

deg.⁻¹ mole⁻¹. This value does not include the contribution due to nuclear spin.

We thank the Shell Development Company for donating the propylene used for these measurements and Dr. R. A. Ruehrwein for assistance with the experimental work.

Summary

The heat capacity of solid and liquid propylene has been measured from 14 to 226°K.

The melting and boiling points are 87.85 and 225.35°K., respectively. (0°C. = 273.10°K.)

The heats of fusion and vaporization were measured calorimetrically and were found to be 717.6 and 4402 cal./mole, respectively.

The vapor pressure of propylene was measured from 165.8 to 225.9°K. and the results have been represented by the equation

$$\log_{10} P_{(\text{inter. cm. Hg})} = -\frac{1196.9}{T} - 3.92 \times 10^{-3}T + 8.07544$$

The gas density of propylene was determined to

be 1.7461 grams per liter at 25.00°C. and 1 atmosphere.

The calorimetric data have been used to calculate the entropy of propylene gas and the value at the boiling point was found to be 59.93 cal. deg.⁻¹ mole⁻¹. The value calculated for this temperature from available molecular data is 61.0 ± 0.3 cal. deg.⁻¹ mole⁻¹. The entropy discrepancy is interpreted as due to random end for end orientation of CH₂=CH—CH₃ molecules in the crystal lattice.

It is concluded that unsymmetrically placed double bonds in otherwise symmetrical hydrocarbons will lead to a disordered arrangement in the crystal lattice and a suitable entropy correction should be made to the $\int C_p d \ln T$.

The most reliable value for the entropy of propylene gas at 298.1°K. and 1 atmosphere is 64.0 cal. deg.⁻¹ mole⁻¹, calculated from molecular data.

BERKELEY, CALIF.

RECEIVED MAY 29, 1939

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TORONTO]

The Vapor Pressure of Aqueous Solutions of Sulfuric Acid

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The growing importance of the isopiestic method of investigating the thermodynamic properties of aqueous solutions has emphasized the need for reliable standards. In their pioneer work in this field, Sinclair and Robinson¹ adopted potassium chloride as reference substance, but, more recently, Scatchard, Hamer and Wood² have selected sodium chloride for their standard curve. While sodium chloride is eminently suitable for the dilute range of concentration, it cannot be employed for solutions in which the activity of the water is less than 0.75; sulfuric acid would seem to be the obvious alternative to serve as standard when studying the more concentrated range. While the vapor pressure and e. m. f. data for sulfuric acid solutions are of high precision and are in satisfactory agreement up to 3 molal, the case is somewhat different for higher concentrations. The vapor pressure measurements of Collins³ (which are usually quoted in

the literature) are not of the highest accuracy, and, moreover, are in disagreement with the e. m. f. measurements. We have therefore measured the vapor pressure of sulfuric acid solutions at 25° for concentrations from 2 molal to 23 molal by the static method.

Experimental

The apparatus was similar to that of Gibson and Adams⁴; we may say at once that we can fully substantiate their claims as to its convenience and accuracy. Since it has been discussed adequately, no lengthy description is needed here; its essential feature is that it is possible to measure the vapor pressure of the solution, the vapor pressure of the pure solvent, and the differential vapor pressure lowering by a suitable manipulation of stopcocks (see Fig. 1 of ref. 4).

In our apparatus, the flasks, containing about 25 cc. of solution or solvent, were of approximately 75 cc. capacity, and were placed symmetrically with respect to regulator, heater and stirrer in a water-bath controlled to 0.01°. The internal diameter of the manometer tubing was 15 mm.; the heights of the manometer liquid were measured by comparing them through a telescope with a vertical plate glass scale, placed immediately in front of the two legs of

(1) D. A. Sinclair, *J. Phys. Chem.*, **37**, 495 (1933); R. A. Robinson and D. A. Sinclair, *THIS JOURNAL*, **56**, 1830 (1934).

(2) G. Scatchard, W. J. Hamer and S. E. Wood, *ibid.*, **60**, 3061 (1938).

(3) E. M. Collins, *J. Phys. Chem.*, **37**, 1191 (1933).

(4) R. E. Gibson and L. H. Adams, *THIS JOURNAL*, **56**, 2679 (1933).

the manometer. The scale had been ruled in millimeters by the dividing engine in the Physics Department of this University, and had been checked by a microscope comparator; interpolation to fractions of a millimeter was accomplished by means of the graticuled scale in the eye-piece of the telescope.

