An Equation of State in Analytical Form

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In most of the text-books of physical chemistry which insert a table of van der Waals' constants a and b, no example of their actual evaluation is given, and students often fall into misconception that the constants are uniquely determinate from the original and its two derived equations at critical points. Concretely speaking, from these equations we obtain $b=V_c/3=RT_c/8p_c$ by substituting for V_c in the former from van der Waals' critical factor, $RT_c/p_cV_c=8/3$, and consequently $a=27p_cb^2=3p_cV_c^2=27(RT_c)^2/64p_c$, whereas for real gases, these two expressions of b give inconsistent values, $V_c/3$ being always less than $RT_c/8p_c$. The latter however has been accepted to make use of calculating molecular diameters.(1) To eliminate this inconsistency from van der Waals' equation, the following correction is needed:

$$b_{corr.}=b\left(\frac{3}{8}\,\frac{RT_c}{p_cV_c}\right)=\frac{V_c}{3}\left(\frac{3}{8}\,\frac{RT_c}{p_cV_c}\right)=\frac{RT_c}{8p_c},$$

where RT_c/p_cV_c in the correction factor is an actual critical factor, ranging from 3.23 to 3.97 for non-polar and larger slightly polar substances. Substitute $a_{corr.}$ for a corresponding to $b_{corr.}$, van der Waals' equation per mol. is

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(1) e.g. Landolt-Börnstein I-1, 1950, p. 325.

Table 1

Validity of van der Waals' Equation for CO_2 at Several Isotherms ($p_c=73.0$ atm.)

30.98°C. (critical temperature)		37.09°C.		41.95°C.		50°C.		100°C.		198 °C.	
p(atm.)	f	p(atm.)	f	p(atm.)	f	p(atm.)	f	p(atm.)	f	p(atm.)	f
63.36	0.982	64.56	0.986	64.85	0.989	50	0.988	50	1.009	50	0.998
69.085	0.989	69.20	0.990	69.81	0.992	100	1.007	100	1.026	100	1.032
72.995	0.955	71.73	0.993	72.78	0.994	200	0.509	200	0.998	200	1.056
75.43	0.864	76.40	0.999	75.48	0.997	400	0.349	400	0.726	400	1.002
86.10	0.763	88.89	0.902	87.18	1.007	600	0.118	600	0.517	600	0.864
106.18	0.662	103.08	0.792	105.01	0.872	800	($V<b_{corr.}$)	800	0.337	800	0.760
138.65	0.568	136.01	0.655	134.85	0.731	1000	〃	1000	0.161	950	0.619

Table 2

Ratios of the Molecular Association Degree to the Correction Factor for Critical Factor

Liquid	V(20°C.) cc.	$b_{corr.}$ cc.	RT_c/p_cV_c	α/β(20°C.)	$A\Big/\frac{3}{8}\frac{RT_c}{p_cV_c}$
Br_2	51.23	58.56	3.46	17.66	0.969
Hg	14.81	17.04	3.40	46.29	1.025
CCl_4	96.45	126.6	3.68	11.51	1.029
CS_2	60.28	75.13	3.49	12.84	1.068
H_2O	18.04	30.49	4.46	3.92	(negative)
$CH_3CO_2C_2H_5$	97.89	141.0	3.95	13.27	1.040
C_2H_5OH	58.35	83.90	4.08	9.65	(1.100)
$C_2H_5OC_2H_5$	103.8	131.8	3.77	8.85	0.986
C_2H_5Br	75.16	84.31	3.14	11.64	1.046
CH_3COCH_3	73.43	86.90	3.02	11.44	(1.159)
C_6H_6	88.85	119.9	3.75	11.11	1.048
C_6H_5Cl	101.8	145.4	3.76	13.07	1.077
$CHCl_3$	80.18	99.42	3.44	12.80	1.046
C_7H_{16}	146.5	205.6	3.85	10.33	1.030
cyclo-C_6H_{14}	108.2	139.8	3.63	10.17	1.027
C_6H_{14}	130.6	174.7	3.80	9.00	1.011
CH_3OH	40.46	53.09	4.75	9.92	(0.927)
C_8H_{18}	162.7	236.1	3.86	11.18	1.052
C_5H_{12}	115.2	145.9	3.76	6.61	1.008
C_3H_7OH	74.74	110.0	3.99	9.80	(1.106)
$C_6H_5CH_3$	106.4	146.4	3.71	12.41	1.054

