and film behavior of various polymeric type compounds.

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Summary

1. Electron diffraction experiments have been carried out upon very thin films of several synthetic polyesters and natural gutta-percha.
2. *Stretched films* show diffraction patterns characteristic of sharply oriented crystals. Measurements upon these patterns are in excellent agreement with existing X-ray data upon the same materials. The utility of the electron diffraction method for structural studies of polymerized substances is thus demonstrated.
3. *Unstretched films of gutta-percha* are found to be composed of relatively large crystallites which are precisely oriented with their fiber axis directions normal to the film surface. It is presumed that the macromolecules are folded back and forth upon themselves in such a way that adjacent sections remain parallel.
4. *Unstretched films of polyethylene sebacate* consist of relatively small crystals which are believed to be oriented with their fiber axis directions approximately in the plane of the film, but with limited rotation around the fiber axis directions.

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Note on a Corresponding-States Equation of Practical Interest for General Physicochemical Computations

By Frederick G. Keyes

During the last few years the desire to compute equilibrium physicochemical quantities under conditions removed from the range of validity of the ideal gas laws has led to a renewed interest in the search for an empirical relation of the corresponding-states character.

One form of this effort has been to test the relation of the fugacity–pressure ratio, γ, to the pressure–critical pressure ratio, π, using the existing p–v–T data for gases, to form a graph of constant temperature–critical temperature, θ, lines. The iso-reduced temperature lines of necessity start from $\gamma = 1$ on the vertical axis[1] and are approximately linear in π for θ large, but become increasingly convex relative to the horizontal, or π, axis for θ small. A chart of this sort for hydrocarbons was prepared and its uses discussed by J. D. Cope, W. K. Lewis and H. C. Weber; W. K. Lewis and C. D. Luke and others.[2] Recently[3] R. H. Newton brought together the data for twenty-four substances and found that within a range of 4%, with some exceptions, the data for the substances in the form $(\gamma)_\theta$ *versus* π fell together. A ficticious critical temperature and pressure, however, had to be selected for H_2 and He to bring the data for these substances into line with other substances.

The existence of an exact, universal correspondence in terms of a relation between θ, π, and φ has, however, good reason to be doubted. The cases of H_2 and He at higher temperatures are well-known examples of how badly the concept works out at ordinary temperatures when the form of the equation of state is based on the van der Waals concept of the molecular field.[4] There does exist, however, a range of temperature for all substances, perhaps, where the van der Waals concept leads to a fair approximation in representing the behavior of individual gases.

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(1) See G. Tunnel's article, *J. Phys. Chem.*, **35**, 2885 (1931), for a comprehensive discussion of the definition and evaluation of the fugacity [G. N. Lewis, *Proc. Am. Acad. Arts Sci.*, **37**, 95 (1901)]. Also, L. H. Adams, *Chem. Rev.*, **19**, 1 (1936).

(2) J. D. Cope, W. K. Lewis and H. C. Weber, *Ind. Eng. Chem.*, **23**, 887 (1931); W. K. Lewis and C. D. Luke, *Trans. Am. Soc. Mech. Eng.*, **54**, 55 (1932); and *Ind. Eng. Chem.*, **25**, 725 (1933); C. W. Selheimer, M. Souders, Jr., R. L. Smith and G. G. Brown, *ibid.*, **24**, 515 (1932); G. G. Brown, W. K. Lewis and H. C. Weber, *ibid.*, **26**, 325 (1936); W. K. Lewis and W. C. Kay, *Oil Gas J.*, **32**, 40, 45 (1934).

(3) R. H. Newton, *Ind. Eng. Chem.*, **27**, 1 (1935). See also, R. H. Newton and B. F. Dodge, This Journal, **56**, 1 (1934).

(4) F. G. Keyes, *Chem. Rev.*, **6**, 175 (1929).

