VOLUMES OF GASEOUS SOLUTIONS OF WATER IN ETHYLENE AT HIGH PRESSURES AND TEMPERATURES

1960

SovietRxiv

Abstract

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PHYSICAL CHEMISTRY

D. S. TSIKLIS, A. I. KULIKOVA, and L. I. SHENDEREI*

VOLUMES OF GASEOUS SOLUTIONS OF WATER IN ETHYLENE AT HIGH PRESSURES AND TEMPERATURES

(Presented by Academician A. N. Frumkin, May 18, 1960)

Using the constant-volume piezometer method, the volumes of gaseous solutions of water in compressed ethylene were measured at temperatures from 200 to 300° and pressures up to 100–150 atm. Into apparatus **1** (Fig. 1) of known volume, definite amounts of water and ethylene were introduced through valve **3** (the composition of the solution was chosen from data on phase equilibria in this system obtained earlier (1)); the apparatus was heated, the gaseous solution was mixed with electromagnetic stirrer **2**, the pressure was measured, and part of the solution was discharged through membrane valve **4** into evacuated, calibrated flasks **13**, condensing the water en route in ampoule **11**. After discharging a sample, the solution was again stirred, the pressure was measured, and part of the solution was again discharged. This was repeated until the entire loaded mixture had been discharged. A balance was then drawn up, the average composition of the mixture was determined, and, knowing the dependence of the molar volume of a solution of this composition on pressure, the molar volume on the saturation line was found.

Membrane valve **6**, mounted in block **5**, served to connect the pressure-measuring system **7**. This system consists of a membrane, which serves as the zero instrument,** and lamp **8**, which lights when the membrane closes an electric circuit. By creating oil pressure with press **9** in the space above the membrane, it is adjusted so that lamp **8** lights and goes out when the pressure changes by fractions of an atmosphere. At this moment the oil pressure (which is equal to the pressure in the apparatus) is measured with standard pressure gauges **10** of class 0.35. When a sample is discharged, water and ethylene are condensed in ampoule **11** at the temperature of liquid nitrogen. The ampoule is then heated to the temperature of a mixture of solid carbon dioxide and acetone, and the evaporating ethylene is pumped off by mercury pump **12** into evacuated flasks of up to 15 l capacity.

The volume of the column was determined by calibration with a gas of known compressibility. The change in the column volume with temperature was calculated from the equation for the volume expansion of stainless steel (3). The experimental data obtained are given in Table 1.

Fig. 1. Apparatus for determining the volumes of gas solutions

Figure 1: Fig. 1. Apparatus for determining the volumes of gas solutions

Fig. 2. Volumes of gas solutions of water in ethylene on the saturation line

Figure 2: Fig. 2. Volumes of gas solutions of water in ethylene on the saturation line

Figure 2 shows the volumes of solutions of water in ethylene on the saturation line, found by extrapolation.

Experimental data

The thermodynamic properties of a substance are most conveniently calculated from pvT data if these data are expressed by an equation of state. We attempted to represent the volumetric behavior of the investigated solutions by an equation —

* V. I. Alisova took part in carrying out the experiments.
** The instrument was constructed by us on the principle of a fully supported membrane, previously used in a membrane valve (^{2}).

state in virial form * (4). Equation (1)

$$pv = RT\left(1 + B(T)/v + C(T)/v^2\right), \tag{1}$$

where p is pressure, v is molar volume, R is the gas constant, and $B(T)$ and $C(T)$ are the second and third virial coefficients; in order to find these

Fig. 1. Apparatus for determining the volumes of gas solutions

coefficients, it was transformed into the equation of a straight line:

$$\left(\frac{pv}{RT} - 1\right) v = B + C/v. \tag{2}$$

If the experimental data are represented by equation (1), then the values of the left-hand side of equation (2), calculated from the experimental data and plotted against $1/v$, should fall on a straight line, which cuts off on the ordinate axis B_p, and the tangent of whose angle of inclination to the abscissa axis is equal to C_p. (B_p and C_p are the second and third virial coefficients of the gas solution of the given concentration.)

