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XLI. *On the Saturation Constants according to van der Waals's Equation.* By JOHN P. DALTON, M.A., *Carnegie Research Scholar* *.

A. *Deduction of Constants.*

FOR the deduction of the saturation constants θ , π , ω_1 and ω_2 , the following different methods are available and have been used :—

1. M. Planck's method for the equation of Clausius may be adapted to that of van der Waals. For this purpose an independent variable ϕ is chosen, such that

$$3\omega_1 - 1 = 3r \sin^2 \frac{1}{2}\phi, \quad \text{and} \quad 3\omega_2 - 1 = 3r \cos^2 \frac{1}{2}\phi.$$

Since

$$\frac{8\theta}{3\omega_1 - 1} - \frac{3}{\omega_1^2} = \pi = \frac{8\theta}{3\omega_2 - 1} - \frac{3}{\omega_2^2},$$

hence

$$r = -\frac{2}{3} \frac{1}{\sin^2 \phi} \left[\frac{\cos \phi + \sin^2 \phi \cdot \log \tan \frac{1}{2}\phi}{\log \tan \frac{1}{2}\phi + \cos \phi} \right].$$

Also

$$\pi = \frac{3\omega_2\omega_1 - \omega_2 - \omega_1}{\omega_1^2\omega_2^2},$$

and

$$\theta = \frac{(\omega_1 + \omega_2)(3\omega_2 - 1)(3\omega_1 - 1)}{8\omega_1^2\omega_2^2}.$$

When $\phi = 90^\circ$, $\omega_1 = 1 = \omega_2$, hence values of ϕ must so be chosen that $90^\circ > \phi > 0$.

This method was used by A. Stoletow ‡ who calculated pressures only, and gave the following results :—

ϕ .	θ .	π .
80°	0.9960	0.984
70	0.9861	0.945
65	0.9780	0.914
60	0.9677	0.876
55	0.9549	0.829
50	0.9396	0.776

* Communicated by Prof. J. P. Kuenen, Ph.D.

† M. Planck, *Wied. Ann.* Bd. xiii. pp. 535-543 (1881).

‡ A. Stoletow, *J. de russ. phys. Ges.* xiv. p. 167 (1882).

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and also by A. Batschinski *, who calculated volumes only:—

ϕ .	θ .	ω_1 .	ω_2 .
90°	1	1	1
40°	0.89894	0.6021	2.3625
25°	0.80247	0.5190	4.1103
15°	0.69682	0.4659	7.9828
8°	0.58213	0.4275	19.585
4°	0.48222	0.4028	57.30
2°	0.40712	0.3877	178.8
0° 15'	0.30723	0.3709	1974

2. The constants may be obtained from the *pv*-isothermals using Maxwell's criterion. This method was employed by H. Hilton †, who gives the following table:—

θ .	π .	ω_1 .	ω_2 .
0.937	0.773	0.660	1.84
0.875	0.587	0.573	2.53
0.844	0.486	0.545	3.31
0.750	0.281	0.495	4.83
0.625	0.090	0.441	—
0.500	0.048	0.418	—

3. They may also be obtained graphically by means of the thermodynamic potential. E. Riecke ‡ using this method obtained the following:—

θ .	π .	ω_1 .	ω_2 .
0.60	0.109	0.432	16.60
0.65	0.137	0.448	10.90
0.70	0.199	0.466	7.75
0.75	0.288	0.489	5.53
0.80	0.384	0.517	4.14
0.85	0.507	0.553	3.05
0.90	0.650	0.602	2.32
0.95	0.807	0.693	1.78

4. A second graphical method is given by the use of the free energy. This method was adopted by Kamerlingh

* A. Batschinski, *Zeits. f. phys. Chemie*, xli. p. 743 (1902).

† H. Hilton, *Phil. Mag.* [6] i. p. 579, and ii. p. 803 (1901).

‡ E. Riecke, *Wied. Ann.* liii. p. 379 (1894).

