stitution suggested by him, the desired functions were obtained from analytical relations between the respective curves.

The similarity in the shapes of the graphs $\ln P_{cr}/P_s$; $\ln V_g/V_{cr}$; $\ln V_g/V_l$ and L_{ev}/T as functions of τ suggested that all these curves belong to one and the same family of algebraic functions and can be expressed by a common equation

$$y = k\left((1 - \tau^2)^m/\tau^n\right)$$

differing only in the values of the parameters k, m and n.

The close interrelation between all these properties is further evident from the fact that the values of the above parameters are close to each other when different properties of one and the same substance are compared, as the following table shows for water.

Property	k	m	n	Substance
Latent heat	17.678	0.41810	1.0129	
Volume ratio	4.122	.3770	1.338	H_2O
Vapor volume	3.281	.47169	1.5190	
Vapor pressure	3.4771	.97084	1.5058	

We have tested here only one substance, water, yet the good results obtained with this substance, having an extremely long saturation line, give every reason to believe that other substances will give support to the above findings.

It remains to see whether the second prediction of Dieterici is correct, namely, that a detailed investigation of reduced properties will lead to the reëstablishment of the principle of corresponding states at least for organic liquids and that the deviations, where encountered, will be found as due to differences in the critical data. This we expect to do in Part II of this study.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Thermodynamic Properties of Substances as a Function of Reduced Temperature. II. Vapor Pressures of Liquids and the Principle of Corresponding States

BY HAROLD A. FALES AND CLARA S. SHAPIRO

In the first part of the present article we calculate the latent heat, the vapor volume and the vapor pressure of water using the equations

$$L_{ev}/T = k''' \frac{(1 - \tau^2)^{m'''}}{\tau^{n'''}} \qquad \text{(Ia)}$$

$$\ln V_g/V_{cr} = k'' \frac{(1 - \tau^2)^{m''}}{\tau^{n''}} \qquad \text{(Ib)}$$

$$\ln P_{cr}/P_s = k' \frac{(1 - \tau^2)^{m'}}{\tau^{n'}} \qquad \text{(Ic)}$$

which are all of the same type but differ in the values of the parameters k, m and n.

In this second part of the paper we will apply the equation of reduced pressure to a large number of substances with a view to arriving at some modification of the principle of corresponding states which might embrace different types of compounds.

The thirty substances selected for the test are the same as chosen previously in the study of orthobaric densities[1] with one exception: carbon dioxide is substituted for sulfur dioxide in view of its greater importance and because its vapor pressure and pressure gradient have been determined recently with great precision by the Bureau of Standards.[2] The calculations for carbon dioxide (entire range of saturation) are shown here in detail in Table I which gives: the observed $\ln P_{cr}/P_s$; the percentage differences between observed and calculated ln values; and the average percentage deviation. The estimated accuracy of the equation for carbon dioxide also is given at the bottom of column 4. In examining the figures we see that the agreement is very good throughout, since the actual average deviation ($\Delta \ln = 0.04\%$) is far smaller than the estimated one ($\Delta \ln = 0.25\%$).

In the last three columns we give the observed and calculated pressures and the percentage differences $\Delta P\%$ including the average percentage difference. This is compared with the average deviation of the empirical equation of the Bureau of Standards.[2]

We see that the pressures themselves are represented with high precision up to the very highest temperatures. In the critical region at 31.0° the difference is only 0.1% and the average deviation for the whole temperature range is only 0.09%.

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[1] H. A. Fales and C. S. Shapiro, THIS JOURNAL, **58**, 2418 (1936).

[2] C. H. Meyers and M. S. Van Dusen, *J. Research Bur. Standards*, **10**, 381 (1933).

This compares rather favorably with the average deviation of the Bureau of Standards equation, 0.01%, the latter having six constants.

Both equations are given for reference in the middle of Table I.

At the bottom of Table I we have shown the pressure gradient of carbon dioxide calculated from the proposed and the Bureau's equations. The differences in percentages also are given, as well as the average difference for the range −56.6 to +20° and the accuracy of the Bureau's $\mathrm{d}p/\mathrm{d}T$ values. The latter are considered correct within 0.10%.[2] The proposed equation yields $\mathrm{d}p/\mathrm{d}T$ values which are quite close—within 0.23% on the average—except at very low and very high temperatures. Above 320° the proposed equation begins to give high values for $\mathrm{d}p/\mathrm{d}T$, the difference rising to 2.5% at $\tau = 0.999$ (30.7°) and to 6% at $\tau = 0.9999$ (30.95°). The latter temperature being only 0.05° lower than the critical, the corresponding value of $\mathrm{d}p/\mathrm{d}T$ is taken as the "critical" value of the pressure gradient, since at the critical point itself the proposed equation would give $\mathrm{d}p/\mathrm{d}T$ = infinity as was explained for the case of water in part I.

TABLE I

CARBON DIOXIDE

Vapor pressures: $k' = 3.1734$; $m' = 0.977256$: $n' = 1.50502$

t, °C.	τ	$\ln P_{cr}/P_s$ Obsd.	$\Delta \ln$ % Obsd.-Calcd.	Pressure bars Obsd.	Pressure bars Calcd.	ΔP% Obsd.-Calcd.
−56.59	0.71201	2.65605	−0.2	5.1798	5.20590	0.5
−50.0	.73367	2.37862	− .08	6.836	6.84916	.20
−40.0*	.76655	1.99235	0*	10.059	10.059	0*
−30.0	.79943	1.64126	+ .03	14.290	14.2828	.05
−20.0	.83231	1.31989	+ .03	19.706	19.6984	.04
−10.0*	.86519	1.02390	0*	26.494	26.494	0*
0.0	.89807	0.74968	− .05	34.853	34.8673	.04
+10.0	.93095	.49387	− .10	45.013	45.0374	.05
+20.0*	.96383	.25304	0*	57.27	57.27	0*
+30.0	.99671	.02262	3.5	72.11	72.048	.09
+31.0	1.00000	0	.....	73.76	73.76	.00

Average deviations $\Delta \ln$ = 0.045%

Estimated accuracy of proposed equation $\Delta \ln$ = 0.25%

Average differences:

Proposed eq.: $\Delta P = 0.09\%$

Bur. Standards eq.: $\Delta P = 0.01\%$

*Asterisks mark reference points

Proposed equation: $\ln P_{cr}/P_s = k' \dfrac{(1 - \tau^2)^{m'}}{\tau^{n'}}$

Bureau of Standards equation $\log_{10} P = a - (1/T)[b - my(10^{ny^2} - 1)]$ Where $y = T - T_1$; T_1 = const.