The van der Waals concept is equivalent to the assumption that molecules may be represented in their physical interaction by the existence of a positive potential which becomes infinite on contact of the supposedly rigid spherical molecules of invariable diameter σ, but zero for all distances of separation of molecular centers greater than σ when a spherically symmetrical negative potential appears. The latter may be represented in the simplest cases by the expression cr^{-m} where m is an integer not smaller than 4. If w represents the potential we may write for the van der Waals field the following relation

$$w = \begin{pmatrix} +\infty;\ r = \sigma \\ 0;\ r > \sigma \end{pmatrix} - cr^{-m}$$

The equation of state for low pressures may then be shown to be, for pure gases

$$p = \frac{RT}{v - B_0}$$

where

$$B_0 = \beta - A/RT \sum_{\nu=0}^{\nu=\infty} \frac{(m-3)^{\nu+1}}{(1+\nu)!\cdot 3^{\nu}[(1+\nu)m-3]} \left(\frac{A}{RT\beta}\right)^{\nu} \tag{1}$$

For mixtures of gases we may write quite generally (p small)

$$p = \frac{RT\Sigma n_1}{V - [B_0]} \tag{1A}$$

$$[B_0] = \frac{1}{\Sigma n_1} [\Sigma B_{0\,11}\, n_1^2 + 2\Sigma B_{0\,12}\, n_1\, n_2] \tag{1B}$$

In the van der Waals form for B_0, β is four times the volume of the spheres contained in the volume v and A is proportional to the constant of the negative potential and an inverse power of σ depending on the exponent m. For $m = 6$ we find the following expression

$$B_0 = \beta - \frac{A}{RT}\left[\left(1 + {}^1/_6\, \frac{A}{RT\beta} + {}^1/_{30} \left(\frac{A}{RT\beta}\right)^2 \ldots\right]\right. \tag{2}$$

The chart produced by Roger H. Newton was based on the computation of γ by the equation

$$\gamma = f/p = \exp.\left[(RT)^{-1}\int_0^p (RT/p - v)\, \mathrm{d}p\right] \tag{3}$$

where p, v and T represent the experimental data for the substances. The integrand has been shown repeatedly not to vanish for $p \rightarrow 0$ but on the contrary to reduce to a pure temperature function and this well-established fact accords with the prediction of the statistical theory of gases using for example the specialized concept of the intramolecular potential of van der Waals. Thus we find using equation (1)

$$\gamma = \exp.\ [(RT)^{-1}(-B_0)p] \tag{4}$$

Now taking the γ, π chart quite literally we would be justified in assuming that whatever the functional relation between γ and π for constant θ, provided only that it is finite and continuous, γ will be linear for π small. We may proceed to write as follows

$$\gamma = 1 + \mathrm{f}(\theta)\pi : \text{for } \pi \text{ small} \tag{5}$$

Expanding γ we obtain further

$$1 - \frac{B_0 p}{RT} = 1 + \mathrm{f}(\theta)\pi \tag{5A}$$

or

$$\frac{B_0 p_c}{T_c} = -R\theta \mathrm{f}(\theta) \tag{6}$$

where the right-hand member is a universal function, the same for every substance in the gaseous state.

In the present state of our knowledge of the molecular field and the available data, no decisive opinion can be formed regarding the degree of exactness of relation (6). We observe, however, that it bears a close relation to Daniel Berthelot's expression for the effect of intramolecular potential in the equation of state.

Some years ago Beattie and Bridgeman[5] formulated the greater part of the existing data for gases using a correlative equation which employs for B_0 the expression

$$B_0 = \beta - \frac{A}{RT} - \frac{c}{T^3} \tag{7}$$

This is equivalent to a van der Waals expression in which the contribution of the series part or coefficient of A/RT of B_0 in equation (1) is represented by $1 + (CR/AT^2)$. I propose to designate this for reasons of convenience by the expression $1 + (\alpha_2)\ [A^2/(RT)^2\beta^2]$ where (α_2) is a quantity which may vary from substance to substance. What is here proposed for later use is the same thing as setting C equal to $(\alpha_2)\ (A^3/R^3\beta^2)$ and we write for B_0 the following equation

$$B_0 = \beta - A/RT - (\alpha_2)\frac{A^3}{(RT)^3\beta^2} \tag{7A}$$

We now obtain however using equations (6) and (7) the relation

$$B_{0\theta} = \beta(p/T)_c - \frac{A}{R\theta T_c}(p/T)_c - \frac{C}{\theta^3 T_0^3}\left(\frac{p}{T}\right)_c = -R\theta \mathrm{f}(\theta) \tag{6A}$$

or

$$B_{0\theta} = \beta_\theta - A_\theta/\theta - C_\theta/\theta^3$$

where the expectation derived from the γ, π chart is that β_θ, A_θ and C_θ will each turn out to be the same number regardless of the substance. Using

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

Beattie and Bridgeman's constants,[6] Table I has been compiled.

