data for the 1,2,3- and 1,3,5- isomers were taken from the literature.[8]

TABLE II

DERIVATIVES OF TRICHLOROBENZENES FROM DEHYDROHALOGENATION OF ISOMERIC BENZENE HEXACHLORIDES

Source	B. p., °C.	M. p., °C.	Derivative, m. p., °C.		
			Mononitro	Dinitro	Anilino
α-Isomer	212–215	11	48–54	99–101	182–183
β-Isomer	210–215	14	55–58	103–104.5	182–183
γ-Isomer	207–214	13	53–58	103–104	183–184
Δ-Isomer	212–215	16	55–58	102–104	183–184
ε-Isomer	.....	..	55–58	102–103.5	183–184
1,2,4-Trichlorobenzene	212–215	15	55–57	102–104	184–185
1,2,3-Trichlorobenzene[a]	218–219	53	55–56	92–93	136–138
1,3,5-Trichlorobenzene[a]	208	63.5	67–68	128.5	179–180

[a] Huntress and Carten, ref. 8.

It is apparent from these data that the dehydrohalogenation product of each of the five isomers of benzene hexachloride under the conditions specified herein is almost exclusively 1,2,4-trichlorobenzene. The three derivatives of 1,2,4-trichlorobenzene may be designated precisely as 2,4,5-trichloro-1-nitrobenzene, 2,4,5-trichloro-1,3-dinitrobenzene and 2,6-dianilino-5-chloro-1,3-dinitrobenzene. Since the α-isomer (m. p. 157°) has been reported[1] to yield also traces of 2,4-dichlorophenol, 2,4,6-trichlorophenol, pyrocatechol and "other products" upon heating with water to 200° in a closed tube, it is reasonable to assume that traces of these materials occurred in the present investigation, although they were not isolated (*cf.* the yields in Table I).

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Dieterici's Equation Modified

BY JOSEPH JOFFE

One of the early attempts to improve on the van der Waals equation of state is the equation

$$p = \frac{RT}{v - b} e^{-a/vRT} \qquad (1)$$

proposed by Dieterici[1] on semi-empirical grounds. The equation has been studied by several investigators[2,3,4] and has been found to possess certain advantages over the van der Waals equation.

Dieterici's equation, however, has achieved its greatest success in a modified form

$$p = \frac{RT}{v - b} e^{-aT_c{}^{1/2}/vRT^{3/2}} \qquad (2)$$

first used by Dieterici[5] in fitting experimental data at temperatures other than the critical. This form was also used by Porter in fitting the Joule–Thomson inversion curves of nitrogen and carbon dioxide[6] and was found by him to give good correspondence with *p-v-t* data at moderate pressures.[7]

TABLE I

COMPARISON OF EQUATIONS OF STATE

	RT_c/p_cv_c	Boyle temp., T_c	Joule–T. max. invers. temp., T_c	$\left(\frac{T}{p}\frac{\partial p}{\partial T}\right)_{\text{crit.}}$
van der Waals eqn.	2.67	3.37	6.75	4
Eqn. (1)	3.69	4.00	8.00	3
Eqn. (2)	3.69	2.52	4.64	4
Eqn. (3)	3.69	2.52	4.64	6.2
Av. obs. value	3.7	2.5	~5	7

It can be seen from Table I, in which several tests are applied to equations of state, that equation (2) should be more successful than equation (1). However, with respect to the critical value of the pressure coefficient at constant volume, $T/p\ \partial p/\partial T$, equation (2) represents but a slight improvement on equation (1).

A further modification of Dieterici's equation is here proposed:

$$p = \frac{RT}{v - b} - \frac{R\sqrt{TT_c}}{v - b}\left(1 - e^{-a/vRT}\right) \qquad (3)$$

The second virial coefficients in the virial expansions of equations (2) and (3) are identical, so that equation (3) reduces to equation (2) at low pressures and large volumes. At the critical temperature equation (3) like equation (2) reduces to equation (1). Equation (3), however, gives a value of 6.2 for the pressure coefficient at the critical point, close to the experimental value of 7 observed for non-polar substances, and may therefore be more satisfactory than equation (2) at higher pressures.

Since nitrogen is representative of the average behavior of non-polar gases,[8] equations (1), (2) and (3) have been compared against smoothed compressibility data of this gas. In each case the volumes tabulated by Deming and Shupe[9] for pressures of 20 to 100 atmospheres between −70 and 600° were used to calculate the pressures. The values of the constants a and b in all three equations were obtained from the critical temperature and pressure of nitrogen with the aid of the relationships $a = 4R^2T_c^2/p_ce^2$, $b = RT_c/p_ce^2$ in accordance with the usual procedure.[10]

Inspection of Table II shows that equation (3) gives better results than either equation (1) or (2), except for a restricted temperature interval

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(1) C. Dieterici, *Wied. Ann.*, **69**, 685 (1899).

(2) J. H. Jeans, "The Dynamical Theory of Gases," Cambridge University Press, 1916, pp. 174–177.

(3) F. H. MacDougall, THIS JOURNAL, **38**, 528 (1916); **39**, 1229 (1917).

(4) S. F. Pickering, U. S. Bureau of Standards Circular No. 279 (1925).