Fig. 2. Volumes of gas solutions of water in ethylene on the saturation line

The calculations we carried out showed that the values of the left-hand side of equation (2)—Δ—lay well on a straight line, and we were able to calculate the values of B_p and C_p for the solutions we studied.

In order to be able to calculate the volumes of a solution of any concentration, and not only of the one investigated, it is necessary to know the concentration dependence of the second and third virial coefficients, which is given by equations (3) and (4)

$$B_p = B_{11}N_1^2 + 2B_{12}N_1N_2 + B_{22}N_2^2; \qquad (3)$$

$$C_p = C_{111}N_1^3 + 3C_{112}N_1^2N_2 + 3C_{122}N_1N_2^2 + C_{222}N_2^3, \qquad (4)$$

where B_{11}, B_{22}, C_{111}, and C_{222} are the second and third virial coefficients of pure water and ethylene, while B_{12}, C_{112}, and C_{122} are the second and third virial coefficients accounting for pair and triple interactions. Knowing B_{12}, C_{112}, C_{122}, one can calculate B_p and C_p, and therefore the molar volumes of solutions of water in ethylene of any composition.

Table 1

Molar volumes (liter/mole) of solutions of water in ethylene. N_2—mole fraction of ethylene in the solution

Temperature	N_2	P, ata	v
200°	0.287	1.97	17.85
200°	0.287	4.70	7.86
200°	0.287	8.16	4.43
200°	0.287	11.7	2.94
200°	0.287	15.9	2.14
200°	0.500	1.77	29.3
200°	0.500	5.16	7.39
200°	0.500	9.13	4.05
200°	0.500	14.07	2.45
200°	0.500	23.75	1.45
200°	0.773	3.70	10.26
200°	0.773	14.45	2.55
200°	0.773	27.1	1.38
200°	0.773	39.85	0.914
200°	0.773	53.80	0.662
200°	0.90	8.8	4.32
200°	0.90	32.6	1.112
200°	0.90	58.6	0.594
200°	0.90	84.3	0.403
200°	0.90	98.3	0.340
250°	0.237	2.3	18.45
250°	0.237	10.1	3.81

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* This idea and the method of calculation were proposed by I. R. Krichevskii.

Temperature	N_2	P, ata	v
250°	0.237	19.3	2.04
250°	0.237	30.2	1.27
250°	0.237	42.2	0.889
250°	0.546	6.3	6.63
250°	0.546	24.6	1.684
250°	0.546	42.6	0.974
250°	0.546	59.6	0.674
250°	0.546	76.0	0.508
250°	0.760	51.0	0.823
250°	0.760	67.8	0.616
250°	0.760	83.8	0.489
250°	0.760	101.2	0.398
250°	0.760	115.7	0.345
250°	0.760	128.8	0.306
250°	0.925	7.8	5.247
250°	0.925	43.6	0.925
250°	0.925	74.1	0.549
250°	0.925	100.2	0.399
250°	0.925	126.8	0.314
300°	0.212	6.4	7.152
300°	0.212	20.4	2.224
300°	0.212	40.9	1.055
300°	0.212	70.4	0.592
300°	0.212	88.1	0.451
300°	0.385	4.7	9.63
300°	0.385	21.8	2.023
300°	0.385	35.5	1.242
300°	0.385	52.2	0.827
300°	0.385	68.0	0.621
300°	0.385	83.7	0.496
300°	0.385	90.5	0.457
300°	0.385	98.8	0.419
300°	0.551	5.8	7.59
300°	0.551	25.2	1.801
300°	0.551	50.4	0.879
300°	0.551	74.4	0.578
300°	0.551	107.5	0.394
300°	0.551	128.3	0.325

