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The Principle of Corresponding States

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The principle of corresponding states in modern form has been applied to the following properties: the critical state, the virial coefficient, the Boyle point, the densities of coexistent phases, the vapor pressure of the liquid, the entropies of evaporation and of fusion, the coefficient of thermal expansion of the liquid, the triple-point temperature and pressure, the heat capacity of the liquid, and the surface tension of the liquid. It has been shown that argon, krypton, xenon, and with less accuracy neon, follow the principle with respect to all these properties. It has further been shown that nitrogen, oxygen, carbon monoxide, and methane follow the principle with fair accuracy as vapors and as liquids, but not as solids. The relations between surface tension, temperature, and densities have been analyzed empirically. For the "ideal" substances under consideration Katayama's modification of Eötvos' relation holds good, but McLeod's relation does not; in the relation $\gamma \propto (\rho_l - \rho_c)^s$, the exponent s is not 4 but much more nearly $3\frac{2}{3}$.

1. INTRODUCTION

THE principle of corresponding states may safely be regarded as the most useful by-product of van der Waals' equation of state. Whereas this equation of state is nowadays recognized to be of little or no value, the principle of corresponding states correctly applied is extremely useful and remarkably accurate.

Pitzer[1] has stated a set of assumptions sufficient to lead to the principle of corresponding states and has shown that argon, krypton, and xenon have several properties in accordance with the principle. In the present paper, I shall draw attention to a number of further relations, not mentioned by Pitzer, all in accordance with the principle of corresponding states. I shall show that the principle is also followed accurately by nitrogen and oxygen, and somewhat less accu-

[1] K. Pitzer, J. Chem. Phys. **7**, 583 (1939). See also Boer and Michels, Physica **5**, 946 (1938).

rately by carbon monoxide and methane. For the sake of continuity and completeness, I shall at small cost of space repeat some of Pitzer's contributions to the subject.

2. ASSUMPTIONS

I shall with the utmost brevity recall Pitzer's list of assumptions and make comments on some of them. They are:

I. "Classical statistical mechanics will be used."
II. "The molecules are spherically symmetrical, either actually or by virtue of rapid and free rotation."
III. "Intramolecular vibrations will be assumed the same in the liquid and gas states."
IV. "The potential energy will be taken as a function only of the various intermolecular distances."
V. "The potential energy for a pair of molecules can be written $A\phi(R/R_0)$ where R is the intermolecular distance, A and R_0 are characteristic constants and ϕ is a universal function."

The precise meaning of assumption 1 is ambigu-

ous. My interpretation of the correct condition is that

(a) any distinction between Fermi-Dirac statistics and Bose-Einstein statistics has a negligible effect;

(b) the effect of quantization of the translational degrees of freedom is negligible.

Both (a) and (b) are satisfied provided $(mkT)^{\frac{1}{2}}v^{\frac{1}{3}} \gg h$, where m denotes molecular mass, T absolute temperature, and v volume per molecule. As pointed out by Pitzer this condition excludes hydrogen and helium owing to their small molecular masses and to some extent limits the applicability of the principle to neon. I can however see no need to assume that degrees of freedom other than the translational must be classical. On the contrary, the vibrational degrees of freedom of diatomic molecules are practically unexcited, and yet it will be shown that such molecules can obey the principle of corresponding states.

The effect of assumption II is that some diatomic and polyatomic molecules may obey the principle in the gaseous and liquid state, but cannot be expected to obey it in the solid state. Assumption III might be more usefully worded: "The intramolecular degrees of freedom are assumed to be completely independent of the volume per molecule." Highly polar molecules are ruled out by conditions II, III, and IV. Metals and molecules capable of forming hydrogen bonds are ruled out by condition IV.

Even when conditions I to IV are fulfilled, there is no *a priori* reason why assumption V should be fulfilled. In fact there is good reason to suppose that it does not hold accurately. The assumption is however accurate for large values of R where the intermolecular potential energy ϵ is proportional to $-R^{-6}$. Moreover many macroscopic properties are insensitive to the precise form of the relation between ϵ and R for small R. Consequently assumption V, though not rigorously true, turns out to be a useful approximation for many non-polar molecules.

3. FORMULATION OF PRINCIPLE

From the above assumptions it follows that the free energy F of a system of N molecules at the temperature T obeys the relation

$$-\frac{F}{NkT} = \frac{3}{2}\log\frac{2\pi mkT}{h^2} + 1 + \log v$$

$$+ \log j(T, I, \nu_i) + \log \psi\left(\frac{kT}{\epsilon_0}, \frac{v}{R_0^3}\right), \quad (3.1)$$

where m is the molecular mass, v is the molecular volume, j is the partition function for the internal degrees of freedom of a molecule and depends only on the temperature T, the principal moments of inertia I, and the frequencies ν_i of the normal modes. Finally ψ is a complicated, but universal function of kT/ϵ_0 and v/R_0^3, where R_0 is the intermolecular distance at which the intermolecular energy has its minimum value $-\epsilon_0$. At infinite dilution ψ tends to unity and formula (3.1) becomes that of a perfect gas.

