A RELATION BETWEEN ORTHOBARIC DENSITIES.

By Jurô HORIUCHI.

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The distribution of infinitesimal molecules in phases having different potential energies is expressed in the following classical equation,

$$\frac{N_1}{N_2}=e^{\frac{-(\psi_1-\psi_2)}{RT,}} \qquad \text{or} \qquad -(\psi_1-\psi_2)=RT\ln\frac{N_1}{N_2}\,,$$

where N_1 and N_2 denote the molecular density in the phase of the potential energy ψ_1 and ψ_2 respectively. Now to discuss the orthobaric state of coexistent liquid and vapour, the molecule cannot be regarded as of infinitesimal size. Consequently we can introduce a proper correction to either side of the above equation. In the following discussion, it is supposed that due correction has been introduced in ψ, so that $\psi_1-\psi_2$ does not express the actual internal heat of evaporation, but the increase of potential energy when the molecule of infinitesimal size be transfered from liquid to the gaseous phase. The foregoing equation can be modified in the following form,

$$-(\psi_1-\psi_2)=\psi=RT\ln\frac{D_l}{D_g}=RT\ln\frac{V_g}{V_l}, \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots(1)$$

where V_l, D_l, V_g and D_g represent the molecular volume and the density of liquid and those of vapour respectively. Under the assumption that the internal pressure should be proportional to the square of the density, van der Waals and his followers gave an expression a/v^2 for the internal pressure. Integrating this, we obtain the following relation for the potential difference between two states having the molecular volume V_g and V_l,

$$\psi=\int_{V_l}^{V_g}\frac{a}{V^2}dV=a\left(\frac{1}{V_l}-\frac{1}{V_g}\right)=RT\ln\frac{V_g}{V_l}\,.$$

It is well known that this does not agree with experiments. However subtracting a certain quantity E, characteristic to individual substances, the resulting equation was found to be concordant with actual measurements i.e.

$$\psi=RT\ln\frac{V_g}{V_l}=A\left(\frac{1}{V_l-E}-\frac{1}{V_g-E}\right)\cdots\cdots\cdots\cdots\cdots(2)$$

where A is a constant characteristic to each substance. This expression may be regarded as a proper form to express virtual internal heat of vaporization for infinitesimal molecules. In the literatures there are found equations analogous to (2). Goebel⁽¹⁾ derived a equation of state for gases, giving an expression $\frac{a}{(V-a)^2}$ for the internal pressure. The region of validity of his equation was found to be $t>t_k$, $p>p_k$, and $V>1.9b$, and it failed at the temperature and pressure below that of the critical point.

Keyes,⁽²⁾ adopting the form $\frac{A}{(V+l)^2}$ for the internal pressure, has shown that the value of l is negative for hydrogen and air, while it is positive for mathane and others.

Now, the calculation of the present author ranges from the critical temperature to those below the room temperature and shows good agreement with the experimental data. Goebel's equation has the purpose to express actual internal pressure, while that of the present author intends to express a relation between orthobaric densities. Consequently these two equations, though resembling in their form, are essentially different, and the numerical values of constants being of course quite different.

If we assume that the internal heat of vaporization L_i can be obtained by integrating Goebel's expression, then we have

$$L_i=\int_{V_l}^{V_g}\frac{a}{(V-a)^2}dV=\frac{a}{V_l-a}-\frac{a}{V_g-a}\quad\cdots\cdots\cdots\cdots\cdots(3)$$

Combining (3) with Dieterici's empirical equation,⁽³⁾ $L=CRT\ln V_g/V_l$, where C is close to 1.7, we obtain a relation

$$CRT\ln\frac{V_g}{V_l}=\frac{a}{V_l-a}-\frac{a}{V_g-a}\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(4)$$

Thus equation (2) is formally equivalent to the Goebel's equation, extended to orthobaric states and combined with Dieterici's rule. In equation (2), however, the actual value of L_i is not taken in consideration, but it simply expresses a relation between orthobaric densities, and agrees excellently with experimental data as is shown in the following tables.