The pressure gradient of carbon dioxide: bars/degrees.

t, °C.	τ	$\mathrm{d}p/\mathrm{d}T$ Bur Stand.	$\mathrm{d}p/\mathrm{d}T$ Proposed	Difference. %
−56.59	0.71201	0.223294	0.223992	+0.3
−50.0	.73367	.2775	.276011	− .6
−40.0	.76655	.3698	.368764	− .3
−30.0	.79943	.4793	.478926	− .08
−20.0	.83231	.6070	.607342	+ .05
−10.0	.86519	.7538	.754995	+ .15
0.0	.89807	.9218	.923258	+ .15
+10.0	.93095	1.115	1.1150	.00
+20.0	.96383	1.344	1.33800	− .45
+30.0	.99671	1.637	1.6581	+1.3
+30.7	.999	(1.661) interpol.	1.700	+2.5
+30.95	.9999	(1.670) interpol.	1.7890	+6.5
+31.0	1.00000	1.672	∞	....
		Proposed eq.: (−56.6 — +20°) =		0.23%
		Bur. Standards eq.: (−56.6 — +25°) =		.10%

Before proceeding with other calculations we have plotted the observed $\ln P_{cr}/P_s$ of other liquids against τ to see how the respective curves are related to each other. Similarly to the volume ratio we find that the ln of reduced pressure again is represented by a family of curves which follow each other in about the same order as that previously found for the ln of the volume ratio.[1]

1 Helium
2 Hydrogen
3 Neon
4 Argon
5 Oxygen
6 Carbon monoxide
7 Nitrogen
8 Ethylene
9 Ethane
10 Hydrogen chloride
11 Nitrous oxide
12 Acetylene
13 Methyl ether
14 Carbon tetrachloride
15 *i*-Pentane
16 Carbon dioxide
17 Benzene
18 Monofluorobenzene
19 Ammonia
20 Methyl formate
21 *n*-Pentane
22 Ethyl ether
23 *n*-Hexane
24 Water
25 Ethyl propionate
26 Acetic acid
27 Sulfur trioxide
28 Methyl alcohol
29 Ethyl alcohol
30 Nitrogen tetroxide

The proposed pressure equation next was applied to every one of these in a manner analogous to water and carbon dioxide and the results recorded briefly in Tables II and III. In Fig. 1 we give 9 typical representative curves $\ln P_{cr}/P_s$, namely: (a) helium, (b) hydrogen, (c) argon, (d) carbon monoxide, (e) methyl ether, (f) *n*-hexane, (g) water, (h) ethyl alcohol, (j) nitrogen tetroxide. In Table II we give the corresponding calculations. (Acetic acid is substituted for water, which has been given in Part I of this paper.)

Table II is constructed similarly to that of orthobaric densities.[1]

For lack of space we give only the percentage differences; (a) between observed pressures and those calculated by the proposed equation; (b) between observed pressures and those calculated by the respective empirical equations used by the different observers.

In examining Table II we wish to speak especially of helium, hydrogen, acetic acid and nitrogen tetroxide.

Helium has an extremely long saturation range when expressed in reduced units (τ = 0.2–1.0). The observers at Leiden used two equations of the same type for this substance, the one equation to represent liquid helium I up to the transition point (2.19°K.), the other to represent liquid helium II from the transition point to the critical

TABLE II

COMPARISON OF THE PROPOSED EQUATION WITH THE OBSERVER'S TEST EQUATIONS AS SHOWN BY THE DIFFERENCES. $P_{\text{obsd.}} - P_{\text{calcd.}}$

Substances	(a) Helium			(b) Hydrogen			(c) Argon	
Equations	Proposed $\Delta P\%$	Leiden		Proposed $\Delta P\%$	Leiden		Proposed $\Delta P\%$	Leiden
0.250	0.00	0.01	Eq. I					
.300	.50	.15						
.350	.10	.30						
.400	1.00	.30						
.450	3.3	.20	Eq. II	..	..	Eq. I		
.500	4.1	.18		1.8	0.30		..	..
.550	1.0	.15		1.12	.35		0.20	0.00
.600	0.20	.00		1.12	.50		.00	.20
.650	0.90	.00		1.35	.46		..	..
.700	1.3	.01		1.45	.35	Eq. II	..	..
.750	1.5	.01		1.50	.30		.27	.42
.800	1.9	.00		1.08	.70		.07	.10
.850	1.4	.05		1.00	.35		.30	.29
.900	0.70	.05		0.85	.20		.60	.20
.950	.00	.10		.48	.20		.50	.20
1.000	.00	5.0[a]		.00	.18		.00	.23
Average diff.:	1.2%	0.10%		1.00%	0.400%		0.23%	0.26%

[a] In averaging the $\Delta P\%$ for helium the deviation for P_{cr} was excluded.

Substances	(d) Carbon monoxide		(e) Methyl ether		(f) *n*-Hexane[b]		
Equations	Proposed $\Delta P\%$	Leiden	Proposed $\Delta P\%$	Cardozo	Proposed	Biot $\Delta P\%$	Cederberg
0.500	..	..			..	..	..
.550	0.02	0.02			0.75	0.70	1.00
.600	.03	.10			.26	.47	0.23
.650	.02	.07	..	..	.20	.10	.40
.700	.22	.56	0.00	1.00	.30	.02	.30
.750	.15	.48	.25	0.00	.18	.10	.20
.800	.20	.20	.15	1.00	.02	.10	.12
.850	.05	.40	.02	0.80	.10	.20	.20
.900	.08	.18	.40	.30	.20	.13	.20
.950	.10	.10	.30	.30	.05	.25	.25
1.000	.00	..	.00	.00	.00	.40	.40
Average diff :	0.094%	0.209%	0.275%	0.517%	0.29%	0.28%	0.36%

[b] Cederberg's "reduced" pressure equation is explained in the text.

Substances	(g) Acetic acid			(h) Ethyl alcohol		(j) Nitrogen tetroxide	
Equations	Proposed $\Delta P\%$	Biot		Proposed $\Delta P\%$	Biot	Proposed $\Delta P\%$	"Int. Crit. Tables"
0.400	..	..					
.450	11.0	7.0					
.500	0.36	0.55		..	..		
.550	.10	.10		5.0	0.03		
.600	.60	.10		0.30	.13	..	..
.650	(1.3)	(1.6)	uncertain	1.40	.60	0.10	1.0
.700	(2.5)	(3.0)	data	0.70	.70	.10	0.10
.750	0.40	0.67		.60	.20	.33	.30
.800	.90	.10		.30	.17	.12	.72
.850	.40	.32		.30	.30	.15	.65
.900	.55	.30		.28	.02	.12	.35
.950	.40	.60		.10	.15	.12	.22
1.000	.00	.15		.00	.20	.00	.50
Average diff.:	0.413%	0.281%		0.440%	0.300%	0.172%	0.433%

point. At the critical point their calculated P_{cr} value is smaller than the observed value by 5%. The eqs. I and II of Leiden are given in the communications of the Leiden Laboratories (see Table IV).

The proposed equation has an average deviation $\Delta P = 1.2\%$ between the melting point and the critical point. This is, however, not outside of the experimental limits for a substance with such an extremely low critical temperature (5°K.).

