1)C_\alpha^\nu / K} = \frac{K^{1/\nu} C_\beta^{1/\nu} + \nu C_\beta}{1 + (\nu - 1)C_\beta}, \tag{4}$$

while for the molar fraction of ether, we get from (2) and (3)

$$C = \left\{1 + (\nu - 1)C_\beta\right\}(1 - x). \tag{5}$$

We shall consider the graphical representations. From (4) we get, by differentiation,

$$\frac{dC_\alpha}{dx} = \frac{\left\{1 + (\nu - 1)\, C_\beta\right\}^2}{1 - (\nu - 1)^2 C_\beta + \nu^2 C_\beta / C_\alpha}.$$

At $x = 0$ and $x = 1$ it becomes

$$\left(\frac{dC_\alpha}{dx}\right)_{x=0} = 1, \quad \left(\frac{dC_\alpha}{dx}\right)_{x=0} = (C_\alpha)_{x=1},$$

respectively. $(C_\alpha)_{x=1}$ denotes the molar fraction of the simple molecule C_3H_6O in acetone in pure state. In the same manner we have

$$\frac{dC_\beta}{dx} = \frac{\left\{1 + (\nu - 1)C_\beta\right\}^2}{\nu + (C_\alpha / \nu C_\beta) - ((\nu - 1)^2 C_\alpha / \nu)}.$$

Hence,

$$\left(\frac{dC_\beta}{dx}\right)_{x=0} = 0 \quad \text{and} \quad \left(\frac{dC_\beta}{dx}\right)_{x=1} = \nu (C_\beta)_{x=1}$$

where $(C_\beta)_{x=1}$ denotes the molar fraction of $(C_3H_6O)_\nu$ in acetone in pure state. Moreover, from (5) we have

$$\frac{dC}{dx} = (\nu - 1)(1 - x)\frac{dC_\beta}{dx} - \left\{1 + (\nu - 1)C_\beta\right\}.$$

Therefore

$$\left(\frac{dC}{dx}\right)_{x=0} = -1 \quad \text{and} \quad \left(\frac{dC}{dx}\right)_{x=1} = -\left\{1 + (\nu - 1)C_\beta\right\}.$$

Now there are the following relations:

$$\begin{aligned} p_\alpha &= C_\alpha \pi_\alpha \\ p_\beta &= C_\beta \pi_\beta \\ p &= C P_0 \end{aligned} \tag{6}$$

and

$$P = C_\alpha \pi_\alpha + C_\beta \pi_\beta + C P_0, \tag{7}$$

where p_α, p_β and p denote the partial pressures of C_3H_6O, $(C_3H_6O)_\nu$ and ether, respectively, in the gas phase, which is in equilibrium with the solution consisting of these chemical species, and π_α, π_β and P_0 denote the vapor pressures of C_3H_6O, $(C_3H_6O)_\nu$ and ether, respectively, when these chemical species exist in pure state. P is the total pressure. (6) is differentiated by x, then

$$\frac{dp_\alpha}{dx} = \frac{dC_\alpha}{dx}\pi_\alpha$$

and

$$\left(\frac{dp_\alpha}{dx}\right)_{x=0} = \pi_\alpha.$$

Therefore, we can know the value π_α by producing the tangent at $x = 0$ to the curve of p_α so as to meet the pressure axis at $x = 1$. The height of the point of intersection is equal to π_α.

On the other hand, the tangent to the total pressure curve may be expressed as follows:

$$\frac{dP}{dx} = \pi_\alpha\frac{dC_\alpha}{dx} + \pi_\beta\frac{dC_\beta}{dx} + P_0\frac{dC}{dx},$$

hence,

$$\left(\frac{dP}{dx}\right)_{x=0} = \pi_\alpha - P_0.$$

In other words, the tangent to the total pressure curve at $x = 0$ intersects the pressure axis at $x = 1$ at the height of π_α.

By these two methods, we have from Figs. 3 and 4

$$\pi_\alpha = 585 \text{ mm. at } 30^\circ$$

and

$$\pi_\alpha = 396 \text{ mm. at } 20^\circ.$$

From the data in Tables VI and VII, the following values of C, C_α and C_β have been obtained by means of Equations 6 and 2:

TABLE VIII.

Molar Compositions of Acetone–Ether System at 30°.

