[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF VERMONT]

Equilibrium and Free Energy Relationships in the System Acetone–Diacetone Alcohol(1)

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The equilibrium between acetone and diacetone alcohol in aqueous solutions of varied concentrations, and the velocity of transformation of diacetone alcohol in 10% aqueous solution into acetone, have been carefully studied by Koelichen.(2)

Owing to the presence of solvent water in the experiments of Koelichen, his results cannot be used for the immediate calculation of the accompanying free energy change, referred to standard states.

In the present work, this same equilibrium has been determined at 25 and 45° in absence of water, and the appropriate vapor pressure measurements have been made.

Reagents

Acetone of tested purity was placed over anhydrous calcium chloride and subsequently carefully fractionated. The refractive index of the product was n^{25}_{D} 1.35668.

A commercial diacetone alcohol, and a sample prepared from pure acetone in this Laboratory, after fractionation under reduced pressure, each gave a product of refractive index n^{25}_{D} 1.42203.

Barium hydroxide, selected as catalyst because of its insolubility in the equilibrium mixture, was prepared from pure octahydrate. This was dehydrated, fused and ground to a coarse powder.

Experimental

Analyses of the equilibrium mixtures gained were made through their refractive indices, since the separate indices differ widely.

The indices of twelve synthetic mixtures of acetone and diacetone alcohol, varying in composition from zero to 100% of acetone, were determined and may be represented by the equation

$$n = 1.42166 - 0.00073416 \times \%\text{ acetone} + 0.0_5 84284 \times (\%\text{ acetone})^2$$

This equation was provided with coefficients by the method of least squares. The probable difference between an observed value of a refractive index and that computed by use of the equation is ±0.00011.

The temperatures of the mixtures as examined in the Pulfrich refractometer were maintained constant within 0.1°. Separately purified samples either of acetone or of diacetone alcohol gave identical readings.

In working with mixtures of these ingredients especial care was taken to avoid changes of composition through evaporation. Constancy of index over considerable periods of time gave evidence that appreciable change due to this cause did not occur during examination.

To attain equilibrium, acetone, diacetone alcohol or suitable mixtures of these, and catalyst, were sealed in Pyrex glass tubes and agitated in the thermostat, maintained constant within 0.05°. At intervals, the tubes were chilled quickly in ice water and placed in a centrifuge to clear the liquid mixture of catalyst. The liquid mixture was then analyzed, with the results shown in Table I.

TABLE I

Duration of heating, hrs.	Index	% acetone	% diacetone alcohol
	25°		
0.0	1.36562	84.38	15.62
1.5	1.36497	85.45	14.55
18.0	1.36333	88.27	11.73
48.0	1.36333	88.27	11.73
0.0	1.36320	88.50	11.50
24.0	1.36328	88.35	11.65
48.0	1.36333	88.27	11.73
	45°		
0.0	1.35668	100.00	0.00
4.0	1.35927	95.00	5.00
6.0	1.35954	94.50	5.50
0.0	1.36625	83.00	17.00
4.0	1.36026	93.50	6.50
6.0	1.35954	94.50	5.50

The equilibrium composition as we have determined it at 25° is close to that found by extrapolating to zero water concentration the values of Koelichen for 25.2°; we find 88.27% acetone as against an extrapolated value of between 88.2 and 88.4%.

Uncertainty as to the extent of deviation of the equilibrium mixture from the ideal solution led to vapor pressure measurements. The method was that of bubbling, using electrolytic gas as suggested by Pearce and Snow.(3) In the present work a copper coulometer replaced that of silver. The coulometer electrolyte was vigorously

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(2) Koelichen, *Z. physik. Chem.*, **33**, 129 (1900).

(3) Pearce and Snow, *J. Phys. Chem.*, **31**, 231 (1927).

stirred by use of carbon dioxide. The yield of electrolytic gas differed by not more than 0.1% from equivalence with the copper deposited.

The vapor pressure of pure acetone was measured largely as a check on the apparatus. Further measurements are those of pure diacetone alcohol and of acetone from the 25° equilibrium mixture. No attempt was made to measure directly the partial pressure of the diacetone alcohol above the equilibrium mixture, and this partial pressure was deemed negligible in the course of measuring the partial pressure of acetone. Indeed the refractometer showed no difference in index between the condensate from the 25° equilibrium mixture and pure acetone.

The results of the vapor pressure measurements are shown in Table II. The vapor pressure determinations of pure diacetone alcohol are here recorded, though not used in our calculations.

TABLE II

VAPOR PRESSURE OF PURE ACETONE AT 25°

Acetone, g.	Cu, g.	Bar., mm.	Pressure acetone, mm.
1.4546	2.4174	758.7	231.4
2.2101	3.6916	759.6	230.9
1.5497	2.5662	756.6	231.4
		Average	231.2

PARTIAL PRESSURE OF ACETONE FROM 25° EQUILIBRIUM MIXTURE

218.7	216.5	218.0
216.0	215.4	215.3
		Average 216.7

VAPOR PRESSURE OF PURE DIACETONE ALCOHOL

Temp., °C.	Pressure, mm.
25	1.68
25	1.72
25	1.65
	Average 1.68
35	3.14
35	3.22
	Average 3.18
45	4.57
45	4.53
	Average 4.55

Calculations

Expressed in terms of mole fractions, the equilibrium constant for the liquid state at 25°, from the data of Table I, and corresponding to the reaction

$$2CH_3COCH_3 = CH_3COHCH_2CH_2COCH_3$$

has the value 0.0714. Whence $\Delta F^\circ_{298} = -RT \ln K = 1570$ cal. This value of ΔF depends for its validity not only on the accuracy of the analysis of the liquid equilibrium mixture, but also on the assumption that the mixture forms an ideal solution.

This assumption is justified by the results of our vapor pressure measurements. From the mole fraction of acetone in the liquid equilibrium mixture at 25°, namely, 0.937, and our average value, 231.2 mm., of the vapor pressure of pure acetone, Raoult's law gives 216.7 mm. as the partial pressure of acetone above this mixture. This is identical with the average of the experimental determinations of the partial pressure of acetone above the equilibrium mixture. In this respect, then, the mixture is ideal in behavior.

Combination of our value of the free energy change of the reaction studied with the average of the values of the free energy of liquid acetone as given by Parks and Huffman,[4] namely, −37,120 cal., gives −72,700 cal. as the free energy of diacetone alcohol.

The equilibrium composition of the liquid mixture at 45°, as given in Table I, yields 0.030 as the constant at this temperature. This value of the equilibrium constant and that at 25° give as the heat of reaction $\Delta H = -8190$ cal.

The heats of combustion of acetone and of diacetone alcohol, given by Koelichen[2] and by the "International Critical Tables," respectively, are −860,100 and −427,000 cal. These thermochemical data give $\Delta H = 6100$ cal., which differs even in sign from our value. Here as frequently the thermochemical calculation involves the inaccuracy inherent in a small difference between large quantities.

Summary

Through equilibrium measurements, the free energy change and the heat of reaction accompanying the transformation of acetone into diacetone alcohol have been determined.

Measurements of the vapor pressure of pure acetone and of its partial pressure above the equilibrium mixture at 25° give evidence that the mixture forms a perfect solution, and confirm the validity of the free energy calculation.

The vapor pressure of diacetone alcohol at each of several temperatures has been measured.

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[4] Parks and Huffman, "Free Energies of Some Organic Compounds," The Chemical Catalog Co., New York, p. 162.