In fact the accuracy for helium was estimated to be Δ ln = 3.7%, while the actual deviation was found to be Δ ln = 1%. It must be noted that in our calculations the observed critical pressure when used in the term ln P_{cr}/P_s gave much inferior results than the P_{cr} obtained from the Leiden pressure equation II. This indicated the possibility of an error in the experimental value of P_{cr} and it was not used in our calculations.

It also is interesting to note that we tried to apply the proposed equation separately to the pressures of liquid helium I and II, but the average deviation, Δ *P*, in each case was far too great, being of the order of 3%.

Hydrogen.—Here the pressures in the range melting point to boiling point were redetermined recently by Leiden and tested by a corresponding pressure formula; the older measurements, between boiling point and critical point, have been checked by a different equation (Leiden). The agreement between the above calculated and observed values is within 0.4% on the average. The proposed equation for hydrogen fits the whole range melting point to critical point within Δ *P* = 1.0%. In view of its low critical temperature (33°K.), we feel that this agreement is satisfactory, since actual average deviation Δ ln = 1.0% is the same as the estimated Δ ln = 1.0%.

Acetic Acid.—This substance is an example of the so-called associated liquids. We see that the proposed equation gives for pressures just as good agreement as the similar equation gives for volume ratios; the behavior of the pressures likewise fails to indicate association in either the liquid or vapor phase.

Nitrogen Tetroxide.—This occupies the highest position among the substances investigated, just as was noted in the case of the volume ratios. The curve ln P_{cr}/P_s differs, however, from the curve ln V_g/V_l in that it is very regularly shaped.[1] In our calculations the three reference points were taken from the pressure values given in the "International Critical Tables" (Vol. III, 1928) which are largely based on the measurements of Baumé and Robert[3] and Scheffer and Treub,[8] but extend only from the boiling point to the critical point. The proposed equation gives excellent agreement with the pressures in the "International Critical Tables" (normal boiling point to critical point). For the lower temperatures we have checked our calculations against the recent values of Mittasch, Kuss and Schleuter[4] and against the old data of Scheffer and Treub[3] and have found that the calculated pressures are very close to those of Scheffer and Treub, deviating from the values of Mittasch and co-workers. The accuracy of the pressures recorded in the "International Critical Tables" (Vol. III, p. 228 top, ed. 1928) was tested by their equation and was estimated to be 0.01 atm., approximately, which amounts to an average Δ *P* = 0.43% (b. p. to T_{cr}). The deviation of the proposed equation is much smaller, since its average Δ*P* = 0.17% (between m. p. and crit. point).

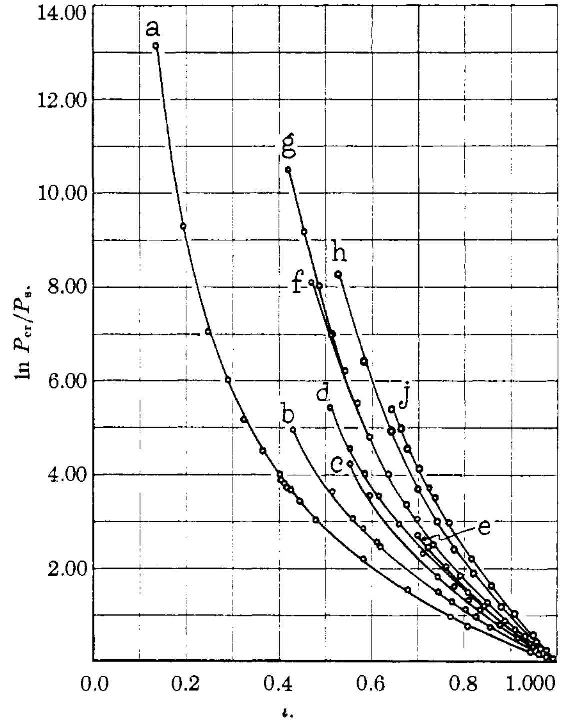

Fig. 1.—ln (P_{cr}/P_s) = $k'(1 - \tau^2)^{m'}/\tau^{n'}$: a, helium; b, hydrogen; c, argon; d, carbon monoxide; e, methyl ether; f, *n*-hexane; g, water; h, ethyl alcohol; j, nitrogen tetroxide.

With regard to the remaining five substances, argon, carbon monoxide, methyl ether, hexane and ethyl alcohol, Table II shows clearly that the proposed equation gives average deviations which are about equal and in the case of methyl ether decidedly smaller than the deviations given by the observers' empirical equations.

Taking the nine illustrative examples as a whole the results show that the proposed equation

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(3) Baumé and Robert, *Compt. rend.*, **169**, 1199 (1919); Scheffer and Treub, *Proc. Roy. Acad. Amsterdam*, **14**, 536 (1912).

(4) Mittasch, Kuss and Schleuter, *Z. anorg. Chem.*, **159**, 29 (1927).

is applicable to the vapor pressures of different liquids in the range boiling point to critical point. At very low temperatures the discrepancy is large compared with experimental precision, but at very high temperatures (τ = 0.9 to 1.0), the deviations from observed data are small, being of the same order as for the moderate temperatures, as was mentioned earlier for the case of water (Part I).

In Table III we give the summary of the pressure calculations for the thirty liquids previously studied for their orthobaric volume ratios.[1] It is constructed exactly like Table III of that article.

In the third column the parenthesized figures indicate the bibliography on experimental vapor pressure and critical pressure data, listed in Table IV.

In the fourth column the observed P_{cr} are given for each substance. The data for helium and ethylene, marked with a *b*, are uncertain since they deviate considerably from the calculated P_{cr} derived from the very accurate Leiden equations. In these cases, it was found accordingly that the Leiden values when substituted in the term ln P_{cr}/P_s gave a smoother observed curve which agreed better with the calculated one.