Empirical molar fraction of acetone. x.	Ether. C.	C_3H_6O. C_α.	$(C_3H_6O)_\nu$. C_β.
0	1.0	0	0
0.0387	0.9652	0.0373	0
0.1327	0.8836	0.1132	0.0032
0.2509	0.7898	0.1824	0.0278
0.3454	0.7193	0.2263	0.0544
0.4958	0.6042	0.2863	0.1095
0.6507	0.4667	0.3439	0.1894
0.7047	0.4118	0.3653	0.2229
0.8381	0.2577	0.4156	0.3267
0.9337	0.1099	0.4561	0.4340
0.9528	0.0856	0.4627	0.4517
0.9799	0.0322	0.4728	0.4950
1.0	0	0.4832	0.5168

TABLE IX.

Molar Compositions of Acetone-Ether System at 20°.

Empirical molar fraction of acetone. x.	Ether. C.	C_3H_6O. C_α.	$(C_3H_6O)_\nu$. C_β.
0	1.0	0	0
0.0520	0.9520	0.0495	0
0.1271	0.8886	0.1056	0.0058
0.2490	0.7903	0.1773	0.0324
0.4570	0.6354	0.2657	0.0989
0.6121	0.5060	0.3202	0.1738
0.6662	0.4483	0.3414	0.2103
0.8416	0.2505	0.4053	0.3442
0.8883	0.1797	0.4240	0.3963
0.9317	0.1089	0.4407	0.4504
0.9358	0.1044	0.4419	0.4537
0.9790	0.0347	0.4581	0.5072
0.9959	0.0041	0.4649	0.5310
1.0	0.0	0.4677	0.5323

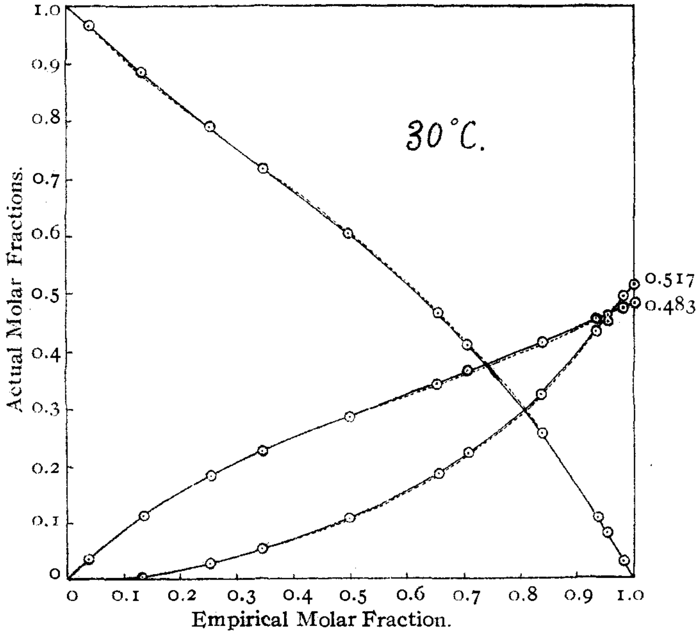

Fig. 5.

These relations are shown in Figs. 5 and 6 marked with circlets. If we use triangular coördinates, we can represent the curves of all temperatures by a single diagram, as shown in Fig. 7.

Now in the reaction

$$\nu C_3H_6O \rightleftarrows (C_3H_6O)_\nu$$

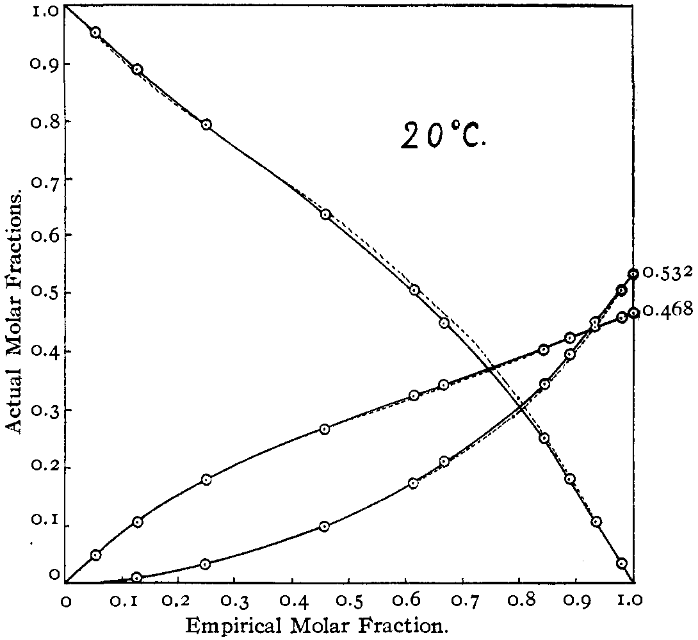
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Actual Molar Fractions.
20°C.
0.532
0.468
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
Empirical Molar Fraction.

