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WORCESTER, MASSACHUSETTS

[CONTRIBUTION FROM THE LABORATORIES OF GENERAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

A STUDY OF THE TERNARY SYSTEM, TOLUENE-ACETONE-WATER

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Toluene and acetone are miscible in all proportions, as are also acetone and water. Water and toluene, however, are practically insoluble in each other. This investigation was undertaken for the purpose of determining the solubility curve for these three compounds.

Reagents.—Acetone was dried over calcium chloride and fractionated, the fraction distilling between 56.05° and 56.16° at 760 mm. being used.

The toluene was dried over sodium, distilled and fractionated. The fraction boiling between 110.65° and 110.75° at 760 mm. was collected.

The water used was a high grade of conductivity water.

Apparatus and Method.—The pipets, burets and flasks were carefully calibrated with air-free water and the pipet also with toluene.

The apparatus in which the determinations were made is shown in Fig. 1. A is a 20 × 2.5cm. test-tube in which the liquids were mixed; P and P′ are two capillary delivery tubes, leading from the burets B and B′ containing the acetone and one of the other liquids. The method of making a determination was as follows. A definite amount, usually 10 cc., of either water or toluene was pipetted into the test-tube, which was then immediately stoppered, placed in the thermostat and allowed to stand for 15 minutes to come to the temperature of the bath. A small amount of the immiscible liquid, 0.2 to 0.5 cc., was then slowly added, the mixture vigorously stirred by means of the motor stirrer and acetone run in slowly, until the solution just cleared. The volumes of the liquids were then read and the temperatures of the burets noted. A new portion of the immiscible liquid was then added, and the process repeated. This was continued until the test-tube was about $^2/_3$ full, when another run was made in exactly the same manner, starting with the other immiscible liquid in the test-tube. This was found necessary because of the small solubility of one liquid in the other in the presence of a small percentage of acetone.

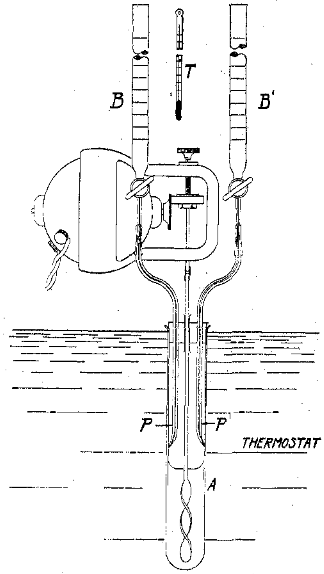

Fig. 1.—Apparatus used for solubility determinations

In order to obtain satisfactory determinations of the parts of the curves where there is only a small percentage of one component in the other (toluene in water, for example), it was found necessary to make a solution of this component in acetone, so that the volumes could be more accurately measured. For this purpose, a 20% solution in acetone was found convenient. The solution was made by weighing 20 cc. of the toluene into a 100cc. flask, filling to the mark with acetone and weighing again.

Because of the high coefficient of expansion of acetone, about 1.00145 per degree at 30°, great care was necessary to control the temperature of the solution. The flask was allowed to come to constant temperature in a thermostat for 15 minutes before it was finally made up to the mark. This solution, which was used in the buret instead of pure liquid, permitted accurate determinations down to about 0.05 cc. of one component in 10 cc. of the other.

The temperature of the liquids in the burets was taken as the average of several readings of the thermometer "T" during the run, the fluctuations usually not being more than a fraction of a degree. The temperature of the liquid placed in the tube was noted at the time it was added from the pipet and its weight and the weights of the others were calculated from their densities at their respective temperatures.

The end-point was taken as the point at which a bright object placed behind the test-tube became sharply defined. It was very sharp between the range of from 5% to 40% of water and especially between 5% and 15% of water. Between the range 15% to 30% of water, the mixture had a very decided colloidal appearance at the end-point, this effect being at a maximum with 20% water. The end-point was very distinct through this whole range, half a drop of acetone being sufficient to change the mixture from a distinct silky appearance, when rapidly stirred, to a distinctly cloudy, but transparent solution. Before adding the half drop, the mixture slowly separated into two layers, but afterward no separation occurred even on prolonged standing. On further additions of successive portions of acetone, the milkiness gradually disappeared, 0.5 to 1 cc. being required to make it disappear entirely.