TABLE I

EQUATION OF STATE CONSTANTS IN REDUCED UNITS (π, φ, θ)

Substance	β	$A_0/R = A'$· 10^{-3}	$C \times 10^{-6}$	β_θ	A'_θ	C_θ
He	14.00	0.2632	0.4	6.08	21.74	1196.0
Ne	20.60	2.590	1.01	12.48	35.34	6.99
A	39.31	15.73	59.9	12.52	33.24	5.57
H_2	20.96	2.41	0.50	8.08	27.95	5.31
N_2	50.46	16.38	42.0	13.42	34.57	5.58
O_2	46.24	18.17	48.0	14.89	37.93	4.21
Air	46.11	15.86	43.4	12.96	33.65	5.24
CO_2	104.8	61.01	660.0	25.14	48.13	5.63
CH_4	55.9	27.75	128.3	13.39	34.82	4.41
C_2H_1	121.56	74.97	226.8	21.88	47.72	1.80
C_2H_6	94.00	71.60	900.0	15.04	37.54	5.07
$(C_2H_5)_2O$	454.46	381.16	333.3	34.54	62.04	0.25

$$\text{Non-polar gases } B_0\theta = 13.29 - \frac{34.9}{\theta} - \frac{5.47}{\theta^3}$$

Substance	β	$A_0/R = A'$· 10^{-3}	$C \times 10^{-6}$	β_θ	A'_θ	C_θ
NH_3	40.86	39.43	3053.0	11.24	26.74	12.59
H_2O	34.05	47.59	8842.0	11.48	24.80	10.99

$$\text{Polar gases } B_0\theta = 11.36 - \frac{25.77}{\theta} - \frac{11.8}{\theta^3}$$

$$\text{Non-polar gas } C_\theta = 0.0227 \frac{(A_\theta)^3}{(\beta_\theta)^2}$$

$$\text{Polar gas} \qquad C_\theta = 0.089 \frac{(A'_\theta)^3}{(\beta_\theta)^2}$$

The units are cc. per mole, atm. °K.

A somewhat astonishing accord of the numbers β_θ, A_θ, and C_θ for the different substances is evident. The case of helium is not significant since helium is the worst known example of a van der Waals molecule even at 100°K. Ether is really a polar gas and moreover the data are neither very exact nor sufficiently extensive in temperature range. The "universal equation" selected to represent the non-polar class of molecules is given at the foot of the table along with a similar one for the polar case. The latter equation is of course based on only two examples, but I have no knowledge of sufficiently precise data for other examples of polar gases. The reason for calling attention to the relation (6A) is solely because it has been found that certain important types of calculations may be facilitated using the "universal" functions B_0 with a combination rule for the constants of mixtures.

The combination rule whereby the constants for a mixture may be computed from the constants (β and A for example) for the pure substances is in a primitive stage. Data for the favorable case of nitrogen–methane mixtures[7] were obtained some years ago for the purpose of investigating the combination rule where the van der Waals form is a reasonable approximation in representing the behavior of the components. It was found that the rule

$$\beta_{12} = {}^1/_2(\beta_1 + \beta_2)\ ;\ A_{12} = (A_1A_2)^{1/2}$$

was suitable for this binary mixture of non-polar molecules. The result accords with quantum theory indications in the case of N_2 and CH_4 molecules as far as the A_{12} rule is concerned but if the van der Waals concept for the positive potential were exact the rule $\sigma_{12} = {}^1/_2(\sigma_1 + \sigma_2)$ would be justified. In the case of polar substances there are definite indications from current quantum theory that the A_{12} rule just given is over simplified. However, even in this case at high temperatures the rule should be a fair approximation.