Fig. 6.

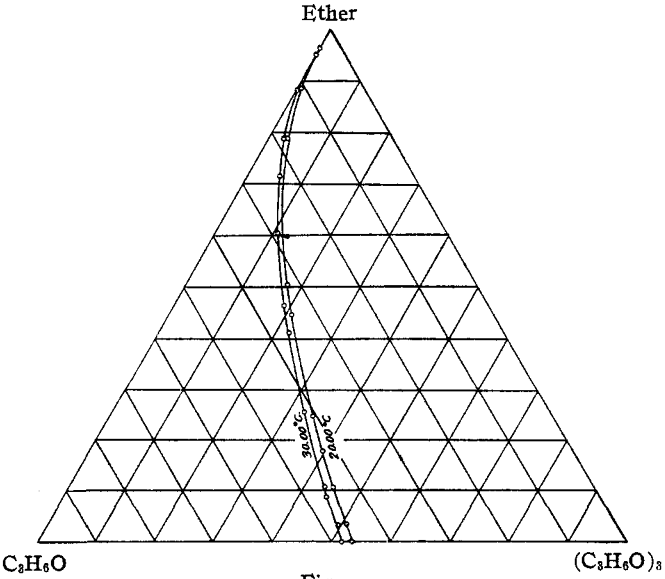
Ether
30.00°C.
20.00°C.
C_3H_6O
$(C_3H_6O)_3$

Fig. 7.

the value of ν can be determined by the following manner. (6) is differentiated with respect to x, thus:

$$\left(\frac{dp}{dx}\right) = P_0\left(\frac{dC}{dx}\right)_{x=1} = -\left\{1 + (\nu - 1)(1 - (C_\alpha)_{x=1})\right\}P_0$$

or

$$\nu = \frac{(-(dp/dx)_{x=1}/P_0) - 1}{1 - (C_\alpha)_{x=1}} + 1.$$

Or, there is another method to determine ν. There are the relations

$$(P)_{x=1} = \pi_\alpha(C_\alpha)_{x=1} + \pi_\alpha(1 - (C_\alpha)_{x=1}),$$

and

$$\left(\frac{dP}{dx}\right)_{x=1} = \pi_\alpha\,(C_\alpha)_{x=1} + \pi_\beta\,\nu(C_\beta)_{x=1} + P_0\left(\frac{dC}{dx}\right)_{x=1}.$$

The value of π_β, *i. e.*, the vapor pressure of $(C_3H_6O)_\nu$ is negligibly small, as we already know, by vapor-density measurements. Hence,

$$\left(\frac{dP}{dx}\right)_{x=1} = (P)_{x=1} - \left\{1 + (\nu - 1)(1 - (C_\alpha)_{x=1})\right\}P_0$$

or

$$\nu = \frac{([(P)_{x=1} - (dP/dx)_{x=1}]/P_0) - 1}{1 - (C_\alpha)_{x=1}} + 1,$$

where $(P)_{x=1}$ denotes the total pressure at $x = 1$. $(dp/dx)_{x=1}$ is the trigonometrical tangent of the angle subtended at $x = 1$ by the curve for p and the axis of x. $(dP/dx)_{x=1}$ is the same with respect to the curve for P. The following data were obtained from Tables VI and VIII and Fig. 3, the temperature being 30°:

$$\left(\frac{dp}{dx}\right)_{x=1} \approx -1340$$

$$P_0 = 646.0$$

$$(C_\alpha)_{x=1} = 0.4832$$

$$(P)_{x=1} = 282.7$$

$$\left(\frac{dP}{dx}\right)_{x=1} \approx -1050.$$

Therefore,

$$\nu = 3.05$$

or

$$\nu = 3.07.$$

At 20°:

