[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 199]

A NEW EQUATION OF STATE FOR FLUIDS. I. APPLICATION TO GASEOUS ETHYL ETHER AND CARBON DIOXIDE[1]

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RECEIVED APRIL 11, 1927 PUBLISHED JULY 5, 1927

The consideration of certain thermodynamic properties of fluids has led the authors to formulate jointly an equation of state which appears to reproduce accurately the pressure-volume-temperature data.

It is believed that this equation has to a unique degree the following desirable qualities. (*a*) The numerical values of the constants can be determined easily and uniquely from the pressure-volume-temperature data, and with one exception can be obtained as the intercepts or slopes of straight lines by suitable treatment of the data. (*b*) The equation is readily amenable to mathematical manipulation since it is completely algebraic. Hence, most of the usual thermodynamic relations can be integrated in terms of elementary functions as, for example, $p\mathrm{d}v$ (and therefore $v\mathrm{d}p$) at constant temperature. (*c*) The equation fits the data over a wide range of pressures and temperatures, reproducing the trends as well as the actual pressures. (*d*) The volume and temperature functions, A, B and ϵ can be expanded further, *if necessary*, without alteration of the general form of the equation. This extension has not as yet been found necessary in the applications which have been made by the authors to gases even up to pressures of 300 atmospheres.

The proposed equation has the following form

$$p = \frac{RT\,(1-\epsilon)}{v^2}\,(v+B) - \frac{A}{v^2}$$

where $A = A_0(1 - a/v)$, $B = B_0\,(1 - b/v)$ and $\epsilon = c/vT^3$. This relation is being tested on all of the available data on fluids, and this extensive application, together with a theoretical basis for the equation and the detailed method for obtaining the numerical values of the constants, will be given later.

In the present article, the equation is applied to the data on gaseous ethyl ether[3] and carbon dioxide,[4] and the numerical values of the constants for these substances are given in Table I. The units of pressure, volume and temperature are the atmosphere, cc. per gram, and degrees absolute where $T^\circ = t^\circ + 273.13$.

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[1] Originally submitted in two articles under separate authorship.

[2] National Research Fellow in Chemistry.

[3] Beattie, THIS JOURNAL, **46**, 342 (1924); **49**, 1123 (1927).

[4] Amagat, *Ann. chim. phys.*, **29**, 109 (1893). For the method used in interpolating to even volumes, and the values of the pressures so obtained see Bridgeman, THIS JOURNAL, **49**, 1130 (1927).

TABLE I

CONSTANTS FOR THE EQUATION FOR GASEOUS ETHYL ETHER AND CARBON DIOXIDE

Constant	R	B_0	b	A_0	a	c
Ethyl ether	1.10777	6.1350	1.6137	5700.0	1.6775	4.5×10^6
Carbon dioxide	1.8650	2.3810	1.6443	2586.0	1.6210	15.0×10^6

The deviations between the observed and calculated values of the pressures for the two gases are presented in Table II.

TABLE II

DEVIATIONS OF PRESSURES CALCULATED BY THE EQUATION OF STATE FROM OBSERVED PRESSURES

(a) Ethyl ether

Temp. °C. Vol., cc./g.	150	175	200	225	250	275	300	325	Av. dev., atm.	Av. press., atm.	Av. dev., %
	$(P_{\text{obs.}} - P_{\text{calcd.}}) \times 10^2$ atm.										
35	1.7	1.2	2.3	0.5	1.3	−0.6	0.5	1.3	0.012	14.42	0.08
30	3.6	1.9	0.5	1.9	2.5	1.0	1.7	3.1	.020	16.52	.12
25	−1.0	0.2	0.5	1.4	0.2	0.1	2.2	−0.1	.007	19.28	.04
20	−2.2	−0.9	0.0	−0.3	0.4	2.6	0.7	1.7	.011	23.14	.05
15		−3.3	−2.5	−1.6	−0.6	−1.7	0.9	0.1	.015	30.11	.05
12.5		−5.2	−4.1	−3.1	−2.6	−1.6	−2.3	−2.2	.030	34.39	.09
10			−2.3	−2.1	−2.4	−3.3	−5.6	−6.1	.036	42.12	.09
7.5			7.2	6.9	5.5	1.9	1.8	−1.6	.042	50.76	.08
5			−2.5	0.6	−0.2	7.7	5.0	6.4	.037	64.52	.06
								Av.	.022		.07