Table 3

($2-\varepsilon$) Values of Ne ($t_c=-228.7$°C, $p_c=26.9$ atm., $d_c=0.484$ g./cc)

$b=13.90$, $\log a=5.147154$, $\log V_0=4.350791$

−213.08°C		−208.10°C		−182.60°C		−141.22°C		−103.01°C		0.00°C	
p(atm.)	$2-\varepsilon$	p(atm.)	$2-\varepsilon$	p(atm.)	$2-\varepsilon$	p(atm.)	$2-\varepsilon$	p(atm.)	$2-\varepsilon$	p(atm.)	$2-\varepsilon$
23.086	1.946	24.071	1.950	32.067	1.973	33.840	1.996	35.558	2.011	22.064	2.093
24.810	1.946	28.844	1.952	32.988	1.973	37.707	1.998	36.697	2.006	23.555	2.078
26.673	1.946	31.948	1.952	36.438	1.976	38.581	1.998	40.610	2.022	25.867	2.107
29.365	1.946	37.856	1.953	36.880	1.977	43.319	2.006	42.107	2.021	28.468	2.115
32.441	1.947	41.798	1.953	41.371	1.977	49.881	2.004	55.136	2.026	30.790	2.118
37.418	1.947	58.472	1.954	42.533	1.981	51.916	2.004	58.583	2.030	39.753	2.059
53.896	1.948	64.451	1.955	49.943	1.981	66.471	2.019	78.110	2.059	44.892	2.072
59.769	1.948	69.692	1.955	50.514	1.980	78.558	2.029			59.777	2.076
66.271	1.948	74.532	1.955	63.320	1.983			mean	2.025	66.104	2.097
72.858	1.950	76.228	1.954			mean	2.007			74.059	2.122
79.698	1.950			mean	1.978					79.108	2.138
		mean	1.953							84.662	2.118
mean	1.947										
										mean	2.099

Table 4

(2−ε) Values at Critical Points and Percentage Divergences of Approximate Formula $RT_c/p_cV_c=2/3\cdot(1+3V_c^{0.077})$ from Experimental Data

Substance	2−ε	Δ	Substance	2−ε	Δ	Substance	2−ε	Δ
He	1.931	+2.50	C_5H_{12}	1.924	+0.52	CH_3SH	1.922	−0.57
Ne	1.935	+2.35	i-C_5H_{12}	1.926	+1.55	C_2H_5SH	1.924	+0.85
A	1.925	+0.84	cyclo-C_6H_{14}	1.931	+3.95	CH_3SCH_3	1.920	−1.37
Kr	1.927	+1.63	C_6H_{14}	1.924	+0.53	$C_2H_5SC_2H_5$	1.933	+4.67
Xe	1.921	−0.89	C_7H_{16}	1.923	+0.28	HCO_2CH_3	1.905	−7.39
H_2	1.936	+4.31	C_8H_{18}	1.923	+0.78	$HCO_2C_2H_5$	1.913	−5.02
N_2	1.928	+1.93	Br_2	1.932	+3.51	$HCO_2C_3H_7$	1.917	−2.75
O_2	1.925	+0.83	Hg	1.915	−2.28	$CH_3CO_2CH_3$	1.909	−6.06
Cl_2	1.921	−0.79	CS_2	1.933	+4.42	$CH_3CO_2C_2H_5$	1.912	−4.82
CO	1.931	+3.01	CCl_4	1.927	+1.96	$CH_3CO_2C_3H_7$	1.914	−4.29
CO_2	1.918	−1.85	$CHCl_3$	1.940	+9.81	$CH_3CO_2CH_2CH(CH_3)_2$	1.937	+7.02
CF_2Cl_2	1.925	+0.96	CH_3OCH_3	1.918	−2.13	$C_2H_5CO_2CH_3$	1.913	−4.34
$COCl_2$	1.933	+4.31	$CH_3OC_2H_5$	1.922	−0.62	$C_2H_5CO_2C_2H_5$	1.915	−3.58
N_2O	1.908	−5.43	$C_2H_5OC_2H_5$	1.922	−0.57	$C_3H_7CO_2CH_3$	1.917	−2.82
PH_3	1.915	−3.13	$C_2H_5OC_3H_7$	1.926	+1.41	$(CH_3)_2CHCO_2CH_3$	1.912	−2.12
SO_3	1.908	−5.93	C_2H_5Cl	1.926	+1.16	$C_3H_7CO_2C_2H_5$	1.932	+4.63
$SnCl_4$	1.927	+2.06	$C_6H_5CH_3$	1.927	+1.87	$(CH_3)_2CHCO_2C_2H_5$	1.937	+7.08
CH_4	1.927	+1.64	C_6H_6	1.922	−0.49	$C_2H_5NH_2$	1.921	−0.82
C_2H_6	1.923	−0.12	C_6H_5F	1.920	−1.00	$(C_2H_5)_2NH$	1.922	−0.59
C_2H_4	1.927	+1.48	C_6H_5Cl	1.923	−0.02	$(C_2H_5)_3N$	1.934	+5.74
C_2H_2	1.915	−2.91	C_6H_5Br	1.921	−0.78	$(CH_3)_2CHCH(CH_3)_2$	1.926	+1.46
C_3H_8	1.921	−1.00	C_6H_5I	1.925	+1.01	$(CH_3)_2CHCH_2CH_2CH(CH_3)_2$	1.926	+1.57