The calculation has been undertaken for the following 21 substances, which are possibly different in chemical nature : hydrogen, oxygen, nitrogen, argon, carbon dioxide, i-pentane, n-octane, benzene, hexamethylene, chlorobenzene, carbon tetrachloride, stannic chloride, methyl acetate, ethyl formate, propyl formate, methyl butylate, ethyl ether, methyl alcohol, ethyl alcohol,

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(1) *Z. phys. Chem.*, **47** (1904), 471; **49** (1905), 129; **50** (1905), 238.

(2) *Proc. Nat. Acad. Sci.*, **3** (1917), 323.
J. Am. Soc. Refrig. Eng., **1** (1914), 9; **7** (1921), 371.
J. Am. Chem. Soc., **41** (1919), 589; **42** (1920), 54; **43** (1921), 1452.
J. Math. Phys. Mass. Inst. Tech., **1** (1922), 89, 191, 211 & 243.

(3) *Ann. Phys.*, **25** (1908), 569.

propyl alcohol and acetic acid. In this paper, however, abridged data⑴ for only 8 substances are shown to save the space. Also the value expressed by the equation $q=RT \ln V+A/(V-E)$, has been calculated for liquid and vapour respectively, and they are given in the table as q_l and q_g. In the calculation the value of R is taken as 1.988 calories.

TABLE 1. Hydrogen.

Temp. C.	D_l	D_g	$RT \ln V_g/V_l$	$A\left(\frac{1}{V_l-E}-\frac{1}{V_g-E}\right)$	q_l	q_g
$-258^\circ.27$	0.07631	0.00020	175.1	178.0	278.3	275.4
-253.76	0.07192	0.00101	163.9	164.3	294.4	294.0
-247.79	0.06416	0.00405	138.6	137.6	319.2	320.2
-245.73	0.06050	0.00613	124.2	124.1	327.4	327.5
-240.57	0.04316	0.01922	52.2	54.0	341.5	339.7
		$A=3958$		$E=4.20.$		

(H. K. Onnes, Crommelin and Cath, *Verhl. Akad. Wet. Amst.*, **26** (1917), 192.)
(Mathias, Crommelin and Onnes, *Compt. rend.*, **172** (1921), 262.)

TABLE 2. Oxygen.

Temp. C.	D_l	D_g	$RT \ln V_g/V_l$	$A\left(\frac{1}{V_l-E}-\frac{1}{V_g-E}\right)$	q_l	q_g
$-210^\circ.4$	1.2746	0.0001	1.2×10^3	1175	1577	1.6×10^3
-182.0	1.1415	0.0051	979	988	1594	1585
-154.5	0.9758	0.0385	761	763	1606	1604
-129.9	0.7781	0.1320	504	499	1634	1639
-120.4	0.6032	0.2701	243	251	1622	1614
		$A=18160$		$E=9.68$		

(Mathias and Onnes, *Comm. Phys. Lab. Leiden*, No. 117 (1917).)

TABLE 3. Isopentane.

Temp. C.	D_l	D_g	$RT \ln V_g/V_l$	$A\left(\frac{1}{V_l-E}-\frac{1}{V_g-E}\right)$	q_l	q_g
0°	0.6393	0.0011	3459	3457	6026	(6028)
40	0.5988	0.004456	3051	3054	6047	6044
70	0.5656	0.01013	2742	2742	6075	6075
100	0.5278	0.02020	2420	2431	6133	6122
130	0.4826	0.03831	2032	2026	6146	6152
160	0.4206	0.07289	1511	1515	6161	6157
180	0.3498	0.1258	923	946	6138	6115
187.4	0.2761	0.1951	319	337	6079	6031
		A$=204300$		$E=53.8.$		

(Young, *Sci. Proc. Roy. Dublin Soc.*, **12** (1910), 374)

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(1) Full data will be published in the *Journal of the Chemical Society of Japan.*

TABLE 4. Chlorobenzene.