The manometer liquid in the earlier runs was butyl phthalate, which has been recommended by Gibson and Adams; we found it necessary to use the special grade supplied by Distillation Products if satisfactory results were to be obtained. Even when distilled into the manometer under high vacuum and shielded from contact with the air, however, it only could be used for about a week or so before it was necessary to replace it. In some later work, Cenco Hyvac pump oil (density at 25°, 0.895) was employed; this was first out-gassed in the vacuum pump, and was then transferred as quickly as possible to the manometer through a side neck, which was then sealed off; the oil was then refluxed in the manometer under high vacuum for several hours. It proved to be a stable and satisfactory manometer liquid, its principal disadvantages as compared with butyl phthalate being its greater viscosity and its somewhat hazier meniscus. Tests showed that both manometer liquids gave identical results (within the limit of error of the experiments) for the activity of the water in the solutions.

The most serious experimental difficulty in a static vapor pressure measurement is the removal of the residual air from the liquid. This was effected by freezing solution and solvent (as well as the solvent in the auxiliary flask⁴ W) while they were boiling under vacuum, the resulting residual pressure being 0.002 mm. or less as determined on the McLeod gage. The flasks were then shut off from the rest of the apparatus, the contents melted, and the whole procedure repeated four or five times. For water, sodium chloride solutions, and for sulfuric acid solutions less than 4 *m*, a mixture of chloroform and dry ice served as freezing mixture, for acid solutions stronger than 4 *m*, liquid air. After out-gassing, the apparatus was allowed to come to temperature equilibrium, and the vapor pressures of water and of solution as well as the differential lowering were followed for a period of from one to three days.

Although the inherent error of a reading is somewhat less than 0.1 mm. of manometer liquid, a fluctuation of bath temperature of 0.01° would cause a change in the vapor pressure of water of nearly twice this amount. However, by having solution and solvent flasks placed symmetrically in the bath, and by always having the contents of the two flasks of approximately the same heat capacity, one would hope that the vapor pressures of both solution and solvent would "hunt" together, and that this error would largely cancel in the ratio. The high reproducibility of the results would seem to show that this is the case. For example, in a series of measurements on a 39.55% by weight solution (6.671 *m*), one result recorded about two hours after the apparatus had been brought on temperature was: $P^0 =$

361.1, $P_1 = 207.4_5$, $\Delta P = 153.7_5$ where P^0 , P_1 and ΔP are the vapor pressure of water, the vapor pressure of solution, and the differential vapor pressure lowering, all expressed in mm. of pump oil. The activity of the water, given by

$$a_1 = 2P_1/(P^0 + P_1 + \Delta P) \quad (1)$$

is thus 0.5744. Twenty-four hours later, a measurement gave $P^0 = 360.1$, $P_1 = 206.7$, $\Delta P = 153.4$, $a_1 = 0.5740$. Thus a_1 only changed by 0.0004, although the individual readings changed by about a part in 300. The mean of all measurements for this run, as recorded in Table I, is $a_1 = 0.5743$ with a mean absolute deviation from the mean of 0.0002.

Chemicals and Analysis.—C. P. sulfuric acid (sp. gr. 1.84) was distilled under vacuum in an all-glass apparatus, the first and last fractions of the distillate being rejected; the final product was free from sulfite. From this acid solutions of desired strength were made up by dilution with a good grade of conductivity water. At the end of each experiment, the acid solutions were analyzed by gravimetric titration with recrystallized sodium bicarbonate which had been fused and cooled in an atmosphere of dry carbon dioxide; after heating to boiling, 0.05 *N* sulfuric acid and carbonate-free sodium hydroxide were used for back titration to obtain the final end-point with methyl red as indicator.⁵ Duplicate analyses agreed to 0.03% or better; in calculating the concentration, all weights were reduced to vacuum.

The sodium chloride was British Drug Houses "Analar"; the unsaturated solution used in one experiment was analyzed by evaporating it to dryness on a steam-bath and then heating to 600°.

Experimental Results

As a check on the apparatus and technique, a few preliminary measurements were carried out on sodium chloride solutions. At 25°, a 21.53% by weight solution gave $\Delta P/P^0 = 0.1801$; a saturated solution at 25° gave 0.2468, and at 20.28°, 0.2456. Gibson and Adams⁴ have studied sodium chloride solutions at 25° by a dynamic method; interpolation⁶ of their results gives for 21.53 weight per cent., 0.1804. By a slight extrapolation of their results to $x_2 = 0.2643$ (6.144 *m*), $\Delta P/P^0$ for the solution saturated at 25° is 0.2469; their result by the static method for the solution saturated at 20.28° is 0.2454. The agreement between our results and theirs in all three cases is satisfactory, and is within the apparent limit of error of either set of experiments. The results recorded in "International Critical Tables"

(5) T. W. Richards and C. R. Hoover, *THIS JOURNAL*, **37**, 95, 108 (1915).