The mean of $(2-\varepsilon)=1.923\pm0.008$, the mean of $\Delta=\pm2.6\%$.

written down:

$$p+\frac{a_{corr.}}{V^2}=\frac{RT}{V-b_{corr.}} \qquad (1).$$

The validity of equation (1) can be tested simply by calculating $f=(p+a_{corr.}/V^2)(V-b_{corr.})/RT$ at different isotherms, which must be unity, if the equation holds good. As seen from Table 1, f deviates from unity as pressure moves slightly away from the critical pressure, so that equation (1) is valid only within narrow limits of pressures, though the range becomes wider as the increase in temperature.

Moreover mere trial for the evaluation of values of $(V-b_{corr.})$ with ordinary liquids at an ordinary temperature proves that the applicability of equation (1) to liquids, should be rejected since all such values become negative (compare column 2 with column 3 in Table 2).

We have the pure thermodynamic equation

$$p+\left(\frac{\partial U}{\partial V}\right)_T=T\left(\frac{\partial p}{\partial T}\right)_V=T\frac{\alpha}{\beta} \qquad (2),$$

where α and β denote thermal expansion coefficient and isothermal compressibility.(2) If there exists an equation of state for liquids, the thermal pressure of which has the form $ART/(AV\text{-}b_{corr.})$, A being a correction factor so as to let the denominator of thermal pressure of equation (1) be positive, the equality:

$$T\frac{\alpha}{\beta}=\frac{ART}{AV-b_{corr.}} \qquad (3)$$

may be satisfied, if A is suitably chosen. Since R (82.06 cc.-atm./deg. mol.) and V (cc./mol.) are both referred to 1 mol. of gases, A may be or may not be proportional to the degree of non-polar association at T°K.

For test of this postulation, 21 kinds of liquids have been adopted from Henning's table.(3) In Table 2 are given A's divided by $3RT_c/8p_cV_c$, from which we can conclude that A is in nearly the same magnitude with $3RT_c/8p_cV_c$, for ordinary liquids except acetone, alcohols and water, or in other words, for liquids having low dielectric constants relation (3) is transformed into

$$T\frac{\alpha}{\beta}=\frac{RT}{V-b} \qquad (4).$$

In accord with the above correction for thermal pressure, an appropriate correction for cohesive pressure will be considered below.

As already known b decreases as V decreases,

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(2) e.g. International Critical Tables IV, p. 19.

(3) F. Henning's "Warmetechnische Richtwerte", p. 17-19, 20-21.

and so the assumption of keeping b to be constant independent of V must yield deviation in thermal pressure, but the deviation therefrom can be attributed to a suitable correction of a in cohesive pressure.

Now assume $a^*_{corr.}$ to vary slightly with V and take the following form:

$$a^*_{corr.} = aV^{\varepsilon},$$

ε = a constant independent of pressure,

then for substances having low dielectric constants it follows from (1), (3) and (4) that

$$p + \frac{a}{V^{2-\varepsilon}} = \frac{RT}{V-b},$$
$$a = 3p_cV_c^2,\ b = V_c/3 \qquad (5).$$

Adopting pv- values of gases from I. C. T.⁽⁴⁾ and Henning's table,⁽⁵⁾ we have calculated $(2-\varepsilon)$ values for several gases. One of them is examplified in Table 3.