In the next column are given the values ln P_{cr}/P_s for τ = 0.6000, which were read directly from the graph; in the following two columns the averages of actual and estimated differences, Δ ln%, were computed by means of accurate graphs for every substance, in a manner analogous to that for orthobaric densities.[1] It will be noticed that the estimated deviations Δ ln for pressures are

TABLE III

SUMMARY OF RESULTS

Substances in this table are arranged in the ascending order of curves

	Substances	*a*	P_{cr}, atm., obsd.	ln P_{cr}/P_s, obsd. τ = 0.600	Average % diff: Actual Δ ln %	Estim. Δ ln %
1	Helium	(2,1)	2.26[b]	2.07	0.7	3.7
2	Hydrogen	(2,1)	12.80	2.15	1.00	0.9
3	Neon	(2,1)	26.86	3.47	0.18	.8
4	Argon	(2,1)	47.996	3.60	.17	.8
5	Oxygen	(3,1)	49.713	3.67	.05	.8
6	Carbon monoxide	(1,2)	34.529	3.75	.08	.8
7	Nitrogen	(3,1)	33.490	3.75	.15	.7
8	Ethylene	(2,1)	50.65[b]	3.90 (interp.)	.15	.5
9	Ethane	(4)	48.8	4.00 (extrap.)	.03	.3
10	Hydrogen chloride	(4)	81.6	4.01	.25	.5
11	Nitrous oxide	(4)	71.7	4.15	.15	.5
12	Acetylene	(4)	62.0	4.20	.08	.5
13	Methyl ether	(5)	52.00	4.35	.23	.30
14	Carbon tetrachloride	(8)	44.975	4.35	.26	.30
15	*i*-Pentane	(8)	32.918	4.40	.21	.30
16	Carbon dioxide	(6)	72.80	4.42	.05	.15
17	Benzene	(8)	47.888	4.42	.29	.30
18	Monofluorobenzene	(8)	44.621	4.55	.29	.30
19	Ammonia	(4)	112.3	4.56	.09	.15
20	Methyl formate	(8)	59.350	4.60	.19	.30
21	*n*-Pentane	(8)	33.026	4.60	.22	.30
22	Ethyl ether	(8)	35.605	4.67	.25	.30
23	*n*-Hexane	(8)	29.618	4.70	.15	.30
24	Water	(7)	218.167	4.95	.12	.15
25	Ethyl propionate	(8)	33.180	5.20	.22	.30
26	Acetic acid	(8)	57.105	5.23	.19	.30
27	Sulfur trioxide[c]	(4)	83.6	5.65	.7	.35
28	Methyl alcohol	(8)	78.500	5.70	.10	.30
29	Ethyl alcohol	(8)	62.961	6.13	.23	.30
30	Nitrogen tetroxide	(4)	99.0	6.40 (extrap.)	.08	.30

[a] The numbers in column 3 indicate the corresponding literature on the observed vapor pressures and critical pressures (listed in Table IV). [b] The observed critical pressures of helium and ethylene differ by 5 and 2%, respectively, from the P_{cr} values calculated by the observers' test equations. The latter values, $P_{cr\,He}$ = 2.15 atm. and $P_{cr\,Ethylene}$ = 49.72 atm., were used in the corresponding observed ln P_{cr}/P_s. [c] Sulfur trioxide is the only substance which shows large discrepancy between observed and calculated ln P_{cr}/P_s.

TABLE III (*concluded*)

Proposed equation: $\ln P_{cr}/P_s = k' \frac{(1 - \tau^2)^{m'}}{\tau^{n'}}$ P_s = vapor pressure (atm.)

					Average % differences of equations		
Substances	K_{cr}[a]	k'[b]	m'	n'	Proposed	Observers	Cederberg
1 Helium	3.264	(1.9506)	(1.03382)	(0.9787)	1.2	0.10	
2 Hydrogen	3.273	2.4088	0.99513	1.0948	1.00	.40	
3 Neon	3.245	2.4805	.90863	1.4426	0.27	.410	
4 Argon	3.426	2.6635	.96339	1.4062	.23	.26	
5 Oxygen	3.421	(2.8374)	(.99493)	(1.3717)	.125	.562	
6 Carbon monoxide	3.440	2.7739	.97352	1.4471	.094	.209	
7 Nitrogen	3.426	2.8539	.98595	1.3883	.445	.352	
8 Ethylene	3.527	2.8905	.98263	1.4420	.124	.100	
9 Ethane	3.587	2.8660	.95195	1.4643	.093	.098	
10 Hydrogen chloride	3.801	3.0254	.97824	1.4206	.37	.10	
11 Nitrous oxide	3.630	3.0363	.98691	1.4737	.126	.461	
12 Acetylene	3.635	3.0729	.96503	1.5012	.133	.670	
13 Methyl ether	3.719	(2.8959)	(.93872)	(1.6322)	.275	.517	[d]
14 Carbon tetrachloride	3.680	2.9996	.95560	1.5533	.347	.150	0.280
15 *i*-Pentane	3.735	3.2158	.98401	1.4849	.400	.205	.210
16 Carbon dioxide	3.585	3.1734	.97726	1.5050	.090	.010	
17 Benzene	3.755	3.0871	.96426	1.5408	.330	.260	.260
18 Monofluorobenzene	3.796	3.1502	.96150	1.5572	.375	.290	
19 Ammonia	4.125	3.3281	.99234	1.4703	.215	.050	
20 Methyl formate	3.922	3.2568	.98283	1.5286	.260	.270	
21 *n*-Pentane	3.766	3.2340	.97783	1.5123	.441	.270	.290
22 Ethyl ether	3.840[e]	3.2440	.96718	1.5551	.410	.158	.175
23 *n*-Hexane	3.830	3.2633	.96326	1.5702	.290	.280	.350
24 Water	4.234	3.4771	.97084	1.5058	.080	.04	
25 Ethyl propionate	3.923	3.3805	.94847	1.6449	.555	.246	
26 Acetic acid	4.991	(3.7852)	(.97659)	(1.4852)	.413	.281	
27 Sulfur trioxide	3.805	(2.7265)	(.85818)	(2.1664)	1.15	.85	
28 Methyl alcohol	4.559	4.0154	.98696	1.5428	0.200	.215	
29 Ethyl alcohol	4.026	3.9880	.97597	1.6690	.440	.300	
30 Nitrogen tetroxide	4.385	5.3981	1.00460	1.2260	.172	.433	

[a] The critical coefficient: $K_{cr} = (RT_{cr})/(P_{cr}V_{cr})$ is given for comparison. [b] The values of k', m', n' in parentheses are not very reliable due to the range of observed pressures being too short, or some P_{obsd} values being unreliable. [c] The range of temperatures is for every substance from melting point to critical point except: ethylene (162K°. − $t°_{cr}$); oxygen (m. p. to 134°K.); carbon tetrachloride (+20° to $t°_{cr}$); monofluorobenzene (+20° to $t°_{cr}$); water (60° to $t°_{cr}$). [d] The average deviations given in the last column refer to Cederberg's equation discussed in the text. [e] The critical coefficient for ethyl ether is that given by Young, corresponding to the P_{cr} = 35.0 atm. This value was used in our calculations of $\ln P_{ci}/P_s$ since it gives better agreement than recent data of Wilip, or Schrör (Landolt's "Tabellen," Erg. I and III).

in each case lower by about 0.15% than the corresponding Δ ln for the volume ratio. This is due to the following consideration: the effect of the errors in T_{cr} is the same for both properties, since the two proposed equations are identical in form. As to the effect of errors in vapor pressure and in P_{cr}, it is almost negligible, since pressures can be measured with an accuracy much greater than in the case of vapor volumes. Accordingly we have assumed that the error in $\ln P_{cr}/P_s$ does not exceed 0.1% for every substance, (the error in $\ln V_g/V_l$ was accepted equal to 0.3%).