$$\left(\frac{dp}{dx}\right)_{x=1} \approx -886$$

$$P_0 = 443.5$$

$$(C_\alpha)_{x=1} = 0.4677$$

$$(P)_{x=1} = 185.2$$

$$\left(\frac{dP}{dx}\right)_{x=1} \cong -656.$$

and

$$\nu = 2.87$$

or

$$\nu = 2.69.$$

It is most probable that $\nu = 3$. Accordingly, at least the chief reaction which takes place in this system must be

$$3C_3H_6O \rightleftarrows (C_3H_6O)_3.$$

Now the former equations pass into:

$$K = \frac{C_\alpha^3}{C_\beta} = \frac{(C_\alpha)^3_{x=1}}{1 - (C_\alpha)_{x=1}} \tag{8}$$

$$x = \frac{C_\alpha + 3\,C_\alpha^3/K}{1 + 2\,C_\alpha^3/K} = \frac{K^{1/3}C_\beta^{1/3} + 3C_\beta}{1 + 2C_\beta} \tag{9}$$

and

$$C = (1 + 2C_\beta)(1 - x), \tag{10}$$

respectively.

We can calculate p, p_α, C, C_α, and C_β from the values of P_0, π_α, $(C_\alpha)_{x=1}$ and the above several equations. From Equation 6 we arrive at

$$C_\alpha = p_\alpha/\pi_\alpha$$

and this value of C_α substituted in (9), then we have

$$x = \frac{p_\alpha/\pi_\alpha + 3/K\,(p_\alpha/\pi_\alpha)^3}{1 + 2/K\,(p_\alpha/\pi_\alpha)^3}$$

This is solved for p_α, whence

$$p_\alpha = \left\{\frac{-\pi_\alpha^3 xK}{2(2x-3)} + \sqrt{\frac{K^2\pi_\alpha^6x^2}{4(2x-3)^2} - \frac{K^3\pi_\alpha^6}{27(2x-3)^3}}\right\}^{1/3} + \left\{\frac{-K\pi_\alpha^3x}{2(2x-3)} - \sqrt{\frac{K^2\pi_\alpha^6x^2}{4(2x-3)^2} - \frac{K^3\pi_\alpha^6}{27(2x-3)^3}}\right\}^{1/3}.$$

The value of p_α, *i. e.*, the partial pressure of acetone corresponding to every amount of x, can be calculated by this equation, K and π_α being known. As the values of C_β and P we have

$$C_\beta = \left[\left\{\frac{x}{6-4x} + \sqrt{\left(\frac{x}{6-4x}\right)^2 + \frac{K}{(9-6x)^3}}\right\}^{1/3} + \left\{\frac{x}{6-4x} - \left(\frac{x}{6-4x}\right)^2 + \frac{K}{(9-6x)^3}\right\}^{1/3}\right]^3$$

and

$$p = CP_0 = P_0(1 + 2C_\beta)(1 - x),$$

respectively. Then C and C_α are readily calculated by (6).

In the above manner we can calculate the partial pressures of ether and acetone, and the actual molar fractions of 3 chemical species corresponding to every value of empirical molar fractions. The results thus obtained are shown in the next tables and by the dotted curves in Figs. 3, 4, 5 and 6.

TABLE X.

Molar Compositions at 30°.

$\pi_\alpha = 585.$ $K = 0.2184.$ $P_\circ = 646.0.$

Empirical molar fraction of acetone. x.	Partial pressure of acetone. p_α.	Molar fr. of $(C_3H_6O)_3$. C_β.	Partial pressure of ether. p.	Molar fr. of C_3H_6O. C_α.	Molar fr. of ether. C.	Total pressure. $P(=p_\alpha+p)$.
0.1	52.9	0.0034	585.4	0.0905	0.9061	638.3
0.3	120.0	0.0395	488.0	0.2051	0.7553	608.0
0.5	167.3	0.1070	392.1	0.2859	0.6070	559.4
0.7	210.3	0.2128	276.3	0.3595	0.4277	486.6
0.9	256.3	0.3849	114.3	0.4381	0.1770	370.6

TABLE XI.

Molar Compositions at 20°.

