An Equation of State in Analytical Form (Concluded)

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(Received June 8, 1954)

The substances already exemplified for the verification of the author's equation of state, $(p+a/V^{2-\varepsilon})(V-b)=RT$, $a=3p_cV_c^2$, $b=V_c/3$, were all non-polar or slightly polar which yielded to the condition that at their critical points the pressure independent constants, ε's, converged to a universal constant, 0.077 ±0.008 when V_c is expressed in cc./mol., and for these substances his newly defined association degree, A, which is the ratio of the critical factor to van der Waals' critical factor, 8/3,

$$A=\frac{3}{8}\left(\frac{RT_c}{P_cV_c}\right), \text{ and } \frac{RT_c}{P_cV_c}=\frac{2(1+3V_c^{\varepsilon})}{3} \tag{1}$$

was found to be from the lowest values of 1.22−1.29 for non-polar molecules such as He, A, Kr, N_2, O_2, and CH_4 to the highest values of 1.47−1.49 for slightly polar molecules such as $CH_3CO_2CH_3$, $CH_3CO_2C_2H_5$, and $CH_3CO_2C_3H_7$[1].

For strongly polar substances such as acetone, lower alcohols, acetic acid, and water, ε's at their critical points always take greater values thus: $(CH_3)_2CO$, $\varepsilon=0.101$; CH_3OH, $\varepsilon=0.139$; C_2H_5OH, $\varepsilon=0.105$; n-C_3H_7OH, $\varepsilon=0.095$; CH_3COOH, $\varepsilon=0.150$; and H_2O, $\varepsilon=0.159$. In these cases, however, A deviates appreciably from the first relation of (1) and takes the form,

$$A=f\cdot\frac{3}{8}\left(\frac{RT_c}{P_cV_c}\right), \tag{2}$$

where f is the deviation factor which may depend upon temperature but can be estimated by putting A from relation (2) into relation (3) in the first report:

$$f=\frac{b}{V-R\beta/\alpha} \tag{3}$$

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[1] T. Ishikawa, This Bulletin, **26**, 78, 530 (1953); ibid., **27**, 226 (1954); T. Ishikawa, M. Ikeda, ibid., **26**, 516 (1953).

where α and β denote the thermal expansion coefficient and the isothermal compressibility.

Taking f at 20°C into account in the calculation of A, we obtain the values, denoted by the author (20°C) in Table I, in which are also shown the association degrees from other methods by several investigators.

TABLE I

ASSOCIATION DEGREES OF STRONGLY POLAR SUBSTANCES

Liquid	Ramsay[2] (20°C)	Traube[3] (15°C)	Bingham & Spooner[4]	The author	
				(20°C)	(crit. pt.)
$(CH_3)_2CO$	—	1.53	1.28—1.31	1.78	1.54
CH_3OH	2.32	1.79	1.89—1.93	1.59	1.71
C_2H_5OH	1.65	1.67	1.90—1.98	1.68	1.53
n-C_3H_7OH	—	1.66	1.78—1.92	1.66	1.50
CH_3COOH	2.13	1.56	1.71—1.95	1.75	1.54
H_2O	1.64	3.06	—	(negative)	1.67

As seen from Table I, the author's values are in fair agreement with other values, his method also may well be applicable to computing the association degree of an abnormal liquid.

The only exceptional case, in which f gives a negative value at 20°C and consequently relation (3) fails, is water. At higher temperatures, however, f changes its sign and this substance behaves like a normal liquid. For example, if we adopt from Kennedy's compressibility data,[5] we can see that e.g., at 200 bars f (α and β being calculated by taking $\Delta t=10$°C and $\Delta p=50$ bars) takes 1.144 at 200°C, 1.106 at 250°C, and 1.011 at 300°C. Judging from these values which approach to 1 as the temperature comes near the critical point, 374.23°C, it is highly probable that even for an abnormal liquid like water, this relation (1) holds good at the critical point (the values of the author [crit. pt.] in Table I are A values thus assumed).

Next, we shall examine the applicability of the new equation to water as an example of the most anomalous case.

Among the critical constants, t_c, p_c, and v_c of water, v_c can not be measured directly and has been obtained by graphical extrapolation from the values of the saturation volume of both liquid and vapour above 340°C.[6] Schroer[7] obtained $v_c=2.56-3.57$ cc./g., but Eck[8] obtained $v_c=2.650-3.630$ cc./g. and decide, as the true critical volume, 3.066 cc./g. which is nearly the value appeared in Henning's "Warmetechnische Richtwerte", p. 17 (VDI-Verlag GMBH, Berlin, 1938), from this the author adopted to evaluate A at the critical point for water in Table I.