From the thermodynamic relation

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = -\frac{1}{N}\left(\frac{\partial F}{\partial v}\right)_{T,N}, \quad (3.2)$$

where P is the pressure, V the volume of the whole system, and v the volume per molecule, it follows that Pv/kT is a universal function of kT/ϵ_0 and v/R_0^3. From the well known conditions for the critical state it follows at once that kT_c/ϵ_0 and v_c/R_0^3, where the subscript c denotes critical values, are both universal constants. The equation of state is therefore of the form

$$\frac{P}{P_c} = u\left(\frac{T}{T_c}, \frac{v}{v_c}\right), \quad (3.3)$$

where u is a universal, but complicated, function. Insofar as the five initial assumptions are fulfilled, Eq. (3.3) is valid for gas, liquid, and solid. This is the general expression of the principle of corresponding states.

I shall now consider various deductions from formula (3.3) and examine to what extent they are borne out by experimental data for neon, argon, krypton, xenon, nitrogen, oxygen, carbon monoxide, and methane.

4. CRITICAL STATE

In Table I, the first row gives the molecular weights, the next four rows[2] the critical tempera-

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[2] The sources of experimental data are collected in an appendix.

TABLE I.

	Formula	Ideal	Ne	A	Kr	Xe	N₂	O₂	CO	CH₄
1.	M		20.18	39.94	83.7	131.3	28.02	32.00	28.00	16.03
2.	$T_c/°K$		44.8	150.7	209.4	289.8	126.0	154.3	133.0	190.3
3.	ρ_c/g cm⁻³		0.484	0.5308	0.9085	1.155	0.311	0.430	0.301	0.162
4.	$v_c/cm³$ mole⁻¹		41.7	75.3	92.1	113.7	90.2	74.5	93.2	98.8
5.	$P_c/atmos.$		26.9	48.0	54.1	58.2	33.5	49.7	34.5	45.7
6.	$P_c v_c/RT_c$	0.292	0.305	0.292	0.290	0.278	0.292	0.292	0.294	0.289
7.	$T_B/°K$		121	411.5			327		∼345	491
8.	T_B/T_c	2.7	2.70	2.73			2.59		2.6	2.58
9.	$T_b/°K$ $(P=1$ atmos.$)$		27.2	87.3	120.9	165.1	77.3	90.1	81.6	112.5
10.	$T_s/°K$ $(P=P_c/50)$		25.2	86.9	122.0	167.9	74.1	90.1	78.9	110.5
11.	T_b/T_c		0.608	0.580	0.577	0.570	0.614	0.583	0.613	0.591
12.	T_s/T_c	0.58	0.563	0.577	0.582	0.580	0.588	0.583	0.593	0.581
13.	$L_e/R°K$		224*	785	1086	1520	671	820	727	1023
14.	L_e/RT_b		8.25	8.98	8.98	9.19	8.68	9.11	8.91	9.10
15.	L_e/RT_s	9.05	8.9	9.04	8.91	9.06	9.06	9.11	9.22	9.26
16.	$10³\alpha$			4.54			5.88	3.85	4.91	
17.	αT_c	0.68		0.68			0.74	0.59	0.65	
18.	$T_t/°K$		24.6	83.8	116.0	161.3	63.1	54.4	68.1	90.6
19.	T_t/T_c	0.555	0.549	0.557	0.553	0.557	0.501	0.352	0.512	0.476
20.	$L_f/R°K$		40.3	141.3	196.2	276	86.8	53.5	100.7	113
21.	L_f/RT_t	1.69	1.64	1.69	1.69	1.71	1.37	0.98	1.48	1.25
22.	$P_t/atmos.$		0.425	0.682	0.721	0.810				
23.	$100P_t/P_c$	1.37	1.58	1.42	1.33	1.39				
24.	$v_l/cm³$			28.14	34.13	42.68				
25.	$v_s/cm³$			24.61	29.65	37.09				
26.	v_l/v_s			1.144	1.151	1.151				
27.	C_P/R at T_s	5.4		5.5	5.35	5.35	6.75	6.45	7.25	

* This is not a measured value, but an approximate value based on vapor pressure measurements.

ture T_c, the critical density ρ_c, the critical molar volume v_c, and the critical pressure P_c. The sixth row gives the values of $P_c v_c/RT_c$, which van der Waals pointed out should have a universal value. It will be seen that the values for argon, krypton, nitrogen, oxygen, carbon monoxide, and methane all lie within 1.5 percent of 0.292. The value for neon is somewhat higher and that for xenon somewhat lower. In the former case the deviation is presumably a quantal effect; in the latter there is no obvious explanation.

