In previous discussions it has been assumed that the reaction

$$OH + OH \longrightarrow H_2 + O_2$$

would have too high a heat of activation to take place. The argument for this is somewhat involved but starts with the fact that no reaction is observed between hydrogen and oxygen at room temperatures. Possible reactions are

$$\begin{aligned} H_2 + O_2 &\longrightarrow H_2O + O && (6)\\ &\longrightarrow OH + OH && (7)\\ &\longrightarrow H_2O_2 && (8)\end{aligned}$$

One may believe that the heats of activation for reactions (6) and (8) are high but these reactions are also inherently improbable and do not concern us here.

Reaction (7), on the other hand, is probably endothermic by 20 kcal. or more so that the failure to observe any reaction between hydrogen and oxygen is not surprising. If the heat of dissociation of the hydroxyl radical is less than 100 kcal. the heat of activation for the reverse reaction may be very small indeed.

There is no direct determination of the heat of dissociation of hydroxyl but the recent work of Dwyer and Oldenberg[7] gives the heat of the reaction

$$H_2O = H + OH, \quad \Delta H = 118 \text{ kcal.}$$

When this datum is combined with the heat of formation of water, we obtain 100 cal. as the heat of dissociation of hydroxyl. In the opinion of the authors, this is an upper limit for the value. The oxygen–hydrogen bond in water has 110 kcal. as its dissociation energy. The loss of one electron could easily reduce the bond strength by 20 kcal. or more.

There is no implication in the foregoing as to the mechanism of the reaction (4) but there are good reasons for assuming that it is a homogeneous reaction. The walls of the apparatus are rendered inactive toward hydrogen atoms by an absorbed layer of water vapor. The recombination of hydrogen atoms has been shown to be due to triple collisions under these conditions. There is no reason, as has been pointed out earlier, to assume that hydroxyl radicals would condense on the walls or that the walls would exert any catalytic activity.

Summary

The formation of hydrogen peroxide from the products of the glow discharge in water vapor is a heterogeneous reaction.

Hydroxyl radicals react rapidly in the vapor phase to form molecular hydrogen and oxygen. This indicates that the heat of dissociation for hydroxyl may be 100 kcal. or less.

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[7] R. J. Dwyer and O. Oldenberg, *J. Chem. Phys.*, **12**, 351 (1944).

[CONTRIBUTION FROM THE NEWARK COLLEGE OF ENGINEERING, NEWARK, N. J.]

A New Equation of State for Gases

BY JOSEPH JOFFE

A new equation of state for gases is proposed in which all the constants are determined from the values of the critical pressure and critical temperature. The equation may be written in generalized form and may be regarded as an analytical expression of the law of corresponding states. This equation differs from generalized equations which have recently been proposed[1,2] in that no fitting of experimental data is required to obtain the values of the constants in the equation.

It is assumed that the equation of the critical isothermal is

$$p = RT/(V - b) - a/V(V - b) + c/V(V - b)^2 - d/V(V - b)^3 + e/V(V - b)^4 \quad (1)$$

The equation is seen to be of the fifth degree in the volume. In this respect it differs from the equations of van der Waals, Clausius, and Berthelot which are of the third degree in the volume, and from the equation of A. Wohl[3] which is of the fourth degree. To obtain the values of the constants the condition is imposed that this fifth degree equation in the volume have five equal roots at the critical point. This leads to the relations

$$\begin{aligned} RT_c &= bp_c + 5p_c\,(V_c - b)\\ a &= RT_cb + 10p_c\,(V_c - b)^2\\ c &= 10p_c\,(V_c - b)^3 \qquad (2)\\ d &= 5p_c\,(V_c - b)^4\\ e &= p_c\,(V_c - b)^5\end{aligned}$$