Trials of the author's equation by Kennedy's data, using $t_c=374.2$°C, $p_c=217.5$ atm., and either of the above extremities of v_c, turned out to give the best constancy for $(2-\varepsilon)$, but with still unsatisfactory results, in the case of $v_c=2.56$ cc./g, the least value among them, this value being nearly equivalent to $d_c=0.4$ g./cc. which appeared in "International Critical Tables", III, p. 248 (1928).

As we know, from van der Waals' b it is possible to calculate the molecular collision diameter, σ, of a gas from the relation:

$$b=4N\frac{4}{3}\pi\left(\frac{\sigma}{2}\right)^3,\qquad \text{where}\quad N\,\text{(Avogadro's number)}=6.025\times10^{23}, \tag{4}$$

but in order to let σ nearly coincide with the molecular collision diameter from viscosity, σ_η, b has usually been taken as

$$b=\frac{RT_c}{8p_c}=\frac{3}{8}\left(\frac{R\,T_c}{p_cV_c}\right)\frac{V_c}{3}=b_{corr}.\qquad\text{(already denoted)}, \tag{5}$$

which is a solution (the other solution being $b=V_c/3$) obtained from van der Waals' equation and its two derivatives, $(\partial p/\partial V)_T=0$, and $(\partial^2 p/\partial V^2)_T=0$ at the critical point, notwithstanding that the selection of $b_{corr.}$ from these two is merely conventional so far as van der Waals' equation is concerned.

Now, in Landolt-Börnstein, I, Teil 1, p. 369 (1950), there appears $\sigma_\eta=2.27$ Å, from which b or otherwise $b_{corr.}$ is calculated to be 14.76 cc./mol., whence $v_c=2.457$ cc./g. or otherwise 1.480 cc./g. The former value is very slightly over the saturation volume, 2.450 cc./g, at 374°C (0.23°C below the critical temperature) observed by Eck and therefore may be acceptable, while the latter is too low and must be rejected.

From complete tests of the author's equation by Henning's tables, p. 25 at 0 to 350°C,

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[2] W. Ramsay, *Z. phys. Chem.*, **15**, 111 (1894).

[3] J. Traube, *Ber.*, **28**, 3292 (1895); ibid., **30**, 273 (1897).

[4] E.C. Bingham, L.W. Spooner, *Physics*, **4**, 387 (1933).

[5] G.C. Kennedy, *Am. J. Sci.*, **248**, 540 (1950).

[6] F.G. Keyes, *J. Chem. Phys.*, **17**, 923 (1949).

[7] E. Schroer, *Z. phys. Chem.*, **129**, 79 (1927).

[8] H. Eck, *Phys. Z.*, **40**, 3 (1939).

the author has learned that this b value gives better constancy for $(2-\varepsilon)$ than $v_c=2.56$ cc./g. i.e., $b=15.39$ cc./mol. above explained, and so the author, adopting also from Kennedy's data, has carried out calculations for $(2-\varepsilon)$ values and their corresponding percentage deviations, $100\ (p_{calc.}-p_{obs.})/p_{obs.}$, for the pressure range 100 to 1000 bars at 200 to 370°C, and 100 to 2500 bars at 380 to 600°C. A half of their results are tabulated in Tables II and III, and the full values of $(2-\varepsilon)$ are diagrammatically shown in Fig. 1, in which the values from Kennedy's data and the values from Henning's tables are denoted by ○ and × respectively.

It follows from Tables II—III and Fig. 1 that the excellent constancies of $(2-\varepsilon)$ and low percentage deviations throughout the temperature studied afford a conclusive proof to the availability of the author's equation for both liquid and vapour states, and that the linearity of $(2-\varepsilon)$ with temperature is strongly confirmed above 250°C as would be expected, the linearity being expressible by $2-\varepsilon=1.771+0.0001683\ (T-T_c)$ where $T_c=647.4$°K.