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Onnes *, but he does not communicate any results. It was used independently by the author. Isothermal ψ , v -curves were constructed by means of the equation

$$-\frac{1}{p_K v_K} \psi = \frac{8\theta}{3} \log_e(3\omega - 1) + \frac{3}{\omega},$$

and a double-tangent drawn to each curve. The slope of these tangents gave the values of π . As it was difficult to read volumes exactly from the curve, values of π were substituted in the "reduced" equation of state, and the volumes determined by calculation. The tabulated results were:—

θ .	π .	ω_1 .	ω_2 .
0.50	0.0280	0.4067	45.62
0.60	0.0869	0.4326	16.72
0.65	0.1364	0.4485	11.16
0.70	0.2007	0.4671	7.799
0.75	0.2825	0.4896	5.642
0.80	0.3840	0.5174	4.162
0.85	0.5058	0.5532	3.113
0.90	0.6494	0.6029	2.337
0.95	0.8095	0.6854	1.744
1.00	1.0000	1.0000	1.000

5. Clausius's method † applied by him to the equation

$$\frac{p}{RT} = \frac{1}{v - \alpha} - \frac{27(\alpha + \beta)}{8\theta(v + \beta)^2},$$

may be easily adapted to the present purpose and the table given by him ‡ (which appears to be very accurate) may be used. He calculates at intervals of $\theta = 0.01$ the corresponding values of $\frac{\Pi}{\Pi_K}$, $\frac{w}{w_K}$, and $\frac{W}{W_K}$, where $\Pi = p/RT$, $w = v_1 - \alpha$, and $W = v_2 - \alpha$.

By comparing his equation with that of van der Waals expressed in the form

$$\frac{p}{RT} = \frac{1}{v - b} - \frac{a}{RTv^2},$$

it will be seen that the saturation constants π , ω_1 , and ω_2

* Kamerlingh Onnes, *Comm. Leid.* no. 66, p. 10 (1900).

† R. Clausius, *Wied. Ann.* Bd. xiv. pp. 279-290 and 692-704 (1881).

‡ *Ibid.* pp. 694-5.

according to van der Waals's equation may be derived from Clausius's table by means of the relations

$$\pi = \theta \frac{\Pi}{\Pi},$$

$$\omega_1 = \frac{2 \frac{w}{w_K} + 1}{3},$$

and

$$\omega_2 = \frac{2 \frac{W}{W_K} + 1}{3}.$$

As these constants are frequently used, the full table is here given:—

θ .	π .	ω_1 .	ω_2 .
0.20	0.000001180	0.35584	448520
1	2646	0.35714	211560
2	5478	0.35846	107120
3	0.000010626	0.35980	57670
4	19536	0.36116	32760
5	34175	0.36254	19509
6	57226	0.36395	12111
7	92232	0.36537	7801.7
8	0.00014367	0.36682	5193.5
9	21701	0.36830	3560.3
0.30	31881	0.36980	2505.9
1	45688	0.37133	1806.1
2	64006	0.37288	1330.1
3	87849	0.37446	998.60
4	0.0011835	0.37608	763.13
5	15673	0.37772	592.61
6	20435	0.37939	466.98
7	26265	0.38109	372.93
8	33318	0.38283	301.49
9	41753	0.38460	246.49
0.40	51744	0.38641	203.63
1	63464	0.38825	169.83
2	77095	0.39013	142.89
3	92833	0.39206	121.20
4	0.011085	0.39402	103.58
5	13134	0.39602	89.147
6	15451	0.39807	77.227
7	18054	0.40017	67.300
8	20966	0.40231	58.969
9	24205	0.40451	51.947
0.50	27789	0.40675	45.984
1	31738	0.40905	40.891
2	36073	0.41141	36.517
3	40812	0.41383	32.741
4	45975	0.41630	29.465
5	51581	0.41884	26.609
6	57646	0.42145	24.109
7	64188	0.42413	21.913
8	71230	0.42687	19.973
9	78783	0.42971	18.256