As a whole, the constancy of $(2-\varepsilon)$ values is fairly good over a wide range of pressures of each isotherm, though the constant range becomes restricted as the temperature decreases. The variation of $(2-\varepsilon)$ values with temperature is similar for all the examined gases except He, their values increasing from a value less than 1.92 to a value slightly greater than 2. Inserting the mean value of $(2-\varepsilon)$ at each isotherm in equation (5), we can obtain the equation of state at respective temperature. The thus analytically determinate equation is, therefore, more reasonable and accurate than a usual equation of algebraic form: $pV = a_0 + a_1/V + a_2/V^2 + a_3/V^3 + \cdots\cdots$.

Besides the gases above examined, all gases and liquids with known critical-point data except those having high dielectric constants take a universal value, 1.923 ± 0.008, for $(2-\varepsilon)$ at critical points (see Table 4).

The following are three formulae at the critical point which can be derived from the new equation of state.

The criteria generally used to determine whether or not any equation of state holds good are RT_c/p_cV_c, T_B/T_c (T_B = Boyle point) and $T_c/p_c \cdot (dp/dT)_c$. These are of course physico-chemical constants giving the values close to 3.7, 2.6 and 7.0 respectively but none of the proposed equations gives concordant values simultaneously.

Inserting $a = 3p_cV_c^2$ and $b = V_c/3$ in equation (5) at the critical point, and rearranging them, it follows that

$$\frac{RT_c}{p_cV_c} = \frac{2}{3}(1 + 3V_c^{\varepsilon}) \qquad (6),$$

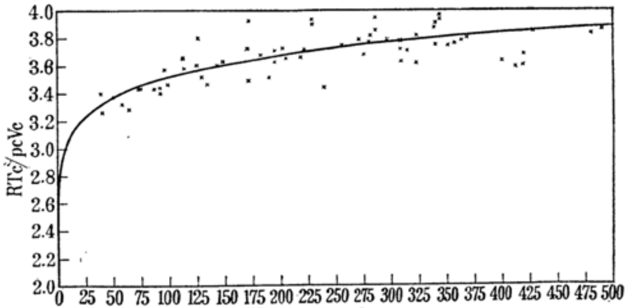

Fig. 1.—Relation between RT_c/p_cV_c and V_c for low dielectric substances.

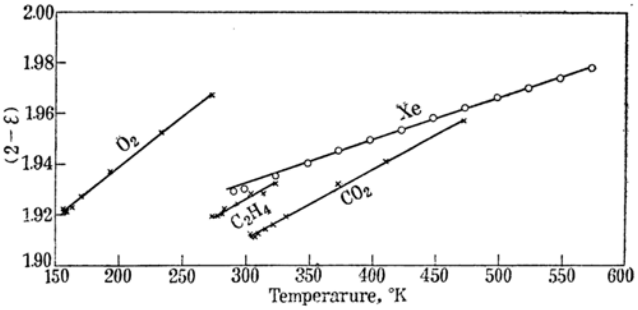

Fig. 2.—The temperature dependence of $(2-\varepsilon)$ for some gases.

here of course ε is its value at the critical point and V_c is expressed in cc.

Firstly, if we take the mean of ε from the results summarized in Table 4, relation (6) becomes

$$\frac{RT_c}{p_cV_c} = \frac{2}{3}(1 + 3V_c^{0.077}) \qquad (7),$$

which serves as an approximate formula. Δ's in Table 4 denote the percentage divergences from experiments and their mean value becomes ±2.6 %. Also the relation between RT_c/p_cV_c and V_c is diagrammatically shown in Fig. 1, in which the curve is plotted by formula (7). Quite recently Himpan⁽⁶⁾ put forward the empirical formula, $RT_c/p_cV_c = 2.92 + 1/3.\log(nM)$, where M is the molecular weight and n the degree of association, but its graphical test has shown that his formula is worse than formula (7).

Secondly, since the Boyle temperature is much higher than the critical temperature, relation $T_B = b/aR = 9p_cV_c/R$ derived from the van der Waals' equation may be allowable. Using this relation in conjunction with formula (7), there results

$$\frac{T_B}{T_c} = \frac{27}{2(1 + 3V_c^{0.077})} \qquad (8).$$

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(4) International Critical Tables III, p. 4-19, 248-249.

(5) F. Henning, l.c., 34-40.

