

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE SOUTHERN BRANCH OF THE UNIVERSITY OF CALIFORNIA]

THE VAPOR PRESSURE OF MONATOMIC ELEMENTS

BY RUSSELL W. MILLAR

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The differential equation, $\frac{d\phi}{dT} = \frac{\Delta H}{T\Delta V}$, which expresses the change of vapor pressure with the temperature in terms of the heat of vaporization and the change of volume, has been integrated heretofore for the purpose of obtaining a vapor-pressure equation.¹ The equation derived contained a "chemical constant" which depended only upon the element under consideration. This constant was determined from the quantum theory, from the relation of Nernst, $C = -1.60 + 1.5 \log w$, where w is the molecular weight of the monatomic gas, or most accurately from two vapor-pressure measurements. It was then possible, using either of the first two methods of determining the chemical constant, to construct an entire vapor-pressure curve from specific heat data of the condensed phase and one point on the vapor-pressure curve.

Investigators² who have provided us with a method of calculating the entropy of a monatomic gas have made possible a simple and straightforward integration of the differential equation. The expression obtained is probably more convenient than that of Nernst for the purpose of calculating vapor pressures in unexplored ranges of temperature.

If we neglect the volume of the condensed phase and let V represent the molar volume of the gas, and assume that $pV = RT$, we have, from the above

$$\frac{d \ln \phi}{d \ln T} = \frac{\Delta H}{RT} = \frac{\Delta S}{R}, \quad (1)$$

an equation used recently by Hildebrand.³ ΔS is the entropy of vaporization, namely $S_g - S_c$, where S_g is the entropy of the gas and S_c that of the condensed phase.

If we express ϕ in atmospheres, then we have from Lewis'⁴ theory of ultimate rational units

$$S_g = R \ln (T^{3/2} w^{3/2} / \phi) - 2.63 \quad (2)$$

where w is the molecular weight of the gas. Also

$$S_c = S_0 + \int_{T_0}^T C_p d \ln T,$$

¹ Nernst, "Theoretische Chemie," Macmillan and Co., 7th ed., 1916, pp. 236, 756. F. Born, *Ann. Physik*, **69**, 473 (1922). Trautz and Stäckel, *Z. anorg. Chem.*, **122**, 81 (1922). Henglein, *ibid.*, **123**, 137 (1922).

² Sackur, *Ann. Physik*, [4] **36**, 598 (1911); **40**, 67 (1913). Tetrode, *ibid.*, [4] **38**, 434 (1912). Lewis, *Phys. Rev.*, [2] **18**, 121 (1921).

³ Hildebrand, *THIS JOURNAL*, **37**, 970 (1915).

⁴ Lewis, Gibson and Latimer, *ibid.*, **44**, 1008 (1922).

neglecting the effect of change of pressure upon the entropy of the condensed phase. Here S_c is the entropy of the condensed phase at some temperature T_0 , and C_p is its molar heat capacity at constant pressure. Now C_p must be expressed as some function of the temperature which will be integrable in the expression above and also give a result which will leave Equation 1 integrable. The simplest function is $C_p = \alpha + \beta \ln T + \gamma(\ln T)^2$. Of course, this function does not express exactly the relation between C_p and T over any extended temperature range, yet it was found that quite accurate calculations of vapor pressure over temperature ranges sufficiently long could be made when γ , and even in some cases β , were omitted. Omitting γ , the inclusion of which, however, in no way complicates the integration of Equation 1, we obtain

$$S_c = S_0 + \alpha \ln T + \frac{\beta}{2} (\ln T)^2 - \alpha \ln T_0 - \frac{\beta}{2} (\ln T_0)^2 \quad (3)$$

Substituting Equations 2 and 3 in 1, we have

$$\frac{d \ln p}{d \ln T} + \ln p = \left(2.5 - \frac{\alpha}{R}\right) \ln T - \frac{\beta}{2R} (\ln T)^2 + \frac{1}{R} \left[1.5 R \ln w + \alpha \ln T_0 + \frac{\beta}{2} (\ln T_0)^2 - 2.63 - S_0\right]$$

This is a differential equation linear with respect to the dependent variable and of the form $\frac{dy}{dx} + y = ax - bx^2 + K$, of which the solution is $y = (a + 2b)x - bx^2 + Ze^{-x} - a + 2b + K$, where Z is the constant of integration. Likewise

$$\ln p = \left(2.5 - \frac{\alpha - \beta}{R}\right) \ln T - \frac{\beta}{2R} (\ln T)^2 + \frac{Z}{T} - \left(2.5 - \frac{\alpha - \beta}{R}\right) + \frac{1}{R} \left[1.5 R \ln w + \alpha \ln T_0 + \frac{\beta}{2} (\ln T_0)^2 - 2.63 - S_0\right]$$