(b) Carbon dioxide

Temp. °C. Vol., cc./g.	0	20	40	60	80	100	Av. dev., atm.	Av. press., atm.	Av. dev., %
	$(P_{\text{obs.}} - P_{\text{calcd.}}) \times 10^2$ atm.								
40	0	−1	0	−1	−1	0	0.005	14.18	0.04
30	−1	−1	−1	−2	−3	−2	.017	18.53	.09
20	−1	−3	−1	−3	−5	−2	.025	26.69	.09
15	−3	−3	−1	−2	−7	−3	.032	34.17	.09
10		−1	4	3	−6	0	.028	49.73	.06
7		6	15	17	3	7	.096	64.76	.15
5			0	2	−1	0	.008	86.28	.01
						Av.	.030		.08

Summary

There is presented a new equation of state which has to a unique extent the desirable features of (*a*) easy and accurate evaluation of the constants from pressure-volume-temperature data, (*b*) ease of mathematical manipulation including the integrability of $v\,dp$ at constant temperature in terms of elementary functions, (*c*) accurate representation of the data and their trends, and (*d*) flexibility, in that without alteration of the general form of the equation more terms can be added, if necessary.

The equation, which contains five constants and the gas constant, reproduces the data on gaseous ethyl ether and carbon dioxide at least to a specific volume of 5 cc. per gram, with an average deviation over the whole range of 0.022 and 0.030 atm., respectively (0.07 and 0.08%). An ex-

tensive application to all the available data and a theoretical basis will be given in a later article.

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[CONTRIBUTION FROM BELL TELEPHONE LABORATORIES, INCORPORATED]

THE SOLID SOLUBILITY OF ANTIMONY IN LEAD AS DETERMINED BY CONDUCTIVITY MEASUREMENTS ON COLD-WORKED ALLOYS

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RECEIVED APRIL 16, 1927 PUBLISHED JULY 5, 1927

Introduction

In 1923, Dean[1] showed the existence of an appreciable solid solubility of antimony in lead at the eutectic temperature. Shortly thereafter Dean, Hudson and Fogler[2] demonstrated that dispersion hardening takes place in these alloys. They found that a 2.5% antimony alloy, a homogeneous solid solution at 247°, precipitated more than half of its antimony from solution after being maintained at room temperature for a short time. A more detailed study of the solubility conditions, using the conductivity method to follow changes of solubility with temperature, was made by Dean, Zickrick and Nix.[3] Unfortunately, at the lower temperatures, they were unable to obtain equilibrium values due to the slow rate of precipitation of the solute.

Recent work indicates that the rate of precipitation of the excess of antimony is greatly accelerated if the alloys are first severely cold-worked. Presumably equilibrium would be reached much more quickly under these conditions. Therefore, it seemed desirable to determine the solid solubility values for antimony in lead on severely cold-worked alloys, hoping thereby to secure more accurate values than those previously obtained.

Photomicrographs Showing the Effect of Cold Work

Several photomicrographs, taken by Mr. F. F. Lucas[4] of these Laboratories, are given to show the structural effect of cold work in these alloys. A lead-antimony alloy containing 1% of antimony and 99% of lead was cast in the form of a rod, 0.5 inch (1.3 cm.) in diameter. This rod was heated at 230° for one hour to get most of the undissolved antimony into solution. The rod was then divided and one section was severely cold-worked by swaging. Both the worked and unworked sections were maintained at room temperature, 20° for five days and then photomicrographs were taken of each. The specimens photographed

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[1] Dean, THIS JOURNAL, **45**, 1683 (1923).

[2] Dean, Hudson and Fogler, *Ind. Eng. Chem.*, **17**, 1246 (1925).

[3] Dean, Zickrick and Nix, *Trans. Am. Inst. Mining Met. Eng.*, **73**, 505 (1926).

[4] Lucas, Preprint No. 1654 E, *Am. Inst. Mining Met. Eng.*, February, **1927**.