At the end of this study we shall add another deduction of the new equation from

TABLE II

$(2-\varepsilon)$ VALUES OF WATER AT 200 TO 600°C

p bars	Temperature in °C										
	200	220	240	260	280	300	320	340	350	360	370
100	1.746	1.748	1.749	1.752	1.754	1.757	(1.745)	(1.756)	(1.763)	(1.768)	(1.774)
150	1.746	1.748	1.750	1.752	1.754	1.758	1.760	1.764	(1.744)	(1.749)	(1.756)
200	1.746	1.748	1.750	1.752	1.755	1.758	1.760	1.764	1.766	1.767	(1.745)
250	1.746	1.748	1.750	1.752	1.755	1.757	1.760	1.764	1.765	1.767	1.769
300	1.746	1.748	1.750	1.753	1.755	1.758	1.761	1.764	1.766	1.767	1.768
350	1.746	1.748	1.751	1.753	1.755	1.758	1.761	1.764	1.766	1.767	1.769
400	1.746	1.748	1.750	1.753	1.755	1.758	1.761	1.764	1.766	1.767	1.769
500	1.745	1.748	1.750	1.753	1.755	1.758	1.761	1.764	1.766	1.768	1.770
600	1.745	1.748	1.750	1.752	1.756	1.758	1.761	1.765	1.766	1.768	1.770
700	1.745	1.747	1.750	1.752	1.755	1.759	1.762	1.765	1.767	1.768	1.770
800	1.745	1.747	1.749	1.752	1.755	1.759	1.762	1.765	1.767	1.769	1.771
900	1.743	1.747	1.749	1.752	1.755	1.758	1.762	1.766	1.767	1.769	1.771
1000	1.743	1.745	1.748	1.752	1.756	1.759	1.762	1.766	1.767	1.769	1.771
mean	1.745	1.748	1.750	1.752	1.755	1.758	1.761	1.765	1.766	1.768	1.770

p bars	Temperature in °C										
	390	410	430	450	470	490	510	530	550	570	590
100	(1.787)	(1.784)	(1.788)	(1.795)	(1.799)	(1.804)	(1.808)	(1.810)	(1.813)	(1.814)	(1.818)
150	(1.767)	(1.776)	(1.784)	(1.791)	(1.798)	(1.805)	(1.812)	(1.816)	(1.820)	(1.822)	(1.826)
200	(1.755)	(1.765)	(1.773)	(1.781)	(1.790)	(1.797)	(1.804)	(1.809)	(1.814)	(1.818)	(1.823)
250	(1.754)	(1.759)	(1.767)	(1.775)	(1.783)	(1.791)	(1.799)	(1.806)	(1.813)	(1.818)	(1.824)
300	1.771	(1.762)	(1.765)	(1.771)	(1.779)	(1.786)	(1.794)	(1.802)	(1.809)	(1.814)	(1.820)
350	1.771	(1.771)	(1.768)	(1.770)	(1.776)	(1.783)	(1.791)	(1.799)	(1.807)	(1.813)	(1.819)
400	1.774	(1.773)	(1.773)	(1.772)	(1.776)	(1.781)	(1.787)	(1.794)	(1.802)	(1.809)	(1.815)
450	1.773	1.776	(1.775)	(1.776)	(1.777)	(1.781)	(1.786)	(1.791)	(1.796)	(1.802)	(1.809)
500	1.773	1.775	1.777	1.778	1.779	1.781	1.786	1.791	1.796	1.801	1.807
600	1.773	1.776	1.778	1.781	1.782	1.784	1.787	1.790	1.795	1.801	1.806
700	1.774	1.777	1.780	1.782	1.784	1.787	1.789	1.792	1.796	1.800	1.804
800	1.774	1.777	1.780	1.783	1.786	1.788	1.791	1.794	1.797	1.801	1.805
900	1.774	1.778	1.780	1.783	1.786	1.789	1.792	1.795	1.798	1.802	1.807
1000	1.774	1.778	1.780	1.783	1.786	1.789	1.792	1.795	1.799	1.803	1.807
1200	1.775	1.778	1.781	1.783	1.786	1.789	1.792	1.795	1.800	1.804	1.808
1400	1.775	1.778	1.780	1.783	1.786	1.789	1.792	1.795	1.799	1.804	1.808
1600	1.775	1.779	1.782	1.786	1.788	1.790	1.793	1.796	1.799	1.803	1.807
1800	1.775	1.779	1.783	1.787	1.790	1.794	1.795	1.797	1.799	1.802	1.806
2000	1.774	1.779	1.784	1.788	1.791	1.794	1.797	1.799	1.801	1.804	1.806
2250	1.774	1.779	1.784	1.788	1.792	1.796	1.799	1.801	1.804	1.806	1.808
2500	1.772	1.778	1.783	1.788	1.792	1.796	1.800	1.803	1.806	1.807	1.810
mean	1.774	1.778	1.781	1.784	1.787	1.790	1.793	1.796	1.799	1.803	1.807

TABLE III

PERCENTAGE DEVIATIONS, 100 $(p_{calc.}-p_{obs.})/p_{obs}$ FOR WATER AT 200 TO 600°C

p bars	Temperature in °C										
	200	220	240	260	280	300	320	340	350	360	370
100	−21.97	+8.29	+7.53	+4.45	+11.47	+11.86	+4.37	+1.91	+0.65	+0.05	+ 0.00
150	−13.15	+3.45	+3.85	+1.76	+ 5.41	+ 7.67	+5.84	+9.51	+9.41	+6.51	+ 4.15
200	−10.59	+2.30	+1.50	−0.88	+ 3.79	+ 5.03	+5.37	+8.37	+3.40	+4.89	+15.95
250	−11.57	+0.66	+1.21	−1.21	+ 1.75	+ 2.89	+3.22	+6.82	+2.87	+5.39	+ 4.74
300	− 5.82	+0.17	+0.45	−1.44	+ 0.69	+ 1.97	+2.05	+5.54	+2.14	+4.71	+ 5.17
350	− 7.50	+1.14	−0.64	−2.95	− 0.65	+ 0.19	+0.83	+4.63	+1.53	+3.80	+ 4.56
400	− 8.94	−0.17	+0.35	−1.43	− 0.08	+ 0.39	−0.02	+3.47	+1.46	+1.85	− 1.66
500	− 2.57	+1.48	+0.22	−1.60	− 0.47	− 0.38	−0.96	+1.73	+0.70	+0.69	+ 1.08
600	− 1.05	+1.84	+0.77	−1.55	− 0.60	− 0.97	−1.36	+1.23	−0.29	+0.09	− 0.58
700	+ 1.19	+2.20	+1.59	−0.80	− 0.90	− 1.08	−1.73	+0.38	−0.97	−0.58	− 0.48
800	+ 2.77	+3.64	+1.63	−0.47	− 0.52	− 1.09	−1.87	−0.13	−0.72	−1.19	− 1.32
900	+ 3.68	+4.52	+2.55	+1.06	− 0.09	− 1.31	−2.15	−0.48	−1.46	−1.59	− 1.75
1000	+ 5.19	+5.17	+3.35	+1.45	+ 0.57	− 1.00	−1.67	−0.44	−1.51	−1.71	− 1.60
mean	7.38	2.69	1.97	1.62	2.08	2.76	2.43	3.43	1.55	2.54	3.31

p bars	Temperature in °C										
	390	410	430	450	470	490	510	530	550	570	590
100	− 1.31	− 0.83	− 0.78	−1.17	−1.56	−1.29	−1.28	−1.10	−0.70	−0.78	−0.67
150	+ 1.58	+ 0.31	− 0.56	−1.09	−1.47	−1.94	−2.12	−2.12	−1.99	−1.75	−1.25
200	+ 7.76	− 4.16	+ 1.99	+0.68	−0.48	−1.15	−1.67	−1.82	−1.86	−1.71	−1.79
250	+18.70	+ 9.27	+ 5.14	+2.61	+1.08	−0.19	−1.20	−1.69	−2.14	−2.11	−2.18
300	+ 7.90	+15.26	+ 9.04	+5.38	+2.80	+1.19	−0.26	−1.26	−1.82	−1.88	−2.01
350	+ 7.34	+11.40	+13.05	+6.34	+4.94	+2.53	−0.67	−0.65	−1.63	−1.93	−2.12
400	+ 4.18	+ 8.98	+10.56	+8.80	+6.28	+3.66	+2.21	+0.72	−0.68	−1.27	−1.67
450	+ 2.60	+ 3.47	+ 7.99	+8.11	+6.68	+4.70	+3.14	+1.86	+0.77	+0.14	−0.52
500	+ 2.12	+ 4.69	+ 5.84	+6.66	+6.30	+5.36	+3.51	+2.17	+1.17	+0.49	−0.01
600	+ 1.45	+ 3.10	+ 3.67	+4.42	+4.55	+4.59	+3.87	+2.89	+1.73	+0.88	+0.36
700	− 0.23	+ 1.77	+ 1.61	+1.94	+2.58	+2.76	+2.88	+2.49	+1.55	+1.33	+0.99
800	+ 0.45	+ 1.20	+ 1.20	+0.83	+1.13	+1.36	+1.47	+1.47	+1.23	+1.00	+0.64
900	+ 0.22	+ 0.65	+ 1.03	+0.84	+0.93	+0.97	+1.06	+0.92	+0.63	+0.39	+0.17
1000	− 0.64	+ 0.40	+ 0.60	+0.80	+0.87	+0.81	+0.89	+0.68	+0.15	−0.08	−0.12
1200	− 1.13	+ 0.17	+ 0.15	+0.71	+0.84	+0.70	+0.64	+0.37	−0.32	−0.54	−0.56
1400	− 0.82	+ 0.06	+ 0.58	+1.02	+1.07	+0.98	+0.94	+0.51	−0.16	−0.66	−0.67
1600	− 0.62	− 0.58	− 1.10	−1.35	−0.99	−0.20	−0.15	+0.27	+0.08	+0.76	+0.01
1800	− 1.53	− 0.86	− 1.51	−1.98	−2.11	−2.72	−1.07	−0.46	−0.14	+0.32	+0.54
2000	− 0.23	− 0.61	− 1.84	−2.54	−2.92	−2.70	−2.34	−1.70	−1.32	−0.29	+0.40
2250	+ 0.04	− 0.48	− 1.89	−2.61	−3.16	−3.23	−3.21	−2.89	−2.68	−1.48	−0.58
2500	+ 1.27	+ 0.28	− 1.07	−2.48	−2.93	−3.35	−3.44	−2.87	−3.14	−2.04	−1.31
mean	2.96	3.26	3.39	2.93	2.65	2.21	1.67	1.47	1.23	1.04	0.88

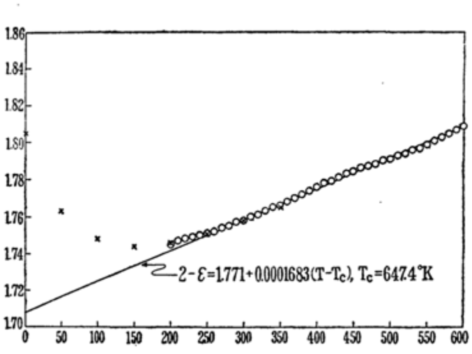

Fig. 1. The temperature dependence of (2−ε) of water.

the standpoint of kinetic theory of gases by taking the idea of molecular association into consideration in the well-known deduction of van der Waals' equation.[9]

In a liquid, single molecules may form themselves into associated molecules[10], each of which is not a fast-combined molecule but is a group composed of no other molecules than singly existing molecules, or more concretely speaking, into cybotactic groups[11], in

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[9] e.g., S. Glasstone, "Textbook of Physical Chemistry", p. 289 (2nd Edition).

[10] T. Ishikawa, This Bulletin, **4**, 5 (1929); T. Ishikawa, T. Baba, ibid., **11**, 64 (1936).

[11] G.W. Stewart, *Rev. Mod. Phys.*, **2**, 116 (1930); *Koll. Z.*, **67**, 130 (1934).

each of which the molecules are arranged in a relatively orderly manner, but the groups are not to be regarded as permanent or as having sharp boundaries, for the movement of the molecules must result in a continual shifting of position and exchange of the members of the cybotactic groups with those in the space between.

If the above idea is extended to the gaseous phase, the force exerted on a single molecule about to strike the wall is, as usually regarded, evidently proportional to the density, ρ, but the number of molecules striking the wall at any instant may be proportional to the density slightly less than ρ, because such molecular groups undoubtedly retard their composition of single molecules striking the wall, that is to say $\rho^{1-\varepsilon}$, if the density under consideration is taken as the simplest power form of ρ, where ε is a correction factor dependent on molecular association and therefore probably independent of pressure, so that the cohesive pressure is proportional to $\rho \cdot \rho^{1-\varepsilon} = \rho^{2-\varepsilon}$. Applying volume correction as is usually done, the author's equation readily follows: $(p + a/V^{2-\varepsilon})(V-b) = RT$, in which constant a is the same as that of van der Waals' equation, if ε is small as compared with unity, and constant b is $V_c/3$ which fits a thermodynamic equality $b = V - R\beta/\alpha$ for normal liquids, hence $a = 3p_cV_c^2$, $b = V_c/3$, and $RT_c/p_cV_c = 2(1+3V_c^{\varepsilon})/3$; this last relation rejects $b = RT_c/8p_c$ (the other solution of b) for the corrected form of van der Waals' equation.

In conclusion, the author expresses his hearty thanks to Nagasaki American Cultural Center who has furnished him with American journals at his request.

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