θ .	π .	ω_1 .	ω_2 .
0.60	0.086868	0.43262	16.730
1	95508	0.43560	15.366
2	0.10470	0.43869	14.147
3	11448	0.44186	13.052
4	12485	0.44513	12.067
5	13584	0.44851	11.177
6	14746	0.45201	10.371
7	15971	0.45561	9.6387
8	17262	0.45934	8.9733
9	18620	0.46319	8.3660
0.70	20046	0.46719	7.8113
1	21541	0.47135	7.3027
2	23108	0.47565	6.8355
3	24747	0.48013	6.4057
4	26459	0.48478	6.0093
5	28246	0.48963	5.6431
6	30109	0.49469	5.3041
7	32048	0.49998	4.9896
8	34064	0.50551	4.6978
9	36160	0.51131	4.4259
0.80	38335	0.51741	4.1725
1	40593	0.52382	3.9356
2	42933	0.53058	3.7141
3	45353	0.53773	3.5064
4	47859	0.54531	3.3113
5	50449	0.55336	3.1276
6	53126	0.56195	2.9545
7	55886	0.57117	2.7910
8	58736	0.58107	2.6361
9	61674	0.59176	2.4889
0.90	64700	0.60339	2.3487
1	67816	0.61615	2.2151
2	71024	0.63019	2.0867
3	74319	0.64592	1.9633
4	77708	0.66368	1.8438
5	81188	0.68412	1.7271
6	84762	0.70817	1.6117
7	88429	0.73746	1.4957
8	92192	0.77535	1.3757
9	96048	0.83028	1.2418
1.00	1.00000	1.00000	1.0000

B. Comparison with Empirical Formulæ.

(1) VAPOUR-PRESSURE LAW.

The values of π given above were used to test the well-known empirical vapour-pressure law of van der Waals, viz.,

$$\log \pi = f \left(1 - \frac{1}{\theta} \right),$$

where f is a constant. Onnes* found that the pressures he obtained by the "free energy" method obeyed the above law

* *Loc. cit.*

with "fair approximation," and gave f (at low temperatures) a value = 3·4, when $\log \pi$ is expressed in natural logarithms.

In the following, the constant has been calculated for both ordinary and natural logarithms :—

θ .	$-\log_{10} \pi$.	$-\left(1 - \frac{1}{\theta}\right)$.	f' .	f .
0·20	5·9281	4·0000	1·4820	3·4124
·25	4·4663	3·0000	1·4888	3·4280
·30	3·4965	2·3333	1·4985	3·4504
·35	2·8049	1·8571	1·5103	3·4776
·40	2·2861	1·5000	1·5241	3·5094
·45	1·8816	1·2222	1·5395	3·5449
·50	1·5561	1·0000	1·5561	3·5830
·55	1·2875	·81818	1·5736	3·6234
·60	1·0611	·66667	1·5917	3·6650
·65	·86697	·53846	1·6101	3·7073
·70	·69797	·42857	1·6286	3·7500
·75	·54904	·33333	1·6471	3·7925
·80	·41640	·25000	1·6656	3·8352
·85	·29715	·17647	1·6839	3·8773
·90	·18910	·11111	1·7019	3·9188
·95	·09051	·05263	1·7197	3·9597
1·00	·00000	·00000	—	—

Fig. 1 shows graphically the deviation of f from a constant.

(2) THE LAW OF CAILLETET AND MATHIAS.

Onnes * found that for the saturation volumes determined by him the law of the diameter held "very well up to quite low temperatures," and A. Batschinski † obtained by plotting mean density against temperature a line that did not "differ much from a straight line."

From the table of saturation constants given above, the following figures were derived :—

θ .	$\frac{1}{\omega_1} + \frac{1}{\omega_2}$.	θ .	$\frac{1}{\omega_1} + \frac{1}{\omega_2}$.
[0·00	3·0000]	·60	2·3713
0·20	2·8103	·65	2·3191
·25	2·7584	·70	2·2685
·30	2·7046	·75	2·2196
·35	2·6492	·80	2·1724
·40	2·5928	·85	2·1268
·45	2·5363	·90	2·0831
·50	2·4802	·95	2·0407
·55	2·4251	1·00	2·0000

* *Loc. cit.*

† *Loc. cit.*

It is known * that the equation

$$\frac{1}{\omega_1} + \frac{1}{\omega_2} = a + b\theta$$

is not an accurate expression of the results of observation, but the curvature shown by plotting the foregoing numbers

* S. Young, Phil. Mag. [5] 1. pp. 291-305 (1900).

(fig. 2) is more marked than that given by experimental results.

Fig. 2.

S. Young (*loc. cit.*) finds as a more correct formula

$$D_t = D_0 + \alpha t + \beta t^2.$$

For all substances α is negative; β is zero only when the ratio of the actual to the theoretical density at the critical point has the normal value 3.77. When this ratio < 3.77, β is positive and the curve is convex to the temperature-axis. This is quite in accordance with fig. 2, where the ratio has the value 2.67.

University College, Dundee,
February, 1907.