$\pi_\alpha = 396.$ $K = 0.1922.$ $P_\circ = 443.5.$

x.	p_α.	C_β.	p.	C_α.	C.	P.
0.1	35.5	0.0037	402.1	0.0895	0.9067	437.6
0.3	79.2	0.0416	336.3	0.2000	0.7583	415.5
0.5	109.9	0.1113	271.1	0.2775	0.6112	381.0
0.7	137.9	0.2198	191.6	0.3483	0.4319	329.5
0.9	167.9	0.3967	79.5	0.4240	0.1793	247.4

Heat of Dissociation.

The heat of dissociation may be calculated simply from the values of K at 20° and 30°, which are directly obtained from Figs. 3 and 4. But in this case the difference in temperature is only 10 degrees and the difference in K is also comparatively small. Since we cannot get reliable results from these data, I used the following more complicated mode of calculation:

The variation of π_α with the temperature is given by the equation of Clapeyron-Clausius,

$$\frac{\partial \ln \pi_\alpha}{\partial T} = \frac{l}{RT^2},$$

where l denotes the latent heat of evaporation of one mol of C_3H_6O. On the assumption that l will be independent of temperature, we have by integration

$$\ln \pi_\alpha = \frac{l}{R}\left(\frac{1}{\tau} - \frac{1}{T}\right),$$

where τ is the hypothetical absolute boiling point of pure C_3H_6O under the pressure of one atmosphere. The atmospheric pressure is taken as the unit of vapor pressure, then we have by Trouton's rule

$$l/R\tau = 10.9$$

hence,

$$ln\ \pi_\alpha/760 = 10.9\ (1 - \tau/T).$$

The value of π_α at 30° is substituted in this equation, and we have $\tau = 310.3$, while from the value at 20° $\tau = 310.5$. The mean value is

$$\tau = 310.4.$$

The hypothetical vapor pressure of the simple molecules of acetone at various temperatures can then be represented by

$$\pi_\alpha = 760e^{10.9(1-310.4/T)}$$

The value of π_α in the following table was calculated by this equation.

Table XII.

$T - 273$.	Vapor pressure of pure C_3H_6O. π_α.	Vapor pressure of pure acetone. $(p_\alpha)_{x=1}$ (observed).	Molar fr. of C_3H_6O in pure acetone. $(C_\alpha)_{x=1}$.	Equilibrium coeff. K.
20.00	397.8	184.8	0.4655	0.1872
30.00	582.4	282.7	0.4854	0.2223
40.00	832.0	421.5	0.5066	0.2636
50.00	1162.7	612.5	0.5268	0.3089

Using the observed values of $(p_\alpha)_{x=1}$ which were already shown in Table V, we can readily calculate $(C_\alpha)_{x=1}$ and then K.

The variation of K with temperature is expressed thus:

$$\frac{\partial\ ln\ K}{\partial T} = \frac{Q}{RT^2},$$

where Q is the heat of dissociation for one mol of C_3H_6O. By integration we have

$$ln\ K = Q/R\ (1/T - 1/T),$$

where T is so-called equipoise temperature, *i. e.*, the temperature at which K becomes unity. From the data of K at 20° and 40° we have $Q = 3115$ calories and $T = 426.4$. From that at 30° and 50° $Q = 3196$ calories and $T = 422.6$. The mean value is $Q = 3156$ calories.

This is the amount of heat which is absorbed when one mol of $(C_3H_6O)_3$ dissociates into 3 mols of C_3H_6O. For the mean equipoise temperature we have $T = 424.5°$. From these values we can easily calculate K, $(C_\alpha)_{x=1}$ and $(p_\alpha)_{x=1}$ at every temperature.

Table XIII.

Temp. $T - 273$.	Equilibrium coeff. K.	Molar fraction of C_3H_6O in pure acetone. $(C_\alpha)_{x=1}$.	Vapor pressure of pure acetone. $(p_\alpha)_{x=1}$ (calc.).	$(p_\alpha)_{x=1}$ (obs.).
10	0.1538	0.4412	119.5	115.6
20	0.1862	0.4639	184.5	184.8
25	0.2040	0.4749	229.4	229.2
30	0.2228	0.4857	282.8	282.7
37.4 ($T = 310.4$)	0.2524	0.5012	380.9	...
40	0.2634	0.5065	421.4	421.5
50	0.3083	0.5265	612.2	612.5

Heat of Evaporation.