5. VIRIAL COEFFICIENT AND BOYLE POINT

The equation of state of a gas up to moderate pressures may be expressed in the form

$$Pv/RT = 1 + B(T)/v, \qquad (5.1)$$

where $B(T)$ is called the second virial coefficient, which is positive at high and negative at low temperatures. The temperature T_B at which $B(T)$ changes sign is called the Boyle point. In the seventh row of Table I are given values of T_B and in the eighth values of T_B/T_c. The values for neon, argon, and oxygen agree within 1 percent; those for nitrogen, carbon monoxide, and methane are 5 to 8 percent lower.

The dependence of $B(T)$ on T is not expressible by any particularly simple relation. $B(T)/v_c$ is plotted against T/T_c in Fig. 1 for neon, argon, nitrogen, and oxygen, for which alone of the substances being considered accurate data at low pressures are available. It will be seen that the three substances are roughly fitted by the same curve.

6. DENSITIES OF COEXISTENT LIQUID AND VAPOR

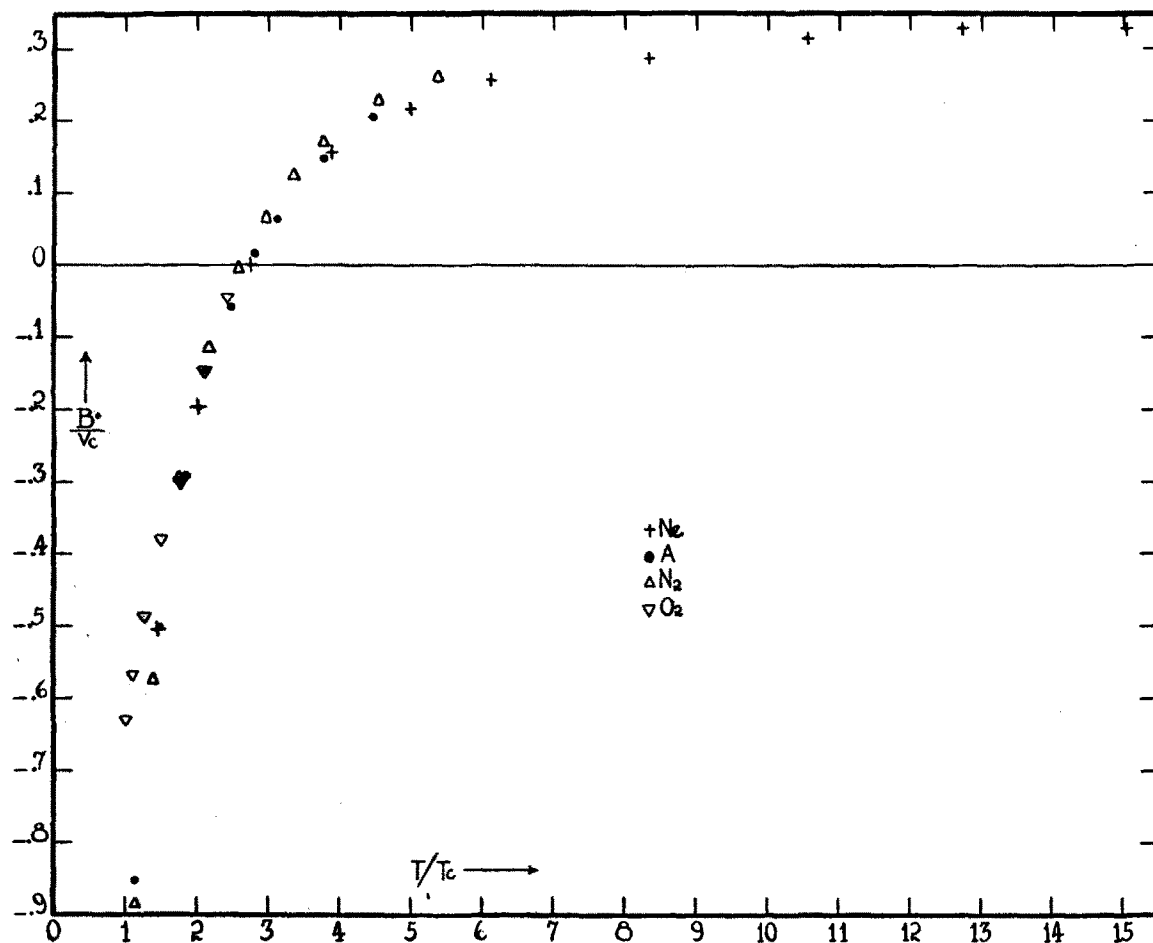If ρ_l denotes the density of the liquid and ρ_g that of the vapor in mutual equilibrium at the

FIG. 1.

temperature T, while ρ_c denotes the critical density, then according to the principle of corresponding states one should expect ρ_l/ρ_c and ρ_g/ρ_c to be universal functions of T/T_c. In Fig. 2 are plotted all the experimental data for the substances under consideration. It will be seen that except for carbon monoxide and methane most of the points lie on or near a single curve.