(6) J. Himpan, *Z. Physik*, **131**, 17 (1951).

Formula (8) gives concordant values with experiments: 2.70 (2.70), 2.60 (2.73), 2.58 (2.59), 2.57 (2.59), 2.56 (2.58) for Ne, A, N_2, CO, CH_4 respectively, the values in parentheses being the observed values.(7)

Thirdly, write equation (5) in the form

$$p=\frac{RT}{V-b}-\frac{a}{V^{2-\varepsilon}},$$

and differentiate with respect to T, remembering ε to be dependent on temperature,

$$\left(\frac{dp}{dT}\right)_V=\frac{R}{V-b}-\frac{a}{V^2}V^{\varepsilon}\log_e V\cdot\frac{d\varepsilon}{dT}.$$

Putting this in the thermodynamic relation, $(dp/dT)_c=[dp/dT)_V]_{T=T_c}$, we readily obtain

$$\frac{T_c}{p_c}\left(\frac{dp}{dT}\right)_c=\frac{3RT_c}{2p_cV_c}-3T_cV_c^{\varepsilon}\log_e V_c\cdot\left(\frac{d\varepsilon}{dT}\right)_c,$$

or replace from formula (7), it follows that

$$\frac{T_c}{p_c}\left(\frac{dp}{dT}\right)_c=1+3V_c^{0\cdot077}-3$$
$$\times 2.303T_cV_c^{0\cdot077}\log_e V_c\left(\frac{d\varepsilon}{dT}\right)_c \qquad (9).$$

For example take CO_2 for which $T_c=304.2$°K., $V_c=44.01/0.460$ cc., $\varepsilon=0.082$ and $T_c/p_c\cdot(dp/dT)_c=7.14$(8) are given, $(d\varepsilon/dT)_c$ is evaluated to be -0.00029, or -0.00032 by the use of formula (9). These values agree well with the experimental value, $-(0.00028\pm0.0004)$, which has been obtained from the mean of $(2-\varepsilon)$ values at several isotherms: 1.912 (30.98°C., critical temperature), 1.916 (48.10°C.), 1.919 (57.75°C.), 1.935 (100°C.), 1.946 (137°C.), 1.969 (198°C.), 1.972 (258°C.).

As already stated, $3RT_c/8p_cV_c$ corresponds to the molecular association factor A at the critical point, so it follows from formula (6) that

$$A=(1+3V_c^{\varepsilon})/4$$

The numerical values of A lie from the lowest value of 1.22−1.29 for non-polar molecules such as Ne, He, A, Kr, N_2 and CO to the highest value of 1.47−1.49 for alkyl esters such as $CH_3CO_2CH_3$, $CH_3CO_2C_2H_5$ and $CH_3CO_2C_3H_7$. Although the former value, to whose class Br_2 and Hg belong, may be inconsistent with ordinary physicochemical knowledge of so-called normal liquids, yet it may be rather conceivable that non-polar association takes place at the critical point where gaseous and liquid states begin to coexist undoubtedly in a molecular aggregation different from the gaseous state, and that such association in the case of normal liquids may keep nearly constant for a wide range, from critical to ordinary temperatures.

Summary

(1) An equation of state in analytical form is proposed:

$$p+\frac{a}{V^{2-\varepsilon}}=\frac{RT}{V-b},\quad a=3p_cV_c^2,\quad b=V_c/3.$$

Values of $(2-\varepsilon)$ keep constant over a wide range of pressures of each isotherm. Taking the mean of $(2-\varepsilon)$ values at each isotherm, we obtain an equation of state which is more reasonable and accurate than the usual isothermal equation of algebraic form.

(2) Tests made with 66 kinds of substances having low dielectric constants prove that values of $(2-\varepsilon)$ at critical points are universal to give 1.923 ± 0.008.

(3) The following three formulae at the critical point are derived from the new equation in which V_c is expressed in cc./mol.

(i) $$\frac{RT_c}{p_cV_c}=\frac{2}{3}(1+3V_c^{0\cdot077}),$$

(ii) $$\frac{T_B}{T_c}=\frac{27}{2(1+3V_c^{0\cdot077})},$$

(iii) $$\frac{T_c}{p_c}\left(\frac{dp}{dT}\right)_c=1+3V_c^{0\cdot077}-3$$
$$\times 2.303T_cV_c^{0\cdot077}\log V_c\cdot\left(\frac{d\varepsilon}{dT}\right)_c.$$

The first formula is concordant with ±2.6% average divergence for 66 kinds of low dielectric substances and the two following are also equally concordant with the experimental data.