The heat of evaporation for one mol of vapor at the boiling point of C_3H_6O has been expressed as

$$L = \frac{1 - (C_\alpha)_{x=1}}{\xi} Q + l,$$

where L = the apparent molecular heat of evaporation,

ξ = the degree of association which is represented by the equation

$$\xi = 3 - (3 - 1)(C_\alpha)_{x=1}.$$

At the temperature τ or 310.4° it becomes $L_\tau = 788 + 6716 = 7504$ calories. The true heat of evaporation of one mol of C_3H_6O is 6716 calories, while the heat of dissociation which is evolved on vaporization is 788 calories.

The calculations according to the equation

$$L = \frac{R(ln\ p_{\alpha_1} - ln\ p_{\alpha_2})}{1/T_2 - 1/T_1}$$

give the following results:

TABLE XIV.

$T_1 - 273$.	$T_2 - 273$.	L.
10	20	7722
20	30	7492
30	40	7519
40	50	7500

Wirtz (1890) determined the heat of evaporation of acetone at its boiling point and obtained the value $L = 7274$ calories.

Heat of Mixing.

Let q be the heat of mixing of one empirical mol of solution, *i. e.*, q calorie of heat is absorbed when

$$\frac{C}{3C_\beta + C_\alpha + C}$$

mol of ether is mixed with

$$\frac{3C_\beta + C_\alpha}{3C_\beta + C_\alpha + C}$$

mol of acetone. In one empirical mol of solution, there is

$$\frac{C_\beta}{3C_\beta + C_\alpha + C}$$

mol of $(C_3H_6O)_3$; and in

$$\frac{3C_\beta + C_\alpha}{3C_\beta + C_\alpha + C}$$

mol of pure acetone, there is

$$\left\{\frac{3C_\beta + C_\alpha}{3C_\beta + C_\alpha + C}\right\} \left\{\frac{1 - (C_\alpha)_{x=1}}{(C_\alpha)_{x=1} + 3(1 - (C_\alpha)_{x=1})}\right\}$$

mol of the polymer. Hence,

$$q = Q\left[\frac{(3C_\beta + C_\alpha)(1 - (C_\alpha)_{x=1})}{(3C_\beta + C_\alpha + C)\{(C_\alpha)_{x=1} + 3(1 - (C_\alpha)_{x=1})\}} - \frac{C_\beta}{3C_\beta + C_\alpha + C}\right].$$

In (2) we have the equation

$$C_\alpha + C_\beta + \mathrm{C} = 1,$$

and from (8) and (9)

$$K = \frac{C_\alpha^3}{C_\beta} = \frac{(x + 2C_\beta x - 3C_\beta)^3}{C_\beta} = \frac{(C_\alpha)^3_{x=1}}{1 - (C_\alpha)_{x=1}}.$$

Hence it follows that

$$q = Q\left\{\frac{1 - (C_\alpha)_{x=1}}{3 - 2(C_\alpha)_{x=1}}\, x - \frac{C_\beta}{2C_\beta + 1}\right\}.$$

Therefore, if we know $(C_\alpha)_{x=1}$ (or K) and Q we can calculate q corresponding to every value of x by means of the above equations. From Table XIII we have at 25°

$$(C_\alpha)_{x=1} = 0.4749, \text{ and } Q = 3156,$$

and the results are

TABLE XV.

Heat of Mixing of Acetone and Ether at 25°.

Molar fraction of acetone.	Heat of mixing. Calories.	
	q (calc.).	q (obs.).
0.1155	77.4	59.6
0.2068	109.0	91.9
0.2943	123.2	110.2
0.4998	121.2	120.7
0.7270	82.8	92.0
0.8295	56.1	61.6
0.9077	32.3	37.9

q (obs.) in this table being determined by H. Hirobe[1] with an isothermal calorimeter.

Volume Contraction.

Let Δv = the volume contraction on mixing for one empirical mol of solution.

V_1 = the molecular volume of C_3H_6O.

V_2 = the molecular volume of $(C_3H_6O)_3$.

Then the volume contracts by the amount $(V_2 - 3V_1)$ when one mol of $(C_3H_6O)_3$ dissociates into 3 mols of C_3H_6O.