In comparing the actual differences: Δ ln% with the estimated ones we see that with the exception of sulfur trioxide all substances here selected give agreement far within the experimental limits. This shows that the pressure equation applies to substances just as well as the equation for volume ratio. The case of sulfur trioxide is not an exception, but rather a result of deficiency in experimental data.

The reference points for sulfur trioxide were taken from the "International Critical Tables" which are largely based on the data of Berthoud.[5] In his original work this author estimates the

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(5) Berthoud, *Helv. Chim. Acta*, **5**, 13 (1922), and *J. chim. phys.*, **20**, 77 (1923).

precision of his measurements as being within 0.3 atm. This he considers good in view of experimental difficulties met with in the handling of sulfur trioxide gas in equilibrium with its liquid. Assuming high accuracy of pressure data, we would estimate the deviation of the proposed equation not to exceed Δ ln = 0.35%. Actually we find the calculated curve follows that of Berthoud within Δ ln = 0.7% in the interval n. b. p. to crit. p. In the range m. p. to n. b. p. the calculated curve deviates very much from this author's values, but is in agreement with the recent measurements of Roth and Grau[6] (given only for that short interval).

In the succeeding four columns of Table III we give the constants k', m', n' of the equation and the critical coefficient K_{cr}, the latter being included just for comparison. In the last three columns we give the average percentage deviations of the proposed equation with regard to pressures themselves, compared with the corresponding deviations of observers' test formulas.

In examining the sets of deviations $\Delta P\%$ we see that in general the proposed equation is quite comparable with the different types of pressure equations used by the experimenters, and having from four to six constants. It is interesting to note that the best agreement is shown by those eight substances which have the most recent and precise pressure data, namely: water, carbon dioxide, ammonia, carbon monoxide, argon, neon, ethylene, oxygen, methyl ether and ethane. Of these the first two were measured at the Bureau of Standards and the Massachusetts Institute of Technology; the next four have been determined at the Leiden Laboratories, and the last three by Dodge and Davis, by Porter, and by Cardozo and Bruno, respectively (see Table IV). For all these substances the proposed equation fits within Δ P = 0.1–0.2%, the observers' test formulas showing equivalent or slightly better accuracy, with the exception of neon, oxygen and methyl ether. In these last three cases our calculations are somewhat closer, the respective ΔP being: 0.27 against 0.40%, 0.13 against 0.56% and 0.28 against 0.52%.

On the other hand, the nitrogen data are better represented by the Dodge and Davis equation (same as for oxygen), the differences being Δ P = 0.35% against ours of 0.45%.

Of the older measurements the proposed equation seems to fit three substances with greater accuracy than that estimated by the "International Critical Tables." These are: nitrogen tetroxide, discussed above; nitrous oxide and acetylene, with respective Δ P = 0.17 against 0.43%, 0.13 against 0.46% and 0.13 against 0.67%. Contrary to this we notice that hydrogen chloride is given in the "International Critical Tables" within 0.1%, while our calculations show a deviation ΔP = 0.37%.

The organic substances measured by Young and checked against Biot's pressure equation indicate the superiority of the latter, with a few exceptions. In general our P values deviate by 0.4–0.5% from the observed ones, the corresponding deviation of Biot averaging about 0.2–0.3%. In the case of *n*-hexane, methyl formate and methyl alcohol the two sets of differences are equivalent (Δ P = 0.3%).

For six of the above liquids we have included the results of Cederberg's calculations. All of them seem to follow the observed data with the same precision as Biot's calculations (Δ P = 0.3%). This shows general applicability of the former to organic liquids with high critical temperatures.

It remains to add that the three substances helium, hydrogen and sulfur trioxide are only approximately (within 1%) represented by the proposed equation, which is to be expected on the ground of the low critical temperatures for the first two and on the ground of low accuracy of pressure measurements for the last one, as was explained above.

In conclusion we can say that out of thirty substances examined seventeen give equal or somewhat better agreement with the proposed equation than with the observers' calculations. Ten substances show slightly larger discrepancy from experiment than that estimated by the observers and only two substances give considerably inferior results.

Taking into consideration that the proposed equation has only three constants, we feel that the results obtained for vapor pressure are rather favorable and quite sufficient for our purpose—the study of the correspondence principle—since they indicate that the equation rests upon sound construction and shows a wide and precise applicability both with respect to type of substance and length of temperature range.

Comparison of the Constants k', m', n', and the Critical Coefficient.—In comparing the con-

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[6] Roth and Grau, *Z. anorg. Chem.*, **188**, 173 (1930).

stants of the equation for different substances we see here as in the case of orthobaric volumes that they vary within narrow limits although the chemical and physical properties differ very much for the examples given; helium and nitrogen tetroxide again are characterized by very low and high parameter values, respectively. For other substances they increase gradually in the order of ascending ln P_{cr}/P_s curves. It must be noted that in the case of pressures not only k' but m' and n' as well show regular increase in the order of the curves. Of these the constant m' shows the least variability, the limits being 0.9086 to 1.0000. The constant n' ranges from 0.9787 to 1.6690, while the constant k' varies most, from 1.9506 to 5.398.

In comparing the parameters for pressure with those for the volume ratio we see that the constant n' is very close to n, averaging 1.40 against 1.30. The constant m' is about 2.5 times larger than m, the respective averages being 0.97 and 0.38. The constant k' is in each case smaller than k. Their ratio varies but little for different substances: from 1.3 to 1.15, the average being $k/k' = 1.2$.

As to the critical coefficient it was found to be almost identical with k of the volume ratio.[1] Accordingly we find that the values of K_{cr} are larger than the pressure constant k' in about the same proportion as above. Their ratio has an average value $K_{cr}/k' = 1.2$ for the thirty liquids given, with the exception of helium (1.6) and nitrogen tetroxide (0.84).

It will be observed from Table III that the k' values follow each other in the same order as the K_{cr} values, which is entirely analogous to the fact observed with respect to the constant k of the volume ratio.

Since the order of succession for K_{cr} and k' parallels that of the curves in the coördinate system, we conclude that the two sets of properties ln P_{cr}/P_s and ln V_g/V_l should have similar relative positions when plotted against reduced temperature. In fact we observe this to be true with but few exceptions. In comparing the Tables III in this and in the previous article, we notice that the first fourteen and the last three liquids (helium to carbon tetrachloride and methyl alcohol to nitrogen tetroxide) have exactly the same location. As to the remaining thirteen substances the general sequence is the same with the following shifts. The pressure curve of benzene is now next to that of monofluorobenzene. Water, acetic acid, sulfur trioxide and ethyl propionate are again close to each other, although the respective order is changed. The n- and i-pentanes are still close to each other, although not adjacent, as was the case for their volume ratios. Carbon dioxide seems to be like sulfur dioxide in that its pressure curve is close to ammonia (between benzene and carbon tetrachloride). On the whole we find that the two properties, reduced pressures and the volume ratio, exhibit striking similarity, since not only their relative positions but the relative parameter values correspond closely in the majority of cases.