Addendum

The constancies of ε were found to be fairly good over a wide range of pressures at each isotherm. Their dependence on temperature, however, was left unsaid since there are but few favorable data from which a conclusion can be deduced.

Quite recently Beattie, Barriault and Brierley(2) reported on the compressibility measurements for gaseous xenon from the critical temperature to 300°C and over the density range of from 1 to 10 mol. per liter, and so by making use of their results we have had an opportunity to certify the linearity between ε and temperature which was already suggested in the case of CO_2.

For xenon we put $b=40.06$ cc. and $\log a=6.3993891$ calculated from their newly determined critical constants, $p_c=57.89$ atm., $d_c=8.32$ mol./liter, $T_c=16.65°C.+273.13$. The $(2-\varepsilon)$ values at every 50°C intervals from 25 to 275°C. are listed

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(7) Adopted from E. A. Guggenheim's "Thermodynamics", p. 140.

(8) Adopted from S. Mizushima's "Physical Chemistry", III, p. 645.

(1) J. A. Beattie, R. J. Barriault, J. S. Brierley, *J. Chem. Phys.*, **19**, 1219 (1951).

Table 5

$(2-\varepsilon)$ for Xenon

mol./liter	$(2-\varepsilon)$					
	25°C.	75°C.	125°C.	175°C.	225°C.	275°C.
10.0	1.934	1.942	1.951	1.960	1.968	
9.0	1.935	1.942	1.951	1.959	1.968	1.977
8.0	1.934	1.942	1.951	1.959	1.967	1.976
7.0	1.932	1.941	1.950	1.958	1.967	1.975
6.0	1.930	1.940	1.949	1.957	1.966	1.974
5.0	1.928	1.939	1.948	1.957	1.965	1.973
4.0	1.926	1.938	1.947	1.956	1.964	1.972
3.0	1.926	1.937	1.947	1.955	1.963	1.971
2.0	1.927	1.938	1.948	1.956	1.964	1.972
1.0	1.931	1.942	1.951	1.959	1.966	1.974
Mean	1.930	1.940	1.949	1.958	1.966	1.974

Table 6

Percent Deviation from Experiments

mol./liter	$100\,(p_{calc.}-p_{obs.})/p_{obs.}$					
	25°C.	75°C.	125°C.	175°C.	225°C.	275°C.
8.0	−6.52	−1.66	−0.824	−0.396	−0.406	−0.473
7.0	−2.93	−1.35	−0.424	−0.073	−0.158	−0.164
6.0	−0.11	−0.10	−0.028	+0.163	+0.079	+0.024
5.0	+1.562	+0.525	+0.288	+0.377	+0.280	+0.213
4.0	+2.095	+0.805	+0.442	+0.493	+0.378	+0.328
3.0	+1.736	+0.724	+0.419	+0.443	+0.371	+0.321
2.0	+0.864	+0.346	+0.184	+0.259	+0.225	+0.205
1.0	−0.121	−0.162	−0.151	−0.034	−0.005	−0.011
Mean	1.99	0.709	0.345	0.258	0.228	0.217
(Beattie-Bridgeman's equation)	1.37	0.282	0.424	0.294	0.171	0.190

in, Table 5, and the percent deviations, $100\,(p_{calc.}-p_{obs.})/p_{obs.}$, from 1 to 8 mol. per liter, in Table 6. As seen from these tables, the constancies of $(2-\varepsilon)$ at respective isotherms are quite satisfactory and the average percent deviations are as small as those of the Beattie-Bridgeman equation of state (the last line in Table 6).

The variation of $(2-\varepsilon)$ with temperature is diagrammatically shown in Fig. 2, in which are also plotted those of CO_2, C_2H_4 and O_2 which were computed from the compressibility data already mentioned.

As to xenon, $(2-\varepsilon)$ is strictly a straight line over the whole range of temperatures. This relationship appears to be equally well for the other gases as judged from their graphical representations. So that we can conclude that the linearity:

$$\varepsilon=\varepsilon_c+c(T-T_c),\quad \varepsilon_c,\ c=\text{consts.}$$

holds true so far as the present data are concerned. Here ε_c is not ε at the critical point but the mean at the critical isotherm.

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