Data

Determinations were made at three temperatures: 0°, 20° and 30°. Four runs were made for each curve, first starting with 20 cc. of toluene in the tube and adding a 20% solution of water in acetone, and acetone, from the burets; second, with 10 cc. of toluene, adding water and acetone; third, with 10 cc. of water, adding acetone and toluene; and fourth, with 20 cc. of water, adding acetone and a 20% solution of toluene in acetone. These runs overlapped to some extent, the first extending from 0.5% water to 5% water, the second from 1.3% water to about 19%, the third from 17% water to 50% and the fourth from 47% water to about 80%. The parts of the curves overlapping checked very closely in all cases.

TABLE I

DATA FOR EQUILIBRIUM LINE BETWEEN THE ONE-LIQUID PHASE AND TWO-LIQUID PHASE SYSTEMS AT 0°

All percentages are by weight

% Water	% Toluene	% Acetone	% Water	% Toluene	% Acetone
0.5	70.3	29.2	15.0	17.5	67.5
1.0	60.0	39.0	20.0	13.6	66.4
1.5	53.3	45.2	25.0	10.1	64.9
2.0	48.6	49.4	30.0	7.1	62.9
2.5	44.9	52.6	34.6	5.0	60.4
3.0	41.6	55.4	37.4	4.0	58.8
4.0	36.8	59.2	41.0	3.0	56.0
5.0	33.2	61.8	45.6	2.0	52.4
7.0	28.1	64.9	48.8	1.5	49.7
10.0	23.0	67.0	53.5	1.0	45.5
13.0	19.4	67.6 (max.)	61.0	0.5	38.5

Duplicate determinations were made on all runs at 0° and 20°, but not at 30°. The results of the duplicates checked very well with one another in every case. The data are given in Tables I, II and III. The data in Table II are shown diagrammatically in Fig. 2. The curves plotted from the data in the other two tables are almost identical with the one in Fig. 2. The results in the tables are interpolated graphically to even percentages of water or toluene.

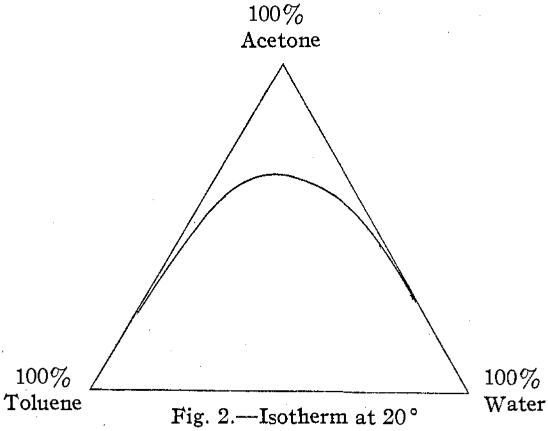

Fig. 2.—Isotherm at 20°

If the solubility surface in the composition temperature prism be drawn from the data of the three isotherms, it will be found that this surface rises abruptly from isotherm to isotherm. Temperature, therefore, has but little effect on the mutual solubility of the three components.

Attempts have been made by numerous authors to obtain mathematical expression for these curves,[1] but with only moderate success. If the

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[1] Bonner, *J. Phys. Chem.*, **14**, 738 (1910).

amounts of the two immiscible liquids soluble in a fixed amount of the consolute liquid are plotted against each other, a curve is secured which can be fairly well expressed by the equation, xy^n = const., in which x is the amount of one liquid, y the amount of the other and n a constant, depending upon the system and the temperature. This expression, however, is by no means exact. If we write the equation in logarithmic form, we have $\log x + n \log y = \log \text{const.}$ Differentiating we find, $d \log x + n\, d \log y = 0$; or,