Temp. C.	D_l	D_g	$RT\ln V_g/V_l$	$A\left(\frac{1}{V_l-E}-\frac{1}{V_g-E}\right)$	q_l	q_g
80°	1.0419	0.0008	5035	5062	8349	8322
100	1.0193	0.0014	4886	4863	8354	8377
120	0.9960	0.0026	4650	4657	8357	8350
140	0.9723	0.004316	4449	4452	8363	8360
160	0.9480	0.006784	4253	4254	8384	8383
180	0.9224	0.01023	4054	4054	8407	8407
200	0.8955	0.01506	3841	3841	8425	8425
220	0.8672	0.02145	3625	3623	8450	8452
240	0.8356	0.03000	3393	3385	8464	8472
260	0.8016	0.04172	3132	3131	8483	8484
		$A=292700$		$E=50.15$		

(Young, ibid.)

TABLE 5. Carbon tetrachloride.

Temp. C.	D_l	D_g	$RT\ln V_g/V_l$	$A\left(\frac{1}{V_l-E}-\frac{1}{V_g-E}\right)$	q_l	q_g
30°	1.5748	0.0012	4326	4339	7101	7088
60	1.5165	0.0033	4059	4054	7116	7121
90	1.4554	0.007955	3760	3762	7138	7136
120	1.3902	0.01639	3471	3470	7172	7173
150	1.3215	0.03040	3172	3173	7221	7220
180	1.2470	0.05249	2855	2851	7271	7265
210	1.1566	0.08787	2475	2479	7313	7309
240	1.0444	0.1464	2004	2023	7342	7323
270	0.8666	0.2710	1256	1326	7327	7257
		$A=232000$		$E=44.3$		

(Young, ibid.)

TABLE 6. Methyl acetate.

Temp. C.	D_l	D_g	$RT\ln V_g/V_l$	$A\left(\frac{1}{V_l-E}-\frac{1}{V_g-E}\right)$	q_l	q_g
0°	0.95932	0.0003	4400	4405	6765	(6760)
50	0.8939	0.002212	3855	3847	6688	6696
110	0.8060	0.01239	3181	3178	6651	6654
170	0.6907	0.04598	2388	2393	6621	6616
230	0.5427	0.2028	803	850	6479	6432
		$A=173700$		$E=37.8$		

(Young, ibid.)

TABLE 7. Ethyl ether.

Temp. C.	D_l	D_g	$RT \ln V_g/V_l$	$A\left(\frac{1}{V_l-E}-\frac{1}{V_g-E}\right)$	q_l	q_g
−101.3°	0.8435	0.40×10^{-6}(M.)	4976	4999	6526	6503
− 81.0	0.8227	3.61×10^{-6}(M.)	4711	4713	6433	6431
− 64.4	0.8056	15.74×10^{-6}(D.)	4499	4498	6374	6375
− 35.0	0.7749	12.59×10^{-5}(T.)	4129	4132	6291	6288
+ 20	0.7135	18.70×10^{-4}(Y.)	3467	3488	6197	6176
+ 60	0.6658	67.71×10^{-4}(Y.)	3039	3042	6179	6176
+ 90	0.6250	0.01477 (Y.)	2698	2699	6188	6187
+140	0.5385	0.04488 (Y.)	2040	2022	6181	6199
+190	0.3663	0.1620 (Y.)	749	769	6114	6094
		$A=185600$		$E=50.0$		

T : Taylor and Smith, *J. Am. Chem. Soc.*, **44** (1922), 2450.
D : Drucker and Kangro, *Z. physik, Chem.*, **90** (1915), 518.
M : Mündel, *Z. physik. Chem.*, **85** (1913), 456.
Y : Young, ibid.

Vapour densities with indices T, D and M have been calculated from vapour tensions given by these authors applying the ideal gas low, and those of liquid at low temperatures have been obtained by interpolation from above mentioned Taylor and Smith's results.

TABLE 8. Methyl alcohol.