Using common logarithms, we have

$$\log p_{\text{atm.}} = \left(2.5 - \frac{\alpha - \beta}{R}\right) \log T - \frac{2.303\beta}{2R} (\log T)^2 + \frac{Z}{T} + \frac{1}{R} \left[1.5 R \log w + \alpha \log T_0 + \frac{2.303\beta}{2} (\log T_0)^2 - \frac{2.63 + S_0 - (\alpha - \beta) + 2.5R}{2.303}\right]$$

Therefore, if, for a condensed phase of any element which vaporizes to a monatomic gas, we know the values of α , β , and the entropy S_0 at some temperature T_0 , and one vapor-pressure measurement, such as the boiling or sublimation point, by means of which Z may be evaluated, the complete vapor-pressure curve for that phase over the temperature range for which α and β are valid may be calculated.

In Table I the calculated values for mercury, sodium, zinc and hydrogen have been compared with the observed values of various investigators. These calculations will now be made to illustrate the use of the equation. The elements named do not by any means exhaust the number of those for which the necessary data exist.

Mercury.—According to Barnes,⁵ the heat capacity of mercury above 120° is about 6.65. Taking this value as constant, and taking with Lewis, Gibson and Latimer $S_0 = 17.81$ at $T_0 = 298^\circ \text{A.}$, and from Smith and Menzies⁶ the value of the boiling point, 357°C., we obtain

$$\log p_{\text{mm.}} = -0.8443 \log T - \frac{3319.6}{T} + 10.5134 \quad (4)$$

Since the heat capacity of mercury increases slightly with decreasing temperature below 160°C., a new equation was used below 120°C. to calculate the vapor pressure at temperatures as far down as the freezing point. In this range Barnes⁵ gives $C_p = 6.70$ (average), and we may take the same value of S_0 and T_0 as before. In order to calculate Z we may take either the calculated or observed value of p . Taking the latter as 0.829 mm. at 394.9°A., we obtain a slightly different equation:

$$\log p_{\text{mm.}} = -0.8694 \log T - \frac{3320.2}{T} + 10.5838 \quad (5)$$

which we can use below 120°C. The values given by this equation are slightly higher than those given by the preceding equation in the lower range of temperature. The results are as accurate as the value of the heat capacity chosen, which, though an average, differs but little from the extreme values.

We are now in a position to calculate the vapor pressure of solid mercury. The data of Pollitzer⁷ for the heat capacity of solid mercury from about 60°A. to the melting point may be expressed with considerable accuracy by $C_p = 1.118 + 1.016 \ln T$. At the melting point, $T_0 = 234.1$, $S_0 = 13.80$. Evaluating Z from the calculated value of p at 234.1°A., we obtain

$$\log p_{\text{mm.}} = 1.4487 \log T - 0.5882 (\log T)^2 - \frac{3621.7}{T} + 9.6814 \quad (6)$$

for solid mercury. At the temperature of boiling liquid air, about 90°A., we find $p = 1 \times 10^{-30}$ mm.

Sodium.—E. Griffiths,⁸ and Griffiths and Griffiths⁹ have measured the heat capacity of sodium for a short distance above the melting point. In the absence of more data, the equation $C_p = 7.40$ has been assumed to hold throughout the range to the boiling point. Using Lewis, Gibson and Latimer's value, $S_{298} = 12.2$, calculating $S_{370.6} - S_{298} = 1.5$ from the data of E. Griffiths⁸ and using Iitaka's¹⁰ value of the entropy of fusion, $\Delta s = 1.6$, we obtain at the melting point, $T_0 = 370.6^\circ \text{A.}$, $S_0 = 15.3$ for liquid sodium. Gebhardt¹¹ gives, at $T = 813^\circ \text{A.}$, $p = 18.5$ mm.

⁵ Barnes, *Rept. Brit. Assoc. Winnipeg*, 1909, p. 403.

⁶ Smith and Menzies. *THIS JOURNAL*, **32**, 1434 (1910).

⁷ Pollitzer, *Z. Elektrochem.*, **19**, 513 (1913).

⁸ E. Griffiths, *Proc. Roy. Soc.*, **89A**, 561 (1914).

⁹ Griffiths and Griffiths, *Phil. Trans. Roy. Soc.*, **213A**, 119 (1913).

¹⁰ Iitaka, *Sci. Rep. Tôhoku Imp. Univ.*, **8**, 99 (1919).

¹¹ Gebhardt, *Dissertation*, Erlangen, 1903.