Accepting the combination rule as stated and extending it to serve for the general case we have the following relationship which may be deduced from (1B)

$$[B_0] = \Sigma\beta_1 n_1 - \frac{(\Sigma A_1{}^{1/2} n_1)^2}{RT\Sigma n_1} - \frac{1}{(RT)^3}\left[\Sigma(\alpha_2)_1 \frac{A_1{}^3}{\beta_1{}^2}\frac{n_1{}^2}{\Sigma n_1} + 2\Sigma(\alpha_2)_{12}\frac{A_{12}^3}{\beta_{12}^2}\frac{n_1 n_2}{\Sigma n_1}\right] \quad (7B)$$

As examples of the practical applications of the "universal" functions, $B_{0\theta}$, and the equation (7), the Haber equilibrium constants ratio K_p/K^* will be computed and also the ratio px_1/p_1 for Gillespie's experiment[8] where ($BaCl_2{\cdot}8NH_3$) was used effectively as a semi-permeable membrane. Here K_p is the equilibrium constant for any pressure p and K^* is the same quantity for pressures approaching zero. For Gillespie's experiment px_1 is the Dalton's law pressure for NH_3 in a mixture of NH_3 and N_2 at total pressure p, while p_1 is the equilibrium pressure of the $BaCl_2{\cdot}8NH_3$ in contact with the gaseous $NH_3:N_2$ mixture. Of course, every sort of calculation for gases may be made subject to the limitations of the $B_{0\theta}$ equations.

The general equation for the equilibrium constant ratio is

$$\ln K_p/K^* = -(RT)^{-1}\Sigma\nu \int_0^p \left[\frac{\partial V}{\partial n_1} - \frac{RT}{p}\right] \mathrm{d}p \quad (8)$$

For Gillespie's experiment we find the following equation from the relation $(\mu_{NH_3})_{p1} = [\mu_{NH_3}]_p$ where

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[6] The constants for NH_3 and H_2O are taken from the author's formulations for these substances. The complete expressions are

$$(B_0)_{NH_3} = 2.4 - 2316\tau \times \text{exp. } 7.744 \times 10^4\tau^2$$

and

$$(B_0)_{H_2O} = 1.89 - 2641.6\tau \times \text{exp. } 1.858 \times 10^5\tau^2$$

where the units are in cc./g. The first two terms of the expanded exponential were assumed the equivalent of $(1 + CR/AT^2)$. This procedure is satisfactory provided the temperature is high enough.

[7] F. G. Keyes and H. G. Burks, THIS JOURNAL, **50**, 1100 (1928). The case is favorable from the point of view of interpretation because chemical action is excluded and the molecules are non-polar.

[8] E. Lurie and L. J. Gillespie, *ibid.*, **49**, 1146 (1927).

$(\mu_{NH_3})_{p1}$ is the chemical potential of the pure gas in equilibrium with the same gas in the mixture the chemical potential of which is $(\mu_{NH_3})_p$.

$$\ln \frac{px_1}{p_1} = (RT)^{-1} \left[\int_0^p \left(\frac{\partial V_1}{\partial n_1} - \frac{RT}{p} \right) \mathrm{d}p_1 - \int_0^p \left(\frac{\partial V}{\partial n_1} - \frac{RT}{p} \right) \mathrm{d}p \right] \quad (9)$$

where p_1 is the $BaCl_2 \cdot 8NH_3$ equilibrium pressure of pure ammonia and p the total pressure.

Using the relations (7) there results

$$\ln K_p/K^* = -(RT)^{-1} \left(\Sigma \nu_1 \frac{\partial [B_0]}{\partial n_1} \right) p \quad (8A)$$

$$\ln px_1/p_1 = (RT)^{-1} [B_{01} p_1 - \partial/\partial n_1 [B_{01}] p] \quad (9A)$$

where in (9A) B_{01} refers to pure ammonia in equilibrium through a semi-permeable membrane with the ammonia in the gaseous mixture $[B_{01}]$. In detail we find using (7) the following equations

$$\ln K_p/K^* = (RT)^{-1} [-\Sigma\beta_1\nu_1 + (RT)^{-1} (A) + (RT)^{-3} (B + C)] \quad (8B)$$

$$(A) = 2(\Sigma A_1{}^{1/2}x_1)(\Sigma A_1{}^{1/2}\nu_1) - (\Sigma A_1{}^{1/2}x_1)\Sigma\nu_1$$