TABLE IV

BIBLIOGRAPHY ON EXPERIMENTAL DATA: VAPOR PRESSURES AND CRITICAL DATA

(1) The new scale of temperatures: (Absolute zero = −273.144°C.) The corrected critical temperatures and the latest data on P_{cr}, V_{cr}, K_{cr} for: helium, hydrogen, neon, argon, oxygen, nitrogen, carbon monoxide and ethylene: Mathias and Crommelin, *Ann. Phys.*, **5**, 137, 143, 144 (1936).

(2) Vapor pressures observed at the Leiden Laboratories: Helium—Comm. No. 202c and suppl. 71d. Hydrogen—Comm. No. 217a, 152a. Neon—Comm. No. 185b, suppl. 64d; T_{cr}—*Ann. Phys.*. [9] **19**, 236 (1923). Argon—Comm. No. 138c. Carbon monoxide—*Ann. Phys.*, **5**, 137 (1936). Ethylene—*ibid.*, [10] **11**, 344 (1929).

(3) Oxygen and nitrogen: vapor pressures (b. p. to crit. p.). Dodge and Davis. THIS JOURNAL, **49**, 610 (1927). Nitrogen: Vapor pressures (m. p. to b. p.). Giauque and Clayton, *ibid.*, **55**, 4879 (1933).

(4) Vapor pressures (norm. b. p. to crit. p.) and critical data recorded in the "I. C. T.," Vol. III, ed. 1928. Acetylene, nitrous oxide, ammonia: pp. 229, 230, 234. Ethane: P_{sat}—p. 230; P_{cr}, V_{cr}, T_{cr}—p. 248. Hydrogen chloride, sulfur trioxide and nitrogen tetroxide, pp. 228–229. Vapor pressures (m. p. to b. p.) for the last three substances: HCl—Giauque and Wiebe. THIS JOURNAL, **50**, 101 (1928). SO_3—Roth and Grau. *Z. anorg. Chem.*, **188**, 173 (1930). N_2O_4—Scheffer and Treub, *Z. physik. Chem.*. **81**, 308 (1912) (6–50°C.).

(5) Methyl ether: (vapor pressures and crit. data) Cardozo and Bruno, *J. chim. phys.*, **20**, 347 (1923).

(6) Carbon dioxide: P_s, dp/dT, crit. data: original paper by the Bur. Stand. Meyers and Van Dusen, *Bur. Standards J. Research*, **10**, 381 (1933).

(7) Water: vapor pressures (m. p. to b. p.), empir. eq. and dp/dT: Osborn and Meyers, *ibid.*. **13**, 1 (1934). Obsd. vapor pressures (b. p. to crit. p.) and crit. data: Keyes. Smith and Gerry, *Proc. Am. Acad. Arts Sci.*. **69**, 139, 285 (1934).

(8) Vapor pressures and critical data observed by S. Young: carbon tetrachloride, benzene, monofluorobenzene i- and n-pentanes, methyl and ethyl alcohols, n-hexane, methyl formate, ethyl propionate, ethyl ether and acetic acid. S. Young, *Proc. Roy. Dublin Soc.*, **12**, 374 (1910).

The most striking example is that of nitrogen tetroxide, where k' and k are 5.4 and 4.9, respectively, while n' and n are 1.24 and 1.22, respectively. We observe finally that adjacent pressure curves have nearly equivalent constants. Here, as in the case of volume ratios, the substances oxygen, carbon monoxide and nitrogen, ethyl ether and *n*-hexane, or methyl and ethyl alcohols serve as good examples. The question arises, however, regarding the relation between the position of the pressure curves (Fig. 1) and the critical values. In the case of the volume ratio the close agreement between K_{cr} and k values,[1] suggests a direct influence of the critical properties on the relative volumes V_g/V_l, as well as on their order in the coördinate system. In the case of pressures we also can state that the critical data have an influence on their order in the coördinate system, because of the parallelism in the succession of K_{cr} and k' values noticed in the majority of the cases.

Discussion of the Correspondence Principle of van der Waals.—The correspondence theorem, as is well known, is a direct deduction from van der Waals equation of state and is based on the assumption that this equation holds both for gaseous and liquid phases, as well as for the equilibrium vapor ⇄ liquid.

In its reduced form this equation contains no constants characteristic of any particular substance, thus:

gases and vapors: $(\pi + 3/\varphi_g^2)(3\varphi_g - 1) = 8\tau$ (1a)

liquids: $(\pi + 3/\varphi_l^2)(3\varphi_l - 1) = 8\tau$ (1b)

where π, φ_g, φ_l, τ are the vapor pressure, the vapor and liquid volumes and the temperature, all expressed in reduced units.

On the basis of Maxwell's theorem of equal areas it has been shown that the above equation will apply to the heterogeneous complex vapor ⇄ liquid in the form

heterogeneous complex: $(\pi + 3/\varphi_g\cdot\varphi_l)(\varphi_g - \varphi_l) = \frac{8\tau}{3}\cdot\ln\frac{3\varphi_g - 1}{3\varphi_l - 1}$ (1c)

From the three equations (1a–1c) defining the behavior of substances during evaporation it obviously follows

$$\pi = f(\tau) \qquad (2a)$$
$$\varphi_g = F(\tau) \qquad (2b)$$
$$\varphi_l = \varphi(\tau) \qquad (2c)$$

The equations (2a–2c) mean that the reduced vapor pressure, vapor volume and liquid volume should be functions of reduced temperature which are entirely independent of the nature of substance, or in other words that the curves ln π–τ and ln φ–τ should coincide for all liquids. Therefore, at equal reduced temperatures the corresponding reduced pressures and volumes should be equal for all substances. This is the essence of the van der Waals theory.[7]

The states at which substences have identical values of π, φ, τ, were called by van der Waals the "corresponding" states for which the condition is with respect to any two substances A and a:

$$\pi_A/\pi_a = 1.000 \qquad (3a)$$
$$\varphi_A/\varphi_a = 1.000 \qquad (3b)$$
$$\tau_A/\tau_a = 1.000 \qquad (3c)$$

The original idea of van der Waals has been subjected to numerous investigations by Young, Onnes, Nernst, Bingham, Shames and others, and it was found that[8] in general the correspondence principle is not valid. This is not astonishing in view of the fact that the van der Waals equation of state has been found inadequate to represent the variety of substances under *all* conditions of pressure and temperature. Thus no direct experimental evidence exists that this equation represents the liquid phase of any substance correctly. For the gaseous phase, all fluids fail to follow the equation, while at pressures approaching the saturated vapor volume the deviations are greatest and become especially large in the critical region. For example at the critical point the van der Waals equation leads to the critical coefficient $K_{cr} = RT_{cr}/P_{cr}V_{cr} = {}^8/_3$ while ${}^{16}/_5$ is the lowest for any actual substance.