Any one of the constants in this set of equations may be assigned an arbitrary value whereupon the values of the other constants and of the critical ratio RT_c/p_cV_c are fixed. It was decided to arbitrarily assign a value to the constant b. Comparison of calculations with experimental data demonstrated that the value $b = V_c/4$, appearing in Berthelot's and Wohl's equations, is more satisfactory than either the van der Waals value $b = V_c/3$, or the Dieterici value $b = V_c/2$, in connection with equation (1) and (2). Substituting $b = V_c/4$ in (2) the following equations are obtained

$$\begin{aligned} RT_c &= 4p_cV_c\\ a &= 53p_cV_c^2/8\\ c &= 270\,p_cV_c^3/64 \qquad (3)\\ d &= 405p_cV_c^4/256\\ e &= 243p_cV_c^5/1024\end{aligned}$$

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[1] S. H. Maron and D. Turnbull, THIS JOURNAL, **64**, 2195 (1942).

[2] G. J. Su and C. H. Chang, *ibid.*, **68**, 1080 (1946).

[3] A. Wohl, *Z. physik. Chem.*, **87** 1 (1914); **99**, 207, 226, 234 (1921).

In evaluating the constants a, b, c, d and e with the aid of equation (3), the critical volume V_c is eliminated through the relation $V_c = RT_c/4p_c$ and the constants are computed from the experimental values of the critical temperature and critical pressure. This procedure is analogous to the one usually employed in the evaluation of the van der Waals constants from critical data.

A comparison of equations (1) and (3) with Wohl's equation, $p = RT/(V - b) - a/V(V - b) + c/V^3$, has been made for the critical isothermal of *i*-pentane. There is substantial agreement of calculated pressures with those calculated with Wohl's equation and with observed pressures down to the critical volume. Below the critical volume equations (1) and (3) give only a qualitative agreement with observed values, while Wohl's equation fails entirely, as can be seen from Table I. The failure of Wohl's equation is due to the fact that his critical isothermal has a maximum instead of a point of inflection at the critical point.[4] Wohl's equation therefore fails to reproduce the continuity of the vapor and liquid states. Equation (1), on the other hand, like the van der Waals equation, gives a critical isothermal which has a point of inflection with a horizontal tangent.

TABLE I

CRITICAL ISOTHERMAL OF ISOPENTANE[a]

Vol. in cc. per g.	p observed in mm.	p calcd. eq. (1), (3)	p calcd. Wohl's eq.
4.0	25.020	25.00	25.00
3.0	26.460	25.48	23.82
2.5	40.560	39.24	14.47
2.4	49.080	52.04	9.04

[a] V_c = 4.266 cc. per g.; p_c = 25.005 mm.; T_c = 461.0°K.

In order to extend equation (1) to temperatures other than the critical the temperature dependence of the constants, a, b, c, d and e must be established.[5] It is assumed provisionally that b is independent of the temperature and that for temperatures other than the critical equation (1) may be written

$$p = RT/(V - b) - aT_c/V(V - b)T + cT_c^{3/2}/V(V - b)^2T^{3/2} - dT_c^2/V(V - b)^3T^2 + eT_c^{5/2}/V(V - b)^4T^{5/2} \tag{4}$$

Equation (4) has been tested against G. J. Su's generalized isometrics based on data of seven hydrocarbons.[2] For the purpose of this comparison the equation is best written in reduced form according to the method suggested by G. J. Su and C. H. Chang.[2] Employing the ideal reduced volume $\varphi = Vp_c/RT_c$, and denoting the reduced temperature with θ and the reduced pressure with π, equation (4) becomes

$$\pi = 16\theta/(16\varphi - 1) - 53/8\theta\varphi(16\varphi - 1) + 135/8\theta^{3/2}\varphi(16\varphi - 1)^2 - 405/16\theta^2\varphi(16\varphi - 1)^3 + 243/16\theta^{5/2}\varphi(16\varphi - 1)^4 \tag{5}$$

The reduced pressures read from the generalized isometrics were compared with those calculated from equation (5), those calculated from the generalized Beattie–Bridgeman equation of Su and Chang,[2] and those calculated from Wohl's equation. The total average per cent. deviation for the 59 points tested is 0.64% for equation (5), 0.66% for the generalized Beattie–Bridgeman equation, and 0.81% for Wohl's equation. Table II gives the average per cent. deviation at each reduced temperature.