The curve drawn through the points for argon is represented by the empirical formulae

$$\frac{\rho_l}{\rho_c}=1+\frac{3}{4}\left(1-\frac{T}{T_c}\right)+\frac{7}{4}\left(1-\frac{T}{T_c}\right)^{\frac{1}{3}}, \quad (6.1)$$

$$\frac{\rho_g}{\rho_c}=1+\frac{3}{4}\left(1-\frac{T}{T_c}\right)-\frac{7}{4}\left(1-\frac{T}{T_c}\right)^{\frac{1}{3}}. \quad (6.2)$$

By addition and subtraction of (6.1) and (6.2)

one obtains

$$\frac{\rho_l+\rho_g}{2\rho_c}=1+\frac{3}{4}\left(1-\frac{T}{T_c}\right), \quad (6.3)$$

$$\frac{\rho_l-\rho_g}{\rho_c}=\frac{7}{2}\left(1-\frac{T}{T_c}\right)^{\frac{1}{3}}. \quad (6.4)$$

Formula (6.3) expresses the well-known law of the rectilinear diameter. Formula (6.4) is new. The inaccuracy of these formulae as applied to argon is generally only one or two parts per thousand of ρ_c or of ρ_l. But the percentage inaccuracy in ρ_g increases with decrease of temperature and becomes serious below $T \simeq 0.65T_c$. In fact according to the formulae, ρ_g would become zero at $T = 0.565T_c$, but this is below the triple point $T_t = 0.58T_c$. It is therefore not recommended that
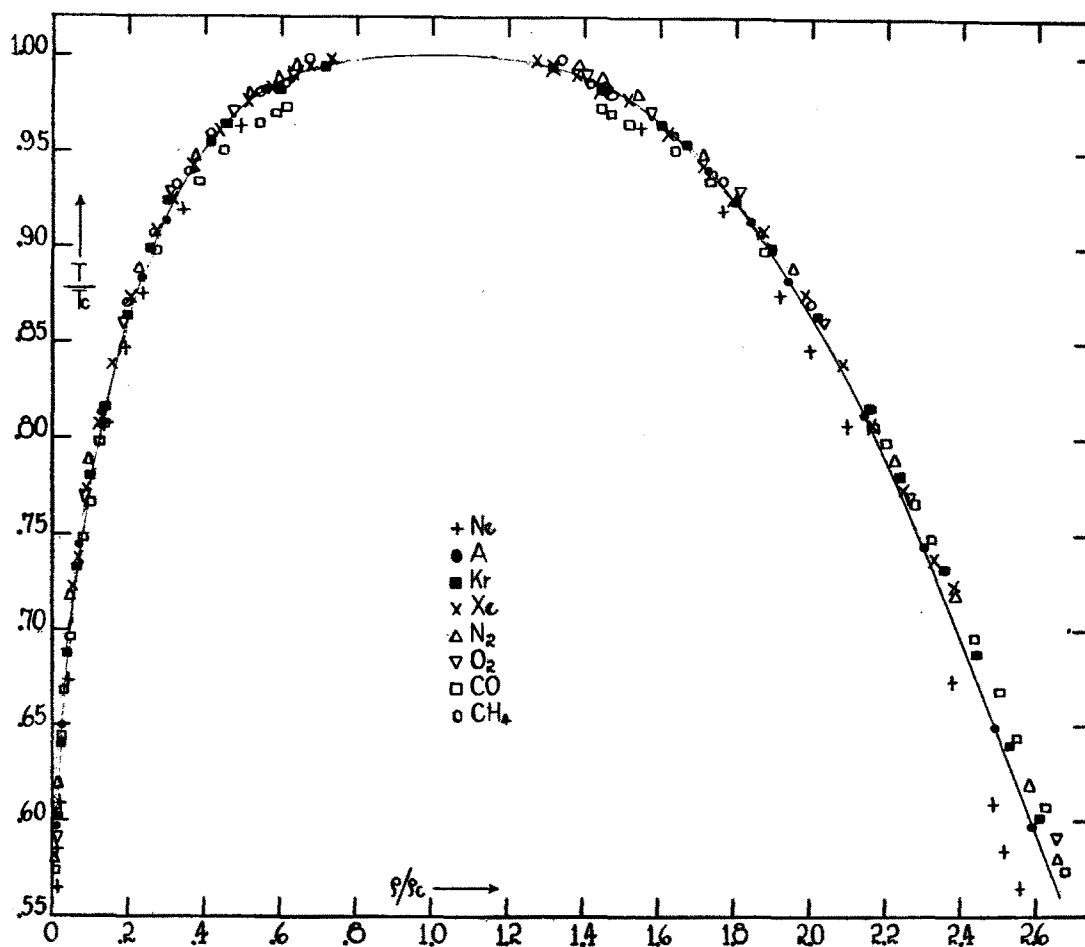
FIG. 2.