$$(B) = \Sigma \mathbf{A}_1 x_1 (2 - x_1)\nu_1$$

$$(C)^9 = 2 \left\{ \begin{matrix} [\mathbf{A}_{12}x_2(1 - x_1) + \mathbf{A}_{13}x_3(1 - x_1) - \mathbf{A}_{23}x_2x_3]\nu_1 \\ [\mathbf{A}_{12}x_1(1 - x_2) + \mathbf{A}_{23}x_3(1 - x_2) - \mathbf{A}_{13}x_1x_3]\nu_2 \\ [\mathbf{A}_{13}x_1(1 - x_3) + \mathbf{A}_{23}x_2(1 - x_3) - \mathbf{A}_{12}x_1x_2]\nu_3 \end{matrix} \right\} \text{for 3 components}$$

$$\ln \frac{px_1}{p} = (RT)^{-1}[-\beta_1(p - p_1) + (RT)^{-1} (Q) + (RT)^{-3} (S)] \quad (9B)$$

$$(Q) = [2(\Sigma A_1{}^{1/2}x_1)A_1{}^{1/2} - (\Sigma A_1{}^{1/2}x_1)^2]p - A_1p_1$$

$$(S) = \{\mathbf{A}_1(2 - x_1)x_1 - [\mathbf{A}_2x_2 - 2\mathbf{A}_{12}(1 - x_1)]x_2\}p - \mathbf{A}_1p_1$$

where $\mathbf{A} = (\alpha_2) \frac{A^3}{\beta^2}$; $(\alpha_2)_{12} = [(\alpha_2)_1(\alpha_2)_2]^{1/2}$; $\mathbf{A}_{12} = (\alpha_2)_{12} \frac{A_{12}^3}{B_{12}^2}$

TABLE II

AMMONIA SYNTHESIS

450 °C.

p	Obsd.[a] (K_p/K^*)	Calcd.[b] (K_p/K^*)	Calcd.[c] (K_p/K^*)	Calcd.[c] mol % NH_3	Obsd. mol % NH_3
100	1.093	1.105	1.110		
300	1.351	1.419	1.454		
600	1.966	2.240	2.384	56.2	53.3
1000	3.483	4.407	4.969	73.1	68.6

[a] L. J. Gillespie, *J. Math. Phys., M. I. T.*, **4**, 84 (1925); L. J. Gillespie and J. A. Beattie, *Phys. Rev.*, **36**, 743 (1930). I have the pleasure of thanking Professor Gillespie for providing me with the ratios in the second column. [b] Computed using the first two terms of (8B). No consideration has been given the fact that 0.3 mol per cent. of argon was present. [c] Computed using all three terms of (8B).

TABLE III

GILLESPIE'S EXPERIMENT[a]

$BaCl_2 \cdot 8NH_3 : N_2$ at 45°

p total	p_1 $BaCl_2 \cdot 8NH_3$	x_1	(px_1/p_1) obsd.	(px_1/p_1) calcd.
60.86	7.44	0.1484	1.214	1.228

[a] E. Lurie and L. J. Gillespie, THIS JOURNAL, **49**, 1146 (1927).

Summary

It is shown that the recent fugacity–pressure ratio charts for constant reduced temperatures *versus* reduced pressure, taken literally, lead at low pressures to a simple reduced equation of state. The constants of this equation are deduced from the values of the van der Waals constants deduced for thirteen substances by Beattie and Bridgeman.

It appears that there is a distinguishable difference in the reduced-constants values for non-polar compared with polar gases. A test of the usefulness of the reduced equation is made by computing the equilibrium constants for the Haber equilibrium for high pressures and for Gillespie's experiment. In applying the equation to mixtures of gases use was made of a "constants" combination rule previously found valid for nitrogen–methane mixtures. The results indicate that the reduced equation is useful for making approximate physico-chemical calculations involving gases under pressure. The present reduced equations suffer from the assumption that a van der Waals type of molecular field is assumed valid, and more precise data for gases and gas mixtures at low pressures are needed before the implications deducible from the existing fugacity–pressure ratio charts can be explored satisfactorily.

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(9) This term is written out for the case of these constituents only.