TABLE II

DEVIATION OF CALCULATED FROM OBSERVED REDUCED PRESSURES FOR GENERALIZED ISOMETRICS[a]

	Average % deviation at following reduced temperatures							
	1.00	1.10	1.20	1.30	1.40	1.60	2.00	2.40
Equation (5)	0.28	0.39	0.66	0.54	0.75	1.08	0.72	0.77
Generalized Beattie–Bridgeman equation	.63	.86	1.10	.92	.61	0.28	.31	.36
Wohl's equation	.46	.48	0.88	.92	.98	1.24	.94	.54

[a] The range covered is $\varphi = 4$ to $\varphi = 2/7$.

Since nitrogen is known to obey the law of corresponding states fairly well,[6] equation (5) has also been tested against compressibility data for nitrogen. Smoothed data of observed pressures[7] for nitrogen were compared with those calculated from equation (5) as well as with values calculated by G. J. Su and C. H. Chang[8] from the generalized van der Waals equation of state. The total average per cent. deviation for the 67 points tested is 0.61% for equation (5) and 1.80% for the generalized van der Waals equation. Table III shows the average per cent. deviation at each of the densities tested.

Additional criteria of agreement with the law of corresponding states which may be applied in testing equations of state are the values of the critical ratio RT_c/p_cV_c, the Boyle temperature, and the Joule–Thomson inversion points. Equation (4) predicts a value of 4 for the critical ratio, 2.57 for the reduced Boyle temperature, and 4.46 for the reduced maximum Joule–Thomson inversion temperature.

TABLE III

DEVIATION OF CALCULATED FROM OBSERVED PRESSURES FOR NITROGEN[a]

	Average % deviation at following densities in moles per liter							
	0.5	1.0	1.5	2.0	3.0	4.0	5.0	5.5
Equation (5)	0.19	0.35	0.54	0.65	0.66	0.82	1.18	1.26
van der Waals equation	0.46	0.91	1.35	1.79	2.55	2.98	3.31	3.60

[a] The temperature range covered is −146.32 to 400°.

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(4) R. Wegscheider, *Z. physik. Chem.*, **99**, 361 (1921).

(5) An equation of the fifth degree in V of the form $P = RT/(V - b) - A_2/(V - b)^2 + A_3/(V - b)^3 - A_4/(V - b)^4 + A_5/(V - b)^5$ has been proposed by R. Plank (*Forsch. Gebiete Ingenieurw.*, **7**, 161 (1936)). However, no general law for the variation of the coefficients A_2, A_3, A_4 and A_5 with temperature has been advanced by Plank.

(6) R. H. Newton, *Ind. Eng. Chem.*, **27**, 302 (1935).

(7) J. A. Beattie and O. C. Bridgeman, *Proc. Am. Acad. Arts Sci.*, **63**, 229 (1928).

(8) G. J. Su and C. H. Chang, *Ind. Eng. Chem.*, **38**, 800 (1946).

The values deduced from van der Waals equation are, respectively, 2.67 for the critical ratio, 3.38 for the reduced Boyle temperature and 6.75 for the reduced maximum inversion temperature. The average experimental value for the critical ratio is 3.7 and that for the reduced Boyle temperature is near 2.5. The maximum inversion temperature has been established for only a few substances. The reduced value for nitrogen[9] is 4.93, that for air[10] is 4.55. It is seen that the values predicted by equation (4) are considerably closer to the experimental ones than those deduced from van der Waals equation.

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(9) J. R. Roebuck and H. Osterberg, *Phys. Rev.*, **48**, 450 (1935).

(10) J. R. Roebuck and H. Osterberg, *ibid.*, **43**, 60 (1933).

Summary

An equation of state for gases, equation (4) is proposed, in which all the constants can be calculated from the critical values of the temperature and pressure in a manner analogous to the evaluation of van der Waals constants. This equation is believed to reproduce the behavior of real gases with a higher degree of accuracy than the van der Waals equation. In the reduced form (5) it represents an analytical expression of the law of corresponding states.