these formulae should be used for computing values of ρ_g. There are however occasions when one requires relatively accurate values not of ρ_g itself but of $(\rho_l - \rho_g)/\rho_c$; on such occasions formula (6.4) in view of its extreme simplicity and surprisingly high accuracy has much to recommend it. An example of its use will occur in Section 16.

7. VAPOR PRESSURE

At temperatures considerably below the critical temperature, say $T < 0.65 T_c$, when formula (6.2) for ρ_g becomes inaccurate it is convenient to consider the equilibrium vapor pressure P rather than ρ_g. According to the principle of corresponding states one should expect P/P_c to be a universal function of T/T_c. In particular the temperatures T_s at which the equilibrium pres-

sure P is one-fiftieth of the critical pressure should be corresponding temperatures for different substances and the ratio of T_s to T_c should have a universal value. On the other hand T_b the boiling points at a pressure of one atmosphere are not corresponding temperatures for different substances. In rows 9 and 10 of Table I are given T_b the boiling point at a pressure of one atmosphere, and T_s the boiling point at a pressure one-fiftieth the critical pressure. In rows 11 and 12 are given the ratios T_b/T_c and T_s/T_c. It will be seen that the values of the latter are, as expected, more nearly the same than the values of the former.

8. ENTROPY OF EVAPORATION

According to Trouton's rule the molar entropies of evaporation for different substances have

roughly the same value at their boiling-points under a pressure of one atmosphere. Hildebrand[3] has found that the molar entropies of evaporation are more nearly the same at temperatures at which ρ_g has the same value. Neither Trouton's rule nor Hildebrand's accords with the principle of corresponding states, which requires rather that the molar entropies of evaporation should be equal at corresponding temperatures. In particular they should be equal at a standard temperature $T_s = 0.58T_c$ at which the vapor pressure is one-fiftieth the critical pressure. In row 13 of Table I are given the molar heats of evaporation L_e divided by the gas constant R. In rows 14 and 15 are given the molar entropies of evaporation divided by the gas constant R at the temperatures T_b and T_s respectively. It will be seen that the values of L_e/RT_s are, as they should be, more nearly alike than the values of L_e/RT_b.

9. COEFFICIENT OF THERMAL EXPANSION

An extremely sensitive test of the accuracy of formula (6.1) for the density ρ_l of the liquid is obtained by using this formula to calculate α the coefficient of thermal expansion. According to this formula α will vary with the temperature, but only slowly at low temperatures. At the temperature $T_s = 0.58T_c$, the calculated value of $\alpha(T_c - T_s)$ is 0.287 and that of αT_c is 0.68. The only experimental values of α are given in row 16 of Table I and the corresponding values of αT_c in row 17. The agreement for nitrogen, oxygen, and carbon monoxide is as good as one could expect. In the case of argon the agreement is exact. This is not an independent test of the principle of corresponding states, but is a demonstration of the high accuracy of formula (6.1) as applied to argon.

10. TRIPLE-POINT TEMPERATURE

As pointed out in Section 2, it is only for monatomic molecules that the principle of corresponding states may be expected to apply to the solid state, because the rotational motion of diatomic and polyatomic molecules can hardly be unrestricted in a crystal. In row 18 of Table I are given the triple-point temperatures T_t and in row 19 the ratios of T_t to T_c. There is good agreement between the monatomic molecules of argon, krypton, xenon, and even neon. For the diatomic molecules and methane the agreement is as expected appreciably less good. The fact that oxygen deviates considerably more than nitrogen and methane is interesting. This may possibly have some connection with the fact that the gaseous molecule O_2 is in a triplet state. The molar entropy consequently contains an electronic contribution $R \log 3$, which presumably persists in the liquid, but has disappeared[4] at the lowest temperatures at which thermal measurements have been made on crystalline oxygen. Whether it disappears by formation of O_4 molecules or otherwise is not known, nor in what temperature range it disappears, but it may be expected to exert a marked effect on the equilibrium properties of the solid phase.

11. ENTROPY OF FUSION

The molar heats of fusion L_f divided by the gas constant R are given in row 20 of Table I and the molar entropies of fusion divided by R in row 21. The agreement between the values for the monatomic molecules is good.