(5) C. Dieterici, *Ann. Physik*, **5**, 51 (1901).

(6) A. W. Porter, *Phil. Mag.*, **19**, 888 (1910).

(7) A. W. Porter in "Glazebrook's Dictionary of Applied Physics," The Macmillan Company, 1922, Vol. I, pp. 892–893.

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

(9) W. E. Deming and L. E. Shupe, *Phys. Rev.*, **37**, 638 (1931).

(10) B. F. Dodge, "Chemical Engineering Thermodynamics," McGraw-Hill Book Co., New York, N. Y., 1944, p. 179.

over which equation (2) fits the data best. It is significant that over the temperature and pressure range studied equation (3) gives a maximum deviation of 1.9% as compared with 6.7% for equation (2) and 20.0% for equation (1), the three maximum deviations occurring at −70° and 100 atmospheres. The over-all behavior of the gas is represented best by equation (3).

It appears from this study that in the case of gases which, like nitrogen, obey the law of corresponding states fairly well, equation (3) has an advantage over other forms of Dieterici's equation heretofore used. Equation (3) does not possess the accuracy of equations of state with several adjustable constants, such as the Beattie–Bridgeman equation. It does, however, retain the theoretical advantage of Dieterici's original equation, since it has only two constants in addition to the gas constant, and since these constants may be eliminated in terms of the critical constants, giving a reduced equation of state.

TABLE II

DEVIATIONS OF CALCULATED FROM OBSERVED PRESSURES FOR NITROGEN[a]

Temp., °C.	Eq. (1)	Eq. (2)	Eq. (3)
−70	11.47	3.32	1.29
−50	9.76	2.08	0.71
−25	8.21	1.18	.29
0	7.02	0.62	.03
20	6.22	.31	.16
50	5.29	.09	.32
100	4.07	.36	.53
200	2.69	.49	.56
300	1.94	.50	.53
400	1.35	.51	.53
500	0.98	.51	.53
600	.73	.49	.49
Total av. % dev.	4.98	.87	.50

[a] The value entered for each temperature is the average of the per cent. deviations of the calculated from the observed pressures at 20, 40, 60, 80, and 100 atmospheres.

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Kinetics of Development by Catechol

BY T. H. JAMES

Catechol as a photographic developer behaves in some ways as a typical singly charged agent[1] and is presumably active in the form of the univalent ion. The way in which the rate of development depends upon the pH cannot be explained, however, simply on the basis of a change in the concentration of the univalent ion. Thus, Bürki and Ostwalt[2] found that the rate of development increased nearly fivefold when the pH was increased from 9.20 to 10.37. The pK_1 value for catechol in a solution of the salt concentration used by them is about 9.20,[3] so that complete primary ionization of the catechol would result in merely doubling the concentration of the univalent ion over its value at pH 9.2. Accordingly, the bivalent ion also must be active. The pK_2 value for the second ionization of catechol has not been determined, and must be higher than 12. Joslyn and Branch have obtained evidence that the bivalent ion is an active absorber of oxygen in the oxygen oxidation of catechol at pH above 10, and have estimated from their kinetic data that the pK_2 value is about 13.

Kinetic experiments on development, carried out under simplified conditions, previously described,[4] indicate that the bivalent ion of catechol is active in the later stages of development even at a pH as low as 7. The catechol was used in phosphate buffered solution and in the absence of sulfite. Development was carried out in the absence of oxygen.

Figure 1 shows the dependence of development rate upon catechol concentration at pH 7.70. The upper curve, R, refers to development rates determined on the basis of the maximum rate of increase of density per unit time, and hence to development well beyond the induction–period. The lower curve, $1/t$, refers to rates which were determined as the reciprocal of the time required to obtain a density of 0.10, or approximately 3% of the maximum density obtainable. These are largely, although not purely, induction–period rates. The slope of the R plot is 0.57, that of the $1/t$ plot is 0.73, indicating adsorption of the developing agent prior to reaction.[4]

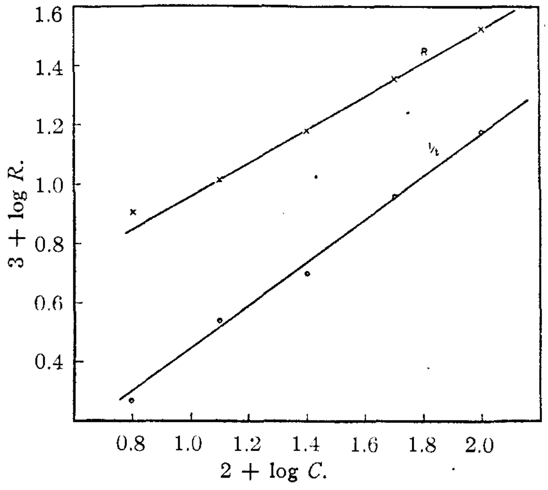

Fig. 1.—Dependence of development rate on catechol concentration at pH 7.70; log E = 1.90.

Figure 2 shows the dependence of development rate upon the pH for constant catechol concentration. The slope of the R plot is 1.01, that of the $1/t$ plot is 0.82. If the univalent ion only were in-

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