Temp. C.	D_l	D_g	$RT \ln V_g/V_l$	$A\left(\frac{1}{V_l-E}-\frac{1}{V_g-E}\right)$	q_l	q_g
0°	0.8100	0.0000562	5195	5217	7214	7192
40	0.7740	0.0004394	4650	4652	6970	6968
80	0.7355	0.002084	4117	4120	6775	6772
120	0.6900	0.007142	3569	3569	6586	6586
160	0.6340	0.01994	2978	2973	6400	6405
200	0.5530	0.05075	2247	2225	6171	6193
230	0.4410	0.1187	1312	1315	5923	5920
237	0.3850	0.1607	886	890	5825	5821
239	0.3504	0.1878	645	638	5774	5771
		$A=78950$		$E=24.40.$		

(Young, ibid.)

These tables show that the deviation between two quantities $RT \ln V_g/V_l$ and $A\left(\frac{1}{V_l-E}-\frac{1}{V_g-E}\right)$ is in most cases less than one percent and it may be concluded that the equation (2) can be applied for whole range of orthobaric state without any considerable error. This relation holds even for alcohols, which contain obviously associated molecules. Only for water it does not hold, because of the abnormal behaviour of its liquid phase.

Values of E used in the foregoing tables are approximately proportional to the critical volume V_k for normal liquids, as shown in Table 9. Consequently E should be an additive quantity, but the data are not sufficient to calculate out reliable additive constants for each atom or radical.

TABLE 9.

Substance	E	$V_{P=\infty}$	E/V_k	A	$T_k/\sqrt{AP_k}$
Hydrogen	4.20	—	0.0596	3958	0.148
Oxygen	9.68	—	0.130	18160	0.162
Nitrogen	12.8	—	0.142	17520	0.164
Argon	10.3	—	0.137	17440	0.165
Carbon dioxide	22.8	—	0.240	33600	0.195
Isopentane	53.8	—	0.175	204300	0.174
Normal octane	87.0	—	0.177	355900	0.180
Benzene	41.5	—	0.162	218500	0.174
Hexamethylene	52.6	—	0.171	249700	0.175
Chlorobenzene	50.15	—	0.163	292700	0.175
Carbon tetrachloride	44.3	—	0.161	232000	0.172
Stannic chloride	58.43	—	0.166	307600	0.176
Methyl acetate	37.8	—	0.166	173700	0.178
Ethyl formate	37.8	—	0.165	174000	0.178
Propyl formate	46.5	—	0.163	232700	0.173
Methyl butylate	59.2	—	0.174	276700	0.179
Ethyl ether	50.0	51.4	0.174	185600	0.181
Methyl alcohol	24.4	23.1	0.207	78950	0.205
Ethyl alcohol	37.8	33.6	0.226	105900	0.200
Propyl alcohol	48.6	—	0.221	143500	0.197
Acetic acid.	30.0	—	0.175	151100	0.202

As shown in Table 9 the ratio E/V_k is 0.169 in the mean, or E is about $V_k/6$ for normal liquids. For carbon dioxide and other abnormal liquids like alcohols the ratio is considerably higher and amounts to 0.21—0.24. The volume correction b in van der Waals' equation being about $V_k/4$ when extrapolated to $T=0$, so it can be said that E is about $2/3 \cdot b$ for almost all normal liquids.

G. Tamman(1) has given the following isothermal equation for liquids under high pressure:

$$(V-V_{P=\infty})(K+P)=A_T K.$$

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(1) *Ann. Phys.*, **87** (1912), 975.

In this equation $V_{P=\infty}$ and K are constants independent of temperature and pressure, while A_T is independent of pressure but varies with temperature. $V_{P=\infty}$ is the molecular volume of the liquid under infinitely large pressure, and is given in the third column in Table 9, which has been obtained by interpolation. As is seen in the table the value of E is nearly equal to $V_{P=\infty}$ of Tammann.

For constant A, there exists a relation that the ratio $T_k/\sqrt{AP_k}$ is roughly constant for normal liquids. For abnormal liquids this ratio is larger than that for normal one, but for alcohols it approaches to that of normal liquids, as the number of carbon atoms in the molecules increases.