12. TRIPLE-POINT PRESSURES

The triple-point pressures P_t of the monatomic species are given in row 22 of Table I and the ratios $100P_t/P_c$ in row 23. The values for argon, krypton, and xenon, but not neon, agree within ± 4 percent. Since an increase of 4 percent in the equilibrium vapor pressure of the crystal, or of the liquid, corresponds to an increase in absolute temperature of only 0.4 percent, this is a much more sensitive test than that of Section 10.

13. EXPANSION ON FUSION

In rows 24 and 25 of Table I are given the molar volumes v_l and v_s of liquid and solid, respectively, at the triple point for the monatomic species. In row 26 are given the ratios of v_l to v_s. As previously pointed out by Clusius and Weigand[5] the uniformity of these ratios is remarkable.

[3] J. Hildebrand, J. Am. Chem. Soc. **37**, 970 (1915); **40**, 45 (1918).

[4] W. Giauque and H. Johnston, J. Am. Chem. Soc. **51**, 2300 (1929).
[5] K. Clusius and K. Weigand, Zeits. f. Physik. Chemie **B46**, 1 (1940).

14. HEAT CAPACITY OF LIQUID

According to the principle of corresponding states the molar heat capacity at corresponding temperatures should be the same for monatomic molecules. That this is at least roughly true is shown by the values given in row 27 of Table I. The application of the principle to diatomic molecules is less simple. One of the assumptions used to deduce the principle is that the molecules should rotate freely in the liquid. If this assumption is accurately fulfilled, then the rotational degrees of freedom should make precisely the same contribution to each of the thermodynamic functions in the liquid as in the gas. In particular the rotational contribution to the molar heat capacity of the diatomic species should be just R. Hence the total molar heat capacity of the diatomic species should exceed that of the monatomic species by just R. Actually the excess, as shown by the values in row 27 of Table 1, is greater than R. This is understandable if there is a small restriction of the rotation increasing with decreasing temperature.

15. EXTENSION OF PRINCIPLE TO SURFACES

In order to extend the principle of corresponding states to surfaces, one needs to revise assumption III as follows: "The intramolecular degrees of freedom are assumed to be completely independent of the volume per molecule and of the distance of the molecule from the surface." From this assumption it follows that the excess free energy F_s due to an interface of area A containing N_s molecules is of the form

$$-\frac{F_s}{N_s kT} = \log \psi_s\left(\frac{kT}{\epsilon_0} \frac{A}{N_s R_0^2}\right), \quad (15.1)$$

where ψ_s is a complicated but universal function of kT/ϵ_0 and $A/N_s R_0^2$. It is also evident that at equilibrium between liquid and vapor $A/N_s R_0^2$ is like v_l/R_0^3 a universal function of T/T_c consequently $F_s R_0^2/kTA$ is a universal function of T/T_c. But for a single component system the surface tension γ is equal to F_s/A. Hence $\gamma R_0^2/kT$ is a universal function of T/T_c. Finally, using the fact that v_c/R_0^3 has a universal value, one concludes that $\gamma v_c^{\frac{2}{3}}/kT$ and so also $\gamma v_c^{\frac{2}{3}}/kT_c$ are universal functions of T/T_c. How well this prediction

is borne out by the experimental data will be examined in the two succeeding sections.

16. TEMPERATURE DEPENDENCE OF SURFACE TENSION

Since the surface tension of a liquid decreases with increasing temperature and vanishes at the critical point, the simplest possible form of empirical relation between γ and T is

$$\gamma = \gamma_0\left(1 - \frac{T}{T_c}\right)^{1+r}, \quad (16.1)$$

where r is a constant. I shall show that this relation with $r = 2/9$ in fact adequately represents the experimental data, but for the moment I leave the value of r unspecified. Van der Waals suggested a formula such as (16.1) with $r = 0.234$ and Ferguson[6] has proposed $r = 0.21 \pm 0.015$.

One of the earliest and best known empirical relations relating to the temperature dependence of γ is that of Eötvos, namely

$$\gamma v_l^{\frac{2}{3}} \propto (1 - T/T_c). \quad (16.2)$$

This relation was however found to be inexact and various modifications of it have been proposed, of which the most satisfactory is that of Katayama,[7] namely

$$\gamma y^{-\frac{2}{3}} \propto (1 - T/T_c), \quad (16.3)$$

where y is defined by

$$y = 1/v_l - 1/v_c, \quad (16.4)$$

or

$$y v_c = (\rho_l - \rho_g)/\rho_c. \quad (16.5)$$

Katayama showed that the experimental data for various organic substances were in excellent accord with his relation (16.3). How accurately this relation fits the data for argon, nitrogen, etc. can only be confirmed by trial, but anticipating such an examination I shall tentatively and provisionally assume that the relation (16.3) holds for these substances.