Since the equation (1a–b) does not hold for the vapor nor the liquid phase, it follows that equation (1c) does not hold for the heterogeneous complex vapor–liquid.

This means that for real liquids the variation of reduced vapor pressures, or of volumes with temperature cannot be expressed by universal functions as in the equations (2a–c). This has been proven definitely by Nernst and by Bingham,[7,8] who have made a graphical examination of the experimental data of a large number of substances. They found that when observed ln π

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(7) J. R. Partington, "Textbook of Thermodynamics." D. Van Nostrand Co., New York, 1913, pp. 231–232.

(8) A complete survey of the modern view upon this subject is found in: K. Jellinek, "Lehrbuch der phys. Chem.," Vol. I, Verlag Ferdinand Enke, Stuttgart, 1928, pp. 672–712—history; pp. 712–720—concept of mechanical similarity and the correspondence principle; pp. 728–730—discussion and criticism of the hypothesis of molecular association as a cause of deviations from this principle,

are plotted against $(1-\tau/\tau)$ a whole array of lines results originating from the critical point.

The cause of the discrepancy between observed fact and van der Waals theory has been given differently by different authors.[8]

The modern view is in accordance with the work of Onnes, who ascribes the chief cause of discrepancies to the differences in chemical composition.[9]

The modern conclusion is that in general this law breaks down, the individual differences between substances being too pronounced, but it is still thought applicable to groups of closely related substances within narrow limits: (I) mono- and diatomic gases; (II) normal organic liquids, which are further subdivided into: (a) paraffins, benzene and the halogenated benzenes, ethyl ether, carbon tetrachloride; (b) fatty esters; (III) associated liquids: (a) water; (b) alcohols; (c) acetic acid.

Within each subdivision there is enough similarity among the members so that the individual deviations are comparatively small.[8]

The mathematical interpretation of the modern correspondence idea can be given as follows. While it has been found impossible to express the reduced vapor pressures, and reduced vapor volumes, as universal functions of reduced temperature, it may be that the behavior of real substances satisfies a number of such equations each one free from individual constants, and applying to a small group of substances, such as the subdivision of the groups I, II, or III listed above.

The particular form of such functions would vary from one type of liquid to another, but all would have the general form

$$\begin{array}{lll} \pi = f_1(\tau)\ \text{(4a)} & \varphi_g = F_1(\tau)\ \text{(4b)} & \varphi_l = \varphi_1(\tau)\ \text{(4c)} \\ \pi = f_2(\tau) & \varphi_g = F_2(\tau) & \varphi_l = \varphi_2(\tau) \\ \pi = f_3(\tau) & \varphi_g = F_3(\tau) & \varphi_l = \varphi_3(\tau) \\ \vdots \quad \vdots & \vdots \quad \vdots & \vdots \quad \vdots \\ \pi = f_n(\tau) & \varphi_g = F_n(\tau) & \varphi_l = \varphi_n(\tau) \end{array}$$

which would give the reduced magnitudes of each member of a given group as identical functions of reduced temperature.

Accordingly, the reduced magnitudes would be represented in the coördinate system by several "ideal" lines, given by eq. (4a–c) and corresponding to each subdivision of the groups I to III above. Around each one of these theoretical lines will cluster the "observed" lines given by the real liquids, members of the particular division.

A careful examination of experimental evidence shows that real substances do not behave in the above manner. This becomes clear from the inspection of Fig. 1 and of Table III, column 5, which gives the observed values of ln P_{cr}/P_s compared at equal reduced temperatures, namely, at $\tau = 0.6000$.

It will be seen, in the first place, that the dispersion of curves is not discontinuous, but gradual. No sharp subdivision into groups can be made, where each group would fluctuate around a single line. Even the pressures of normal organic liquids, which according to Dieterici should show very similar behavior, are found to occupy a rather broad region between carbon tetrachloride (adjacent to curve e in Fig. 1) and ethyl propionate (adjacent to curve g). This shows that even with respect to this small group of substances (group II above) it hardly can be said that their lines ln P_{cr}/P_s represent small deviations from an ideal line.

We come to the conclusion that the theorem of corresponding states is not supported by experimental evidence and has neither universal application assumed by van der Waals, nor regional application thought of by the modern investigators. Hence the coefficients relating the reduced properties of any two substances at equal reduced temperatures can in general never be equal to unity

$$\pi_A/\pi_a \neq 1.000 \qquad (5a)$$
$$\varphi_A/\varphi_a \neq 1.000 \qquad (5b)$$
$$\text{when } \tau_A/\tau_a = 1.000$$

The question now can be asked: "If substances do not show an identical behavior along the saturation line, is there not some other regularity governing this behavior? If the relating coefficients in the equations (5a–b) are not equal to unity, is there not some other definite relationship between reduced magnitudes when compared at equal reduced temperatures?"

The answer to this question is given by the fact that it is possible to express quantitatively the change of reduced vapor pressure, or vapor volume, with reduced temperature of all liquids by introducing three individual constants into the general functions of eq. (4a–b). These will now have the form

$$\pi = f(\tau, k', m', n') \qquad (6a)$$
$$\varphi = F(\tau, k'', m'', n'') \qquad (6b)$$

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(9) The view of Onnes is based on the concept of mechanical similarity which has been developed by Newton and extended by Bertrand: see H. K. Onnes, *Arch. Néerl.*, **30**, 112 (1897).

We shall now imagine two substances A and a which follow the proposed equation Ia–Ic. This can be written in the forms

$$\pi = e^{-z} \tag{7a}$$

where

$$z = \left[k'' \frac{(1 - \tau^2)^{m'}}{\tau^{n'}}\right] \tag{7b}$$

$$\varphi = e^{Z} \tag{8a}$$

where

$$Z = \left[k'' \frac{(1 - \tau^2)^{m''}}{\tau^{n''}}\right] \tag{8b}$$

It is obvious that at equal τ the reduced pressures and reduced volumes of A and a will be related in a definite manner.

$$\pi_A/\pi_a = e^{z_a - z_A} = j \tag{9a}$$

$$\varphi_A/\varphi_a = e^{Z_A - Z_a} = J \tag{9b}$$

Substituting the values z and Z given by (7) and (8) and transforming, we get

$$\ln j = z_a - z_A = \left[k' \frac{(1 - \tau^2)^{m'}}{\tau^{n'}}\right]_a - \left[k' \frac{(1 - \tau^2)^{m'}}{\tau^{n'}}\right]_A \tag{10a}$$

$$\ln J = Z_A - Z_a = \left[k' \frac{(1 - \tau^2)^{m''}}{\tau^{n''}}\right]_A - \left[k'' \frac{(1 - \tau^2)^{m''}}{\tau^{n''}}\right]_a \tag{10b}$$

From the equations (9) and (10) it follows that at equal reduced temperatures the reduced magnitudes of two chemically different substances will not be equal to each other, but will be related in a definite way, the relating coefficients j and J being exponential functions of the reduced temperature and of the respective parameters k, m, n, of the equation.