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Atomic Radii and Interatomic Distances in Metals[1]

BY LINUS PAULING

The problem of the nature of the interatomic forces in the elementary metals and in intermetallic compounds and other alloys continues to be puzzling, despite the clarification of some questions which has been provided by quantum mechanical considerations.[2] It has been my opinion,[1,3] contrary to that of other investigators,[4,5] that the metallic bond is very closely related to the covalent (shared-electron-pair) bond, and that each atom in a metal may be considered as forming covalent bonds with neighboring atoms, the covalent bonds resonating among the available interatomic positions. It was shown in the first paper of this series[1] that the number of covalent bonds resonating among the available positions about an atom (the metallic valence of the atom) increases from one to nearly six (5.78) in the sequence K, Ca, Sc, Ti, V, Cr in the first long period of the periodic table, remains nearly constant from Cr to Ni, and begins to decrease with Cu. This concept, which is substantiated by the magnetic properties of the metals and their alloys, provides a qualitative explanation of many properties of the transition metals (including those of the palladium and platinum groups), such as characteristic temperature (heat capacity at low temperatures), hardness, compressibility, coefficient of thermal expansion, and the general trend of interatomic distances. It will be shown in the following pages that it also permits the formulation of a system of atomic radii which can be used for the calculation of interatomic distances in metals and intermetallic compounds and for the interpretation of observed interatomic distances in terms of the electronic structure of the crystals. These atomic radii (which may be called metallic radii) are found, as expected, to show an intimate relation to the covalent radii of the atoms—a relation which, in its general nature, permitted Goldschmidt[6] over twenty years ago to use data taken from both metals and ordinary covalent crystals in formulating a table of atomic radii, and which has been recognized[3] as providing very strong support for the concept that metallic bonds are essentially resonating covalent bonds.

The Relation of Atomic Radius to Bond Type

In the discussion of metallic radii we may make a choice between two immediate alternative procedures. The first, which I shall adopt, is to consider the dependence of the radius on the type of the bond, defined as the number (which may be fractional) of shared electron pairs involved (corresponding to the single, double, and triple bonds in ordinary covalent molecules and crystals), and then to consider separately the effect of resonance in stabilizing the crystal and decreasing the interatomic distance. This procedure is similar to that which we have used in the discussion of interatomic distances in resonating molecules.[7a] The alternative procedure would be to assign to each bond a number, the bond order, to represent the strength of the bond with inclusion of the resonance effect as well as of the bond type.[8]

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(1) "The Nature of the Interatomic Forces in Metals. II." For paper I of this series see L. Pauling, *Phys. Rev.*, **54**, 899 (1938).

(2) A. Sommerfeld and H. Bethe, "Handbuch der Physik," Vol. 24, second edition; N. F. Mott and H. Jones, "The Theory of the Properties of Metals and Alloys," Oxford University Press, Oxford, 1936; F. Seitz, "The Modern Theory of Solids," McGraw-Hill Book Co., New York, N. Y., 1940.

(3) L. Pauling, "The Nature of the Chemical Bond," 2nd ed., Cornell University Press, 1940, chap. XI.

(4) J. D. Bernal, *Trans. Faraday Soc.*, **25**, 367 (1929).

(5) W. L. Bragg, *J. Roy. Soc. Arts*, **85**, 430 (1937).

(6) V. M. Goldschmidt, "Geochemische Verteilungsgesetze der Elemente," Vol. VII, Oslo, 1926.

(7) L. Pauling, *Proc. Natl. Acad. Sci.*, **18**, 293 (1932); L. Pauling, L. O. Brockway and J. Y. Beach, THIS JOURNAL, **57**, 2705 (1935); L. Pauling and L. O. Brockway, *ibid.*, **59**, 1223 (1937); ref. 3, Chap. V.

(8) W. G. Penney, *Proc. Roy. Soc.* (London), **A158**, 306 (1937).