(6) For the concentrations studied by Gibson and Adams, $\Delta P/x_2P^0$ is practically linear in x_2 , the weight fraction of the salt.

(based on unpublished work of Negus⁷) correspond to $a_1 = 0.1793$ for the 21.53% solution, and, by a slight extrapolation, to $a_1 = 0.2464$ for the solution saturated at 25°, the apparent uncertainty in both cases being ± 0.0005 .

Table I summarizes the results for sulfuric acid; the first column gives the weight fraction of the acid, the second the molality, and the third the mole fraction of the water defined by

$$X_1 = (x_1/18.016)/(x_1/18.016 + x_2/49.04) \quad (2)$$

where x_1 is the weight fraction of the water. The fourth column gives the mean observed value of a_1 , the activity of the water in the solution (see Eq. 1); as a rule the individual values of a_1 showed a mean absolute deviation from the mean of 0.0002 or less, although in a few cases the deviation was somewhat larger.

TABLE I
25°

x_2	m	X_1	a_1 obsd.	a_1 (II)	a_1 (III)
0.1583 ₅	1.918	0.9354	0.9174	0.9173	
.1800 ₅	2.239	.9254	.8995	.8994	
.2641 ₀	3.659	.8835	.8048	.8049	
.2702 ₅	3.776	.8802	.7964	.7963	
.2926 ₅	4.218	.8681	.7627	.7630	
.2956 ₀	4.279	.8663	.7586	.7585	
.2985 ₀	4.339	.8648	.7539	.7539	
.3267	4.947	.8487	.7062	.7070	
.3485	5.454	.8357	.6679	.6678	
.3639	5.833	.8263	.6379	.6382	
.3955	6.671	.8062	.5743	.5740	0.5740
.4251	7.540	.7863	.5110	.5112	.5110
.4512	8.383	.7680	.4542		.4545
.4797	9.400	.7470	.3934		.3932
.4985	10.13 ₅	.7325	.3537		.3533
.5242	11.23 ₅	.7119	.2993		.3007
.5551	12.72	.6857	.2404		.2406
.5973	15.12	.6473	.1667		.1667
.6695	20.65	.5733	.0720		.0718
.6894	22.63	.5509	.0538		.0538

For convenience in representation, two deviation functions were computed, defined by

$$0 < m < 8 \quad a_1 = 1 - 0.02678m - 0.00922m^2 + 0.000556m^3 + \delta_1 \quad (3)$$

$$0.52 < X_1 < 0.82 \quad a_1 = f_1 X_1 + \delta_2 \quad (4)$$

where $\log f_1 = -5.5254 + 11.422X_1 - 5.8966X_1^2$. These forms are, of course, entirely empirical, but have the advantage that the resulting δ_1 and δ_2 are everywhere less than 0.01, and consequently can be handled graphically; see Figs. 1 and 2. From our values, and from those computed from the vapor pressure data of Grollman

(7) "International Critical Tables," Vol. III, p. 297.

and Fraser⁸ and from the electromotive force measurements of Harned and Hamer⁹ for concentrations less than 3 molal, the smooth curves in the figures were drawn. From these again, with the aid of Eqs. 3 and 4, values of a_1 at round values of the molality for the dilute range (Table II) and at round values of the mole fraction of the water for the concentrated (Table III) were obtained. The interval in both tables is sufficiently fine to permit interpolation by the method of mean second differences¹⁰ and still obtain results numerically accurate to a unit or so in the fourth decimal place; this is illustrated in the last two columns of Table I, which give the values obtained by interpolation in Tables II and III.

TABLE II

m	a_1	m	a_1	m	a_1	m	a_1
0.5	0.9821	2.5	0.8838	4.5	0.7415	6.5	0.5868
1.0	.9620	3.0	.8514	5.0	.7030	7.0	.5497
1.5	.9389	3.5	.8164	5.5	.6642	7.5	.5140
2.0	.9129	4.0	.7795	6.0	.6252	8.0	.4798

TABLE III

X_1	a_1	X_1	a_1	X_1	a_1	X_1	a_1
0.52	0.0346	0.66	0.1892	0.72	0.3208	0.78	0.4912
.56	.0607	.68	.2285	.74	.3736	.80	.5542
.60	.0996	.70	.2724	.76	.4307	.82	.6183
.64	.1546						

Discussion

A glance at Fig. 1 will show that, where they overlap, our results are consistent with those of Grollman and Fraser, who used a Rayleigh gage, although the scattering of their points from the curve at their highest concentrations would seem somewhat greater than their apparent experimental error. Figure 1 also shows the results of Collins, obtained by an isoteniscope with mercury manometer (his Table II). He records his results only to the nearest 0.1 mm. in the more dilute solutions, so that the smoothed entries in his table might be in error by 0.0040; actually, the agreement with our results is a good deal closer. For solutions between 50 and 65% by weight, however, his results disagree with ours by as much as 0.008 in a_1 , and would be entirely off Fig. 2.