From these equations it is seen further that the coefficients j and J increase with decrease of τ, hence the dispersion of curves is the greater the lower the temperature, which is supported by experimental evidence. Finally, it is evident that in general the coefficients j and J will be equal to unity at $\tau = 1.000$; hence the curves will coincide at one point only, at the critical point. This is the only temperature then, at which all substances show identical behavior, as also can be seen from Fig. 1.

Under two conditions, however, the coefficients j and J become unity at temperatures other than critical: (1) when the constants k, m, n, of one substance are very close to those of the other substance. This happens for nitrogen and carbon monoxide, for *i*- and *n*-pentane, etc. It follows that substances closely related chemically will show nearly identical behavior along the saturation line as was shown by Onnes.[8] This is true both for organic liquids and permanent gases, when treated individually rather than as a group. (2) It also may happen that the two sets of constants $(k, m, n,)_A$ and $(k, m, n)_a$ while not equal to each other, will be so interrelated as to give equal values to the exponents z_A and z_a, and Z_A and Z_a. This will make the equations (10a) and (10b) equal to zero and the quotients j and J again will be equal to unity. Such is the case with water and acetic acid, which follow closely adjacent curves (Fig. 1, g), although they have very different values of the parameters and different chemical properties.

Since it was found above that the proposed pressure equation holds for different types of substances, it follows that at least with respect to this property substances show definite regularity, which can be expressed by equations (10a–b).

We come to the conclusion that the dispersion of curves ln π–τ is a natural phenomenon, which can be explained readily if we replace the concept of identity (the basis of correspondence principle) by the concept of relatedness, as defining the properties of substances at equal distances from the critical point (*i. e.*, at equal reduced temperatures). It is to be pointed out that since the pressure equation has shown no exception this concept of relatedness will apply to water, alcohol, acetic acid and similar substances, just as strictly as to the remaining substances studied. Therefore, contrary to the view of Nernst, Schames, and others given above,[8] the behavior along the saturation line gives no ground for the segregation of substances into two classes.

We can now determine to what extent the prediction of Dieterici quoted in Part I of this article is verified, as regards the correspondence theorem and its relation to the critical data of liquids.[10] We have seen above that even the organic liquids deviate from the van der Waals theorem, consequently, the expectation of Dieterici that this theorem will be reëstablished after a careful investigation of organic liquids, has not been fulfilled. Also, we no longer can regard the departure of the pressure curves from each other as deviations from ideal lines. However, if we substitute the term "degree of dispersion" for the term "deviation," then we shall find that Dieterici was right in suspecting the influence of critical properties on the extent of this dispersion.

[10] C. Dieterici, *Ann. Physik*, **25**, 569, 578 (1908).

This is evident from eq. (10a–b), namely, the relating coefficients j and J are functions of the constants k', k'', respectively, which in their turn stand in definite relationship to the critical coefficient K_{cr} of each particular substance. In general we can say that the dispersion is greater where K_{cr} is small (as in permanent gases), and that the curves run closer to each other where the K_{cr} lies between 3.7–3.9 (normal organic liquids).

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Conclusions

1. The reduced vapor pressures of chemically different substances are found to be expressible in terms of reduced temperature within the limits of experimental error and in agreement with the accurate test formulas used by observers to check their data.

2. The form of the vapor pressure function is entirely analogous to that of the volume ratio, namely

$$\ln P_{\text{cr}}/P_{\text{s}} = k' \frac{(1 - \tau^2)^{m'}}{\tau^{n'}} = z \qquad (11a)$$

$$P_{\text{s}} = P_{\text{cr}}\, e^{-z} \qquad (11b)$$

3. The parameters k', m', n' vary with the chemical nature of substances. Their values increase parallel to the ascending order of curves and to the increase of the critical coefficient K_{cr}, exceptions being very few. The ratio K_{cr}/k' varies from 1.3 for permanent gases to 1.15 for organic liquids, while for helium and nitrogen tetroxide it is, respectively, 1.6 and 0.84.

4. The fact that the reduced vapor pressures are given accurately by the proposed equation leads to the possibility of defining the behavior of all substances when compared at equal reduced temperatures. At equal τ the reduced vapor pressures of two substances are related definitely to each other. The relating coefficients are in general different from unity and are exponential functions of temperature and of the parameters k, m, n

$$\pi_{\text{A}}/\pi_{\text{a}} = e^{Z_{\text{a}} - Z_{\text{A}}} = j \qquad (12)$$

5. The coefficients become unity only at the critical point, this being the only temperature at which the properties of substances are identical. At other temperatures the coefficients increase with decrease of τ.

6. Accordingly, the dispersion of curves ln π–τ is a normal phenomenon for all substances. Since the coefficients j are functions of the k' and the latter are related to the K_{cr}, it follows that the degree of dispersion is somehow influenced by the critical coefficient, the true mechanism of this influence being at present obscure.

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The Structure of the Hydrides of Boron. V. Tetraborane B_4H_{10} and the Pentaborane B_5H_{11}

BY S. H. BAUER*

The hydrides of boron have been classified into two groups on the basis of their constitution, B_nH_{n+4} and B_nH_{n+6}.[1] It has been suggested that corresponding differences in physical and chemical properties exist; these differences are, however, not distinct, and, indeed, the first member of the B_nH_{n+4} series, diborane, behaves as though it belonged with the B_nH_{n+6} group.[2] Of the numerous theories which have been proposed during the last decade and a half, only that of Wiberg is sufficiently complete to

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(1) Except when otherwise specified, the chemical information quoted in this paper has been obtained from: A. Stock, "The Hydrides of Boron and Silicon," Cornell Univ. Press, Ithaca, N. Y., 1931; E. Wiberg, *Ber.*, 69, 2816 (1936).

(2) Unlike B_5H_9 and $B_{10}H_{14}$, but like B_4H_{10}, B_5H_{11}, and B_6H_{10}, diborane melts at a temperature at which its vapor tension is not observable on an ordinary mercury manometer. Diborane, tetraborane and the unstable pentaborane also react far more readily with water and ammonia than does the stable pentaborane or decaborane. In further contrast to the latter two compounds, B_2H_6 reacts with hydrochloric acid to give a chloro derivative and hydrogen, a behavior shown also by B_4H_{10} and B_5H_{11} (except that the derivatives of these cannot be isolated). It is significant that di-, tetra- and the unstable pentaboranes are converted easily one into the other by the proper choice of experimental conditions, while B_5H_9, B_6H_{10}, and $B_{10}H_{14}$ are formed slowly and irreversibly from that equilibrium mixture. Hence the classification of the boranes into the series B_nH_{n+4} and B_nH_{n+6} is purely formal, and has no chemical basis.