TABLE II

DATA FOR EQUILIBRIUM LINE BETWEEN THE ONE-LIQUID PHASE AND TWO-LIQUID PHASE SYSTEMS AT 20°

% Water	% Toluene	% Acetone	% Water	% Toluene	% Acetone
0.5	76.0	23.5	15.0	19.0	66.0
1.0	68.9	33.1	20.0	14.9	65.1
1.5	58.5	40.0	25.0	11.5	63.5
2.0	53.6	44.4	30.0	8.5	61.5
2.5	49.4	48.1	35.0	6.0	59.0
3.0	45.9	51.1	37.6	5.0	57.4
4.0	40.6	55.4	40.5	4.0	55.5
5.0	36.6	58.4	43.8	3.0	53.2
7.0	30.6	62.4	48.3	2.0	49.7
10.0	25.0	65.0	52.1	1.5	46.4
14.2	19.8	66.0 (max.)	57.0	1.0	42.0
..	..	..	65.2	0.5	34.3

TABLE III

DATA FOR EQUILIBRIUM LINE BETWEEN THE ONE-LIQUID PHASE AND TWO-LIQUID PHASE SYSTEMS AT 30°

% Water	% Toluene	% Acetone	% Water	% Toluene	% Acetone
1.5	61.5	37.0	25.0	12.2	62.8
2.0	56.1	41.9	28.7	10.0	61.3
2.5	51.6	45.9	34.3	7.0	58.7
3.0	48.5	48.5	39.0	5.0	56.0
4.0	43.1	52.9	42.1	4.0	53.9
5.0	38.6	56.4	46.0	3.0	51.0
7.0	32.3	60.7	50.8	2.0	47.2
10.0	26.0	64.0	54.4	1.5	44.1
15.0	19.7	65.3	59.4	1.0	39.6
14.6	20.1	65.3 (max.)	68.3	0.5	31.2
20.0	15.5	64.5	71.5	0.4	28.1

$$\frac{d \log x}{d \log y} = -n$$

Plotting $\log x$ against $\log y$ should give a straight line, if n is a constant. As a matter of fact, for this system the line is distinctly curved. Plotting y as the amounts of toluene and x as the amounts of water for a given weight of acetone, the curve is concave toward the $\log x$ axis. Other formulas have been suggested but none of them fits the curves satisfactorily.

Summary

1. The isotherm curves for the system, water-toluene-acetone, have been experimentally determined at three temperatures, 0°, 20° and 30° An apparatus suitable for such determinations is described.

2. Temperature has but little effect on the mutual solubility of the three components.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF CLARK UNIVERSITY, NO. I, 30]

EQUILIBRIA IN SYSTEMS INVOLVING CALCIUM, HYDROGEN AND NITROGEN

BY CHARLES A. KRAUS AND CHARLES B. HURD

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The reactions of the more electropositive elements with hydrogen and with nitrogen and the interaction between the corresponding hydrides and nitrides, as well as the interaction of these compounds with nitrogen and hydrogen, possess considerable interest from the standpoint of the chemistry of nitrogen compounds. Up to the present time the available data are extremely meager. The present investigation was undertaken for the purpose of supplying further data in this field.

1. Action of Ammonia on Calcium and Barium Nitrides

Among the more recent and important investigations may be mentioned that of Mentrel,[1] who studied the reaction, $Ba(NH_2)_2 = Ba_3N_2 + 4NH_3$. He states that this reaction is reversible.

As is well known, calcium amide loses ammonia at higher temperatures and is ultimately converted to the nitride. Experiments were accordingly carried out in which the nitride was subjected to the action of ammonia in order to determine whether this reaction was reversible in the case of calcium.

Calcium amide was first prepared by treating the metal with liquid ammonia in a quartz tube in the presence of a trace of iron oxide, which served as catalyst. After vaporization of the excess ammonia, the resulting hexammoniate[2] was converted to the amide at temperatures slightly above that of the surroundings. The tube containing the amide was connected with a manometer, a vacuum pump, and a source of pure ammonia vapor. In a series of experiments, extending over a period of two months and at temperatures ranging from 200° to 850°, no indication of an equilibrium was observed. At higher temperatures, gradual decomposition of the amide took place with loss of ammonia and in the end there was left behind a yellow, porous material which consisted of calcium nitride.

[1] Mentrel, *Compt. rend.*, **135**, 740 (1902).

[2] Kraus, THIS JOURNAL, **30**, 653 (1908).