The position with respect to Harned and Hamer's electromotive force measurements (their Table II) is a curious one. Up to 3 m , the agreement with the vapor pressure data is excellent, the deviations corresponding to less than 0.05 mv.; at 5 and 7 m , however, the discrepancy is

(8) A. Grollman and J. C. W. Fraser, *THIS JOURNAL*, **47**, 712 (1925).

(9) H. S. Harned and W. J. Hamer, *ibid.*, **57**, 27 (1935).

(10) H. L. Rice, "Theory and Practice of Interpolation," or any standard text on the calculus of finite differences.

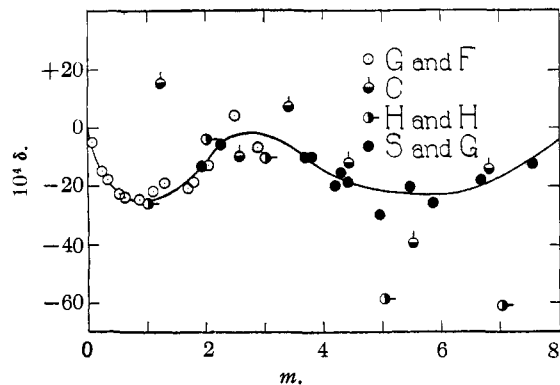


Fig. 1.

striking, and is several times their estimated experimental error. The discrepancy is also apparent if the activity coefficient of the acid be computed from the vapor pressure data (see Table IV) by means of the Gibbs relation¹¹

$$d \ln \gamma m = -(55.51/3m) \cdot d \ln a_1 \quad (5)$$

One is naturally hesitant to assert that the results of such a manifestly careful research as that of

TABLE IV

<i>m</i>	$V \gamma_p$	E. m. f. γ	<i>m</i>	$V \gamma_p$	E. m. f. γ
1	(0.130)	0.130	8	0.385	0.397
2	.125	.124	10	.557	.553
3	.141	.141	12	.763	.743
4	.168	.171	14	1.008	.969
6	.254	.264	16	1.288	1.235

Harned and Hamer are in error. However, when one considers the difficulties encountered in e. m. f. measurements in strong solutions, and the possibility that the cell reaction in such solutions is not that postulated, and then contrasts this with the simplicity and directness of a vapor pressure measurement, it would seem advisable on the whole to place considerable reliance on the vapor pressure data.

Recently, Scatchard, Hamer and Wood² have compared isopiesticly sodium chloride and sul-

(11) In effecting the integration of Eq. 5, Harned and Hamer's value of γ for $m = 1$ was adopted.

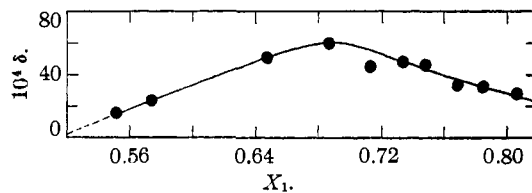


Fig. 2.

furic acid solutions. Up to 3 molal, values of a_1 , computed from the osmotic coefficients in their Table IIa, agree with our Table II within a unit or so in the fourth decimal place; for 3.5 and 4 m , their ϕ yield values of a_1 which are 0.0003 and 0.0014 less than the values in Table II. The isopiestic results will be discussed in detail in a forthcoming paper; it is sufficient for the moment to say that their isopiestic ratios of concentration are in satisfactory agreement with the results of similar measurements carried out in this Laboratory, and, moreover, are consistent with the measurements of Gibson and Adams and ourselves for sodium chloride and the results recorded here for sulfuric acid. We feel fairly confident that vapor pressures of sulfuric acid solutions at 25° may be obtained from our Tables II and III accurate to 0.01 mm. or better.

Summary

The vapor pressure of sulfuric acid solutions at 25° has been measured by the static method for concentrations ranging from 2 to 23 molal. The results are in good agreement with the vapor pressure measurements of Grollman and Fraser, and are consistent with the vapor pressure measurements of Collins up to 8 molal. They agree with the results of e. m. f. measurements up to 3 molal, but are in definite disagreement at higher concentrations.

Values of the activity of the water and of the activity coefficient of the acid in the solutions have been tabulated at round values of the concentration.