By substitution of (16.5) into formula (6.4), one sees that this can be expressed in the form

$$y \propto (1 - T/T_c)^{\frac{1}{3}}. \quad (16.6)$$

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[6] A. Ferguson, Trans. Faraday Soc. **19**, 407 (1923); Proc. Phys. Soc. **52**, 759 (1940).
[7] Katayama, Science Reports Tôhoku Imperial University **4**, 373 (1916).

TABLE II. $\gamma = \gamma_0(1 - T/T_c)^{11/9}$.

Ne			A			N$_2$			O$_2$		
$T_c = 44.8°$K $\gamma_0 = 15.1$ dyne/cm			$T_c = 150.7°$K $\gamma_0 = 36.31$ dyne/cm			$T_c = 126.0°$K $\gamma_0 = 28.4$ dyne/cm			$T_c = 154.3°$K $\gamma_0 = 38.4$ dyne/cm		
T °K	γ dyne/cm calc.	obs.	T °K	γ dyne/cm calc.	obs.	T °K	γ dyne/cm calc.	obs.	T °K	γ dyne/cm calc.	obs.
24.8	5.64	5.61	85.0	13.16	13.19	70.0	10.54	10.53	70.0	18.34	18.35
25.7	5.33	5.33	87.0	12.67	12.68	75.0	9.40	9.39	75.0	17.02	17.0
26.6	5.02	4.99	90.0	11.95	11.91	80.0	8.29	8.27	80.0	15.72	15.73
27.4	4.75	4.69				85.0	7.20	7.20	85.0	14.44	14.5
28.3	4.45	4.44				90.0	6.14	6.16	90.0	13.17	13.23
$V_c = 41.7$ cm^3/mole $\gamma_0 V_c^{\frac{2}{3}} T_c^{-1}$ $= 4.05$ erg deg.$^{-1}$ mole$^{-\frac{2}{3}}$			$V_c = 75.3$ cm^3/mole $\gamma_0 V_c^{\frac{2}{3}} T_c^{-1}$ $= 4.3$ erg deg.$^{-1}$ mole$^{-\frac{2}{3}}$			$V_c = 90.2$ cm^3/mole $\gamma_0 V_c^{\frac{2}{3}} T_c^{-1}$ $= 4.5$ erg deg.$^{-1}$ mole$^{-\frac{2}{3}}$			$V_c = 74.5$ cm^3/mole $\gamma_0 V_c^{\frac{2}{3}} T_c^{-1}$ $= 4.4$ erg deg.$^{-1}$ mole$^{-\frac{2}{3}}$		

Now eliminating y between (16.3) and (16.6), one obtains

$$y \propto (1 - T/T_c)^{11/9}, \qquad (16.7)$$

which can also be written

$$\gamma = \gamma_0(1 - T/T_c)^{11/9}, \qquad (16.8)$$

in agreement with (16.1) with $r = 2/9$.

To recapitulate, for argon, nitrogen, and other substances under consideration the validity of formula (16.6) has already been established in Section 6. Taking account of this, formula (16.8) and Katayama's formula (16.3) are mutually inter-dependent. Verification of either implies the accuracy of the other and conversely. I shall now show that formula (16.8) holds satisfactorily for the substances under discussion for which experimental data exist, namely neon, argon, nitrogen, and oxygen.

In Table II at the top, are given the experimental value of the critical temperature T_c and the arbitrarily assumed value of γ_0 for each substance. Below this the values of γ calculated according to (16.8) are compared with the observed values over a range of temperatures. The agreement is good throughout and could hardly be improved by amending the value 2/9 assumed for r.

If now instead of eliminating y between (16.3) and (16.6) to obtain (16.7), one eliminates T/T_c one obtains

$$\gamma \propto y^s, \quad s = 3(1+r) = 3\tfrac{2}{3}. \qquad (16.9)$$

This is in definite disagreement with the better

known relation of McLeod[8] according to which s is 4. Actually McLeod based his relation on half a dozen organic compounds, but a mere glance at his figures is sufficient to show that γ in fact varies as some power of y less than 4.

It is outside the scope of the present paper to discuss the best value of s to represent the over-all average behavior of organic compounds. I merely wish to emphasize that for the substances having the simplest and most symmetrical molecules the value of s is not 4 but $3\tfrac{2}{3}$. Any molecular theory[9] or model of the simplest molecules leading to $s = 4$ is therefore spurious.

17. ABSOLUTE VALUE OF SURFACE TENSION

In Section 15 it was shown that according to the principle of corresponding states $\gamma v_c^{\frac{2}{3}} T_c^{-1}$ should be a universal function of T/T_c. Seeing that for the substances under consideration the dependence of γ on the temperature is represented by formula (16.8), it follows that $\gamma_0 v_c^{\frac{2}{3}} T_c^{-1}$ should have a universal value. How nearly this is the case is shown at the bottom of Table II. The agreement between argon, nitrogen, and oxygen is remarkable; that of neon is less good, presumably owing to quantal effects.