Consequently

$$\Delta v = (V_2 - 3V_1)\left\{\frac{1 - (C_\alpha)_{x=1}}{3 - 2(C_\alpha)_{x=1}}\, x - \frac{C_\beta}{2C_\beta + 1}\right\}.$$

The volume of one empirical mol of acetone is expressed by

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[1] This investigation has not yet been published.

$$V = \frac{V_1(C_\alpha)_{x=1} + \{1 - (C_\alpha)_{x=1}\}V_2}{(C_\alpha)_{x=1} + 3\{1 - (C_\alpha)_{x=1}\}}.$$

Since if we know the amount of Δv at one point of composition, we can calculate $(V_2 - 3V_1)$ provided $(C_\alpha)_{x=1}$ and K are known. Furthermore, V_1 and V_2 are easily ascertained, because V is directly measured by a pycnometer, and Δv is calculated at every value of x.

We find by direct measurement that

$$\Delta v = 0.175 \text{ cc. at } x = 0.5.$$

Hence,

$$V_2 - 3V_1 = 4.56,$$

and thus:

TABLE XVI.

Volume Contraction on Mixing Acetone and Ether at 25°.

Molar fraction of acetone. x.	Molecular volume contraction. Cc.	
	Δv (calc.).	Δv (obs.).
0.2	0.155	0.104
0.4	0.183	0.168
0.5	(0.175)	0.175
0.6	0.156	0.171
0.8	0.093	0.120

The molecular volume of acetone has been measured and found to be $V = 73.8835$, from which we have $V_1 = 72.7$ and $V_2 = 222.7$, or the specific volumes of C_3H_6O and $(C_3H_6O)_3$ are 1.253 and 1.279, respectively.

Summary.

1. A new apparatus for vapor-density measurement has been described and the molecular weights of ethyl ether and acetone in the vapor state have been determined by this apparatus.

2. A new method for measurement of the vapor pressure of binary mixtures has been described. The total and partial vapor pressures of mixtures of acetone and ethyl ether at 20° and 30° were measured and the vapor pressures of pure acetone at various temperatures were also determined.

3. The chemical action which takes place in the mixed liquid of acetone and ether was studied, and it was found that the reaction

$$3C_3H_6O \rightleftarrows (C_3H_6O)_3$$

takes place in acetone in the liquid state.

4. Many characteristic constants of the reaction were determined. The vapor pressures of the acetone-ether system, those of pure acetone at various temperatures, the evaporation heat of acetone, the heat of mixing of acetone and ether, and the volume contraction on mixing these two substances were calculated by means of these characteristic constants,

and the results were compared with the values directly observed. The agreement is sufficiently good to indicate that these constants may now be considered as fairly well known, and affords striking support to Professor Ikeda's considerations concerning quasi-ideal solutions.

The present study was carried out under the kind guidance of Professor K. Ikeda, to whom my best thanks are due. Moreover, I express my thanks to Professor T. W. Richards for his valuable suggestions.

TOKYO, JAPAN.

[CONTRIBUTION FROM THE CHEMICAL INSTITUTE OF THE SCIENCE COLLEGE, IMPERIAL UNIVERSITY OF TOKYO.]

ON THE SYSTEM BENZENE-CARBONDISULFIDE.

BY JITSUSABURO SAMESHIMA.

Received April 9, 1918.

There are a great many cases in which solutions do not obey the criteria of ideal solutions, even when both components are considered to be normal substances and no chemical reaction takes place between them. When a solution is ideal no heat and volume changes occur on mixing. Furthermore, the vapor pressure of the solution should be equal to the sum of the partial vapor pressures of both components, which is calculated as the product of the molar fraction of the component in solution and the vapor pressure of that component in pure state. But in actual cases, most solutions deviate more or less from the above conditions. In order to discover whether there is any relation between the total energy change and free energy change occurring on mixing, I have carried out the vapor pressure measurement of binary mixtures.

Materials.

Benzene.—Chemically pure material from Merck was dehydrated over calcium chloride and frozen twice. The substance thus obtained had the melting point 5.4–5.5°. By fractionation it gave the boiling point 80.05–80.08° under 760 mm. pressure. The specific gravity was 0.87345 at 25°.

Carbondisulfide.—Commercially pure material was allowed to stand over calcium oxide and then distilled. The distillate was well shaken with potassium permanganate powder, and decanted over metallic mercury and mercuric sulfate and again well shaken. Finally, it was fractionated over metallic mercury. The boiling point was 46.27–46.31° under 760 mm. pressure, and the specific gravity was 1.25585 at 25°.

Vapor Pressures.

The method of vapor-pressure measurement was the same as described in the previous paper. The vapor pressures of the mixtures of benzene and carbondisulfide were as follows: