Note on the Constancy of ϵ in the New Equation of State

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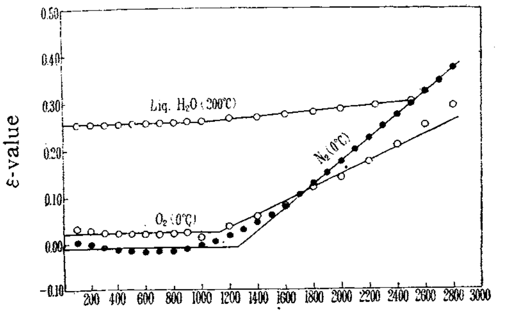
From the successive studies[1], I am convinced that in my equation of state, $(p+$

$a/V^{2-\varepsilon})(V-b)=RT$, $a=3p_cV_c^2$, $b=v_c/3$, which is valid for gases and liquids, an analytically determinable constant, ε, depends upon the molecular association, and isothermal ε values keep constant so far as the molecular association is little affected by applied pressures.

If the above conception of isothermal ε values is right, the change in molecular association, and hence the change in isothermal ε values at elevated pressures should go in the direction of increasing their values.

For water, as would be expected, isothermal ε values at 200°C for the critical temperature have been found to increase above 1000 bars, the manner of which is exemplified in Fig. 1 which shows ε -- p(pressure) diagram at 200°C, the lowest temperature taken by Kennedy[2]. The constant range of ε is fairly good, and the change in ε at elevated pressures above 1000 bars is strictly linear up to his applied highest pressure, 2500 bars.

Similar phenomena are also observed for gaseous nitrogen and oxygen (see Fig. 1), which are the only two cases of being adoptable from International Critical Tables[3]. In these cases, however, the points which should belong to the constant range of ε are somewhat doubtful, and so it may be necessary to test percentage deviations of the calculated pressures from the observed pressures, 100 $(p_{calc.}-p_{obs.})/p_{obs.}$ (see Table I). As seem from Table I, the deviations are probably within the error limits, so that in these cases also the constant ranges of ε undoubtedly exist up to about 1000 atm., but the increasing rates of ε above 1000 atm. seem to be different from each other: for nitrogen the rate is linear at 1000 to 1600 atm. but strictly constant above 1600 up to 2800 atm., whereas for oxygen the rate is nearly constant at 1100 to 2400 atm.



Pressure, bars for H_2O, atm. for N_2 atd O_2

Fig. 1. ε-p Diagrams for Livuid H_2O at 200°C and for N_2 and O_2 at 0°C.

The above analyses lead to the conclusion that isothermal ε values against pressures are composed of two parts, the one being that of a constant range where no change in molecular association occurs at low to moderately high pressures, and the other being that of linear range, where molecular association is forced into a greater degree at elevated pressures above the limiting pressure which may be particular for a particular substance.

TABLE I

PERCENTAGE DEVIATIONS FOR THE CONSTANT RANGE OF ε AT 0°C

	Nitrogen	Oxygen
	$b=30.03$	$b=24.81$
	$\log a=5.911459$	$\log a=5.916842$
	$\log V$(0°C, 1 atm.) $=4.350323$	$\log V$(0°C, 1 atm.) $=4.350134$
p(atm.)	% deviation	% deviation
100	+1.10	+1.27
200	+1.09	+1.14
300	+0.21	+0.53
400	−0.59	−0.34
500	−1.44	−0.68
600	−1.56	−0.83
700	−1.38	−0.99
800	−1.25	−0.71
900	−0.48	−0.31
1000	+0.63	+0.42
	mean 0.97	mean 0.72

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[1] T. Ishikawa, This Bulletin, 26, 78, 530 (1953), 27, 226, 570 (1954); T. Ishikawa, M. Ikeda, ibid., 26, 516 (1953).

[2] G. C. Kennedy, *Amer. J. Sci.*, 248, 540 (1950).

[3] International Critical Tables, III, p. 8 for O_2, and p. 17 for N_2, both being the measurements by Amagat.

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