18. DEVIATIONS FROM THE PRINCIPLE

In the column of Table I preceding neon and labelled "Ideal," are given values of those quantities which should be common to all sub-

[8] J. McLeod, Trans. Faraday Soc. 19, 38 (1923).
[9] Fowler and Guggenheim, Statistical Thermodynamics (Cambridge University Press New York, 1939), p. 451.

stances conforming to the principle of corresponding states. It has been shown that argon, krypton, and xenon conform with a high degree of accuracy to the principle in all their properties; that nitrogen, oxygen, carbon monoxide, and methane also conform with fair accuracy in the gaseous and liquid states but not in the solid state. The behavior corresponding to argon, krypton, and xenon should be considered as an ideal one to which other substances may be expected to conform more or less according to the extent to which the assumptions of Section 2 are or are not satisfied. Departures of a particular substance from this ideal behavior must not be regarded as unsatisfactory flaws in the principle, but rather as giving interesting information concerning fundamental differences between the molecules of the substance in question and the ideal molecule visualized in Section 2. The varied effects of such deviations from the ideal have been discussed by others, notably by Hildebrand,[10] by Bernal,[11] and by Pitzer.[1]

APPENDIX

The following sources of experimental data have been used:

1. Critical data, densities of coexistent liquid and vapor.
   Neon: Mathias, Crommelin, and Onnes, Comptes rendus **175**, 933 (1922).
   　　　Mathias and Crommelin, Comm. Leiden Supp. 52 (1924).
   Argon: Onnes and Crommelin, Comm. Leiden No. 131a (1912).
   Krypton: Mathias, Crommelin, and Meihuizen, Comptes rendus **204**, 630 (1937).
   Xenon: Patterson, Cripps, and Gray, Proc. Roy. Soc. **86**, 579 (1912).
   Nitrogen: Mathias, Onnes, and Crommelin, Comm. Leiden No. 145c (1914).
   Oxygen: Mathias and Onnes, Comm. Leiden No. 117 (1911).
   Carbon monoxide: Crommelin, Bijleveld, and Grigg, Comm. Leiden 20 No. 221b (1932).
   Methane: Cardoso, J. Chim. Phys. **13**, 312 (1915).

[10] J. Hildebrand, J. Chem. Phys. **7**, 233 (1939).
[11] J. Bernal, Address to Chemical Society, February 3, (1938).

2. Boyle points.
   Neon, argon, nitrogen: Holborn and Otto, Zeits f. Physik **33**, 9 (1925).
   Carbon monoxide: rough interpolation of data of Bartlett, J. Am. Chem. Soc. **52**, 1374 (1930).
   Methane: Keyes and Burkes, J. Am. Chem. Soc. **49**, 1403 (1924).

3. Virial coefficients.
   Holborn and Otto, Zeits f. Physik **33**, 5 (1925).

4. Vapor pressures.
   Landolt-Börnstein tables.

5. Heats of evaporation and of fusion, triple-points, heat capacities of liquids.
   Neon: Clusius, Zeits. f. Physik. Chemie **B4**, 1 (1929).
   　　　Clusius, and Riccoboni, Zeits. f. Physik. Chemie **B38**, 81 (1937).
   Argon: Eucken and Hauck, Zeits. f. Physik. Chemie **134**, 161 (1928).
   　　　Clusius, Zeits. f. Physik. Chemie **31**, 459 (1936).
   　　　Frank and Clusius, Zeits. f. Physik. Chemie **B42**, 395 (1939).
   Krypton: Clusius, Kruis, and Konnertz, Ann. d. Physik **33**, 642 (1938).
   Xenon: Clusius and Riccoboni, Zeits. f. Physik. Chemie **B38**, 81 (1937).
   Nitrogen: Giauque and Clayton, J. Am. Chem. Soc. **55**, 4875 (1933).
   Oxygen: Giauque and Johnston, J. Am. Chem. Soc. **51**, 2300 (1929).
   Carbon monoxide: Clayton and Giauque, J. Am. Chem. Soc. **54**, 2610 (1932).
   Methane: Frank and Clusius, Zeits. f. Physik. Chemie **B36**, 291 (1937).

6. Coefficients of thermal expansion.
   Baly and Donnan, J. Chem. Soc. **81**, 907 (1902).

7. Densities of liquid and crystal at triple-point.
   Clusius and Weigand, Zeits. f. Physik. Chemie **B46** (1940).

8. Surface tensions.
   Neon: van Urk, Keesom, and Nijhoff, Comm. Leiden No. 182b (1926).
   Argon: Baly and Donnan, corrected by Rudorf, Ann. d. Physik [4] **29**, 764 (1909).
   Nitrogen, oxygen: Baly and Donnan, Trans. Chem. Soc. **81**, 907 (1902).