To calculate B_{12}, the values of the right-hand side of equation (5) were plotted against $N_1 N_2$, and, drawing a straight line by the method of least squares, the tangent of the angle of inclination of this straight line was calculated

$$[2B_{12}N_1N_2 = (B_p - B_{11}N_1^2 - B_{22}N_2^2). \tag{5}$$

Table 2

Values of the second (cm^3/mole) and third ($cm^6/mole^2$) virial coefficients of equations (3) and (4)

Temp., °C	B_{11}	B_{12}	B_{22}	$C_{111} \cdot 10^3$	$C_{112} \cdot 10^3$	$C_{122} \cdot 10^3$	$C_{222} \cdot 10^3$
200	−213	−488	−71	+0.50	+263	−43	+60
250	−154	−61	−18	−0.18	−123	+72	−18
300	−117	−58	−39	+0.82	+24	+2.2	+7.4

Next, using equation (3), the values of B_p were again calculated. They agreed satisfactorily with those calculated from equation (2). Then, by the method of least squares, the slopes of the straight lines passing (in coordi-

in the coordinates $\Delta - 1/v$ through the values of B_p calculated by equation (3) and the experimental values of Δ. The tangent of the angle of inclination of this straight line is equal to C_p.

The obtained values of C_p were used to calculate C_{112} and C_{122}. Transforming equation (4) into the equation of a straight line

$$(C_p - C_{111}N_1^3 - C_{222}N_2^3)/N_1^2N_2 = 3C_{112} + 3C_{122}N_2/N_1, \tag{6}$$

we drew, by the method of least squares, a straight line through the points on the plot in the coordinates

$$\frac{C_p - C_{111}N_1^3 - C_{222}N_2^3}{N_1^2N_2}$$

against $N_2 : N_1$. On the ordinate axis the straight line cuts off the value $3C_{112}$, and the tangent of its angle of inclination is equal to $3C_{122}$. Table 2 gives the values of all virial coefficients*, necessary for calculation by equation (1).

The cubic equation (1) was solved with respect to pressure, and, in order to check the accuracy of the calculations, we calculated not the volumes, which would have been very complicated, but the pressures from the volume values found experimentally, and compared the data obtained with the pressure values recorded in the experiment. The comparison data are given in Table 3.

Table 3

Pressures calculated by equation (1) and read from the manometer in the ethylene–water system at 300°

$N_2 =$ 0.212	$N_2 =$ 0.212	$N_2 =$ 0.212	$N_2 =$ 0.385	$N_2 =$ 0.385	$N_2 =$ 0.385	$N_2 =$ 0.551	$N_2 =$ 0.551	$N_2 =$ 0.551
v, l/m	P, ata exp.	P, ata calc.	v, l/m	P, ata exp.	P, ata calc.	v, l/m	P, ata exp.	P, ata calc.
2.224	20.4	20.3	9.63	4.7	4.8	7.49	5.8	6.23
1.055	40.9	41.1	2.023	21.8	22.41	1.801	25.2	25.27
0.592	70.4	69.7	1.242	35.5	35.75	0.879	50.4	50.37
0.451	88.1	89.1	0.827	52.5	52.39	0.578	74.4	75.10
			0.621	68.0	68.26	0.394	107.5	108.7
			0.496	83.7	83.90	0.325	128.3	132.1
			0.457	90.5	90.48			
			0.419	98.8	98.00			

As can be seen from Table 3, the difference between the calculated and experimental pressure values is, as a rule, small. Such good agreement shows that equation (1) describes the volumetric behavior of solutions of water in ethylene at pressures up to 150 atm and temperatures of 200–300°.

The authors express their gratitude to I. R. Krichevsky for his interest in the work and valuable advice.

State Scientific-Research and Design Institute
of the Nitrogen Industry
and Products of Organic Synthesis

Received
18 V 1960

CITED LITERATURE

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* The coefficients of pure water and ethylene were calculated from data in (5, 6).