We can thus formulate as follows:

$$E=0.17\ V_k \quad\cdots\cdots\cdots\cdots(5)$$

$$A=32.3\frac{T_k^2}{P_k} \quad\cdots\cdots\cdots\cdots(6)$$

Putting $T/T_k=\theta$ and $V/V_k=\varphi$, we obtain from equations (5), (6) and (2),

$$R\theta\ln\frac{\varphi_g}{\varphi_l}=32.3\frac{T_k}{P_kV_k}\left(\frac{1}{\varphi_l-0.17}-\frac{1}{\varphi_g-0.17}\right)=1.47\left(\frac{1}{\varphi_l-0.17}-\frac{1}{\varphi_g-0.17}\right).$$

This equation is of reduced form and is in accord with the theory of the corresponding state, as the ratio P_kV_k/T_k is almost universal for normal liquids.

By slightly modifying the equation (2) we obtain

$$q=RT\ln V_g+\frac{A}{V_g-E}=RT\ln V_l+\frac{A}{V_l-E} \quad\cdots\cdots(7)$$

each side having V_g or V_l only. By actual calculation, it was found that q is a linear function of temperature, thus

$$q=C+BT \quad\cdots\cdots\cdots\cdots(8)$$

B, the temperature coefficient of q, is very small for normal liquids, and has considerable negative values for abnormal liquids. This enables us to calculate every pair of orthobaric densities as two roots of the equation (8), provided the values of C and B are known.

Next, an equation for vapour pressure at low temperatures can be derived from equation (2). By neglecting $A/(V_g-E)$, and regarding the vapour as an ideal gas, we can transform the equation (2) as follows:

$$\ln P=\ln\frac{RT}{V_l}-\frac{1}{RT}\ \frac{A}{V_l-E} \quad\cdots\cdots\cdots\cdots(9)$$

where vapour pressure P is given by the molecular volume of the liquid. As an example of the verification of this equation, the data for ethyl ether are given in the following table.

TABLE 10.

Temp. C.	Vapour press. (obs.) mm.	Vapour press. (calc.) mm.	Observer
−101.3°	0.058	0.0535	Mündel
− 95.2	0.118	0.118	„
− 88.1	0.270	0.276	„
− 81.0	0.584	0.588	„
− 75.8	0.953	1.18	Drucker and Kangro
− 64.4	2.77	2.81	„ „
− 57.3	5.12	5.18	„ „
− 44.2	14.17	13.6	„ „
− 35.0	26.95	25.4	Taylor and Smith
− 32.4	31.93	30.1	„ „
− 20	63	63.7	Ramsay and Young
− 10	111.8	110	„ „
0	184.9	181	„ „

The vapour pressure calculated by the equation (9) agrees well with the observed value even at the temperature more than 100 degrees below the room temperature.

Sammary.

1. There exists a relation

$$RT\ln\frac{V_g}{V_l}=A\left(\frac{1}{V_l-E}-\frac{1}{V_g-E}\right)$$

between orthobaric densities for normal and abnormal liquids.

2. By modifying the above equation, we obtain

$$RT\ln\ V_g+\frac{A}{V_g-E}=RT\ln\ V_l+\frac{A}{V_l-E}\ ,$$

each side being proved to be a linear function of temperature.

3. For constants A and E it was found that $A=32.3\ \frac{T_k^2}{P_k}$ and $E=0.17\ V_k$ for normal liquids. E is, therefore, an additive quantity if V_k is additive.

4. By dint of the relation for constants A and E mentioned above, we have a reduced equation

$$R\theta\ln\frac{\varphi_g}{\varphi_l}=1.47\left(\frac{1}{\varphi_l-0.17}-\frac{1}{\varphi_g-0.17}\right).$$

5. For lower temperatures, we have derived a vapour pressure equation

$$\ln P = \ln \frac{RT}{V_l} - \frac{1}{RT}\,\frac{A}{V_l - E}\,.$$

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Chemical Institute, Faculty of Science,
Tokyo Imperial University.