The equation then becomes

$$\log p_{\text{mm.}} = -1.20 \log T - \frac{5135}{T} + 11.071 \quad (7)$$

For solid sodium we obtain from E. Griffiths $C_p = -20.2808 + 4.6869 \ln T$, an equation which reproduces the results fairly accurately from room temperature to the melting point. Taking T_0 as equal to the melting point 370.6°A. , $S_0 = 13.7$, and evaluating Z from the calculated value of p at 370.6°A. , we obtain

$$\log p_{\text{mm.}} = 15.0560 \log T - 2.7136 (\log T)^2 - \frac{7091.9}{T} - 4.6050 \quad (8)$$

This equation gives $p = 1.7 \times 10^{-8}$ mm. at 298°A.

Zinc.—According to Iitaka,¹⁰ the heat capacity of liquid zinc is 7.91 and is nearly independent of the temperature. The same observer gives 2.19 as the entropy of fusion. Using his data for the heat capacity of solid zinc from 298°A. to the melting point, and $S_{298} = 9.83$ as given by Lewis, Gibson and Latimer, we obtain $S_0 = 17.46$ for liquid zinc at the melting point, $T_0 = 692^\circ\text{A.}$ The boiling point of zinc is taken as 1193°A. From these data we obtain

$$\log p_{\text{mm.}} = -1.4779 \log T - \frac{68336}{T} + 13.1558 \quad (9)$$

Iitaka's values of the heat capacity of zinc from room temperature to the melting point are fairly well represented by $C_p = -1.7437 + 1.3550 \ln T$. Taking $T_0 = 298^\circ\text{A.}$, $S_0 = 9.83$, and the vapor pressure at the melting point as calculated from Equation 9 we obtain

$$\log p_{\text{mm.}} = 4.0583 \log T - 0.7845 (\log T)^2 - \frac{6823.1}{T} + 3.7555 \quad (10)$$

Hydrogen.—According to Eucken,¹² the heat capacity of hydrogen gas below 60°A. is that of a monatomic gas, and consequently Lewis, Gibson and Latimer⁴ have applied the Sackur equation to the calculation of the entropy of hydrogen gas at the boiling point. If that application is valid, we are justified in using the method of this paper to calculate the vapor pressure of hydrogen.

Keesom and Onnes,¹³ and Eucken¹² give consistent values for the heat capacity of liquid hydrogen which may be represented closely by $C_p = -6.14 + 3.55 \ln T$. Keesom and Onnes¹³ measurements of the heat capacity of solid hydrogen give 0.6 as the molar entropy of hydrogen at the melting point, 14°A. The same authors, and also Dewar,¹⁴ have determined the molar heat of fusion of hydrogen to be about 30, from which we find 2.14 as the entropy of fusion. Taking, then, $S_0 = 3.00$ at

¹² Eucken, *Ber. physik. Ges.*, **18**, 4 (1916).

¹³ Keesom and Onnes, *Comm. Phys. Lab. Leiden*, **153a** (1917).

¹⁴ Dewar, *J. Chem. Soc.*, **73**, 528 (1898).

$T_0 = 14^\circ\text{A.}$, and Cath and Onnes'¹⁵ boiling point, 20.39°A. , we obtain

$$\log p_{\text{mm.}} = 7.3725 \log T - 2.0572 (\log T)^2 - \frac{26.8679}{T} - 1.9280 \quad (11)$$

The values given by this equation do not, however, agree with the experimental values of Keesom and Onnes.

It will be noted that the vapor-pressure equation is of the form, $\log p = A \log T + B(\log T)^2 + \frac{Z}{T} + C$, and that A and B are determined solely by the heat-capacity curve of the condensed phase, here liquid hydrogen. If Keesom and Onnes' and Eucken's determinations of this curve are correct, and if, indeed, the application of the Sackur equation to gaseous hydrogen at these temperatures is valid, we should be able to obtain a vapor-pressure equation by evaluating both Z and C by means of two determinations of the vapor pressure. It will be noted that here we are not depending upon any of the experimental determinations of the heat capacity of solid hydrogen and the heat of fusion of hydrogen, since S_0 occurs only in the constant C. The equation obtained by this method is

$$\log p_{\text{mm.}} = 7.3715 \log T - 2.0572 (\log T)^2 - \frac{40.733}{T} - 1.2537 \quad (12)$$

It will be noted in Table I that the calculations from this equation agree with the determinations of Keesom and Onnes but little better than those from Equation 11. The failure of Equation 12 indicates that the Sackur equation is not applicable, that the heat-capacity measurements of Keesom and Onnes are uncertain, or that the vapor-pressure measurements are themselves uncertain, or a combination of these circumstances.

Finally, a calculation of the heat of fusion was made on the assumption that Keesom and Onnes' values of the vapor pressure and the heat capacity of the solid are correct, and that the application of the Sackur equation is valid. From the last we calculate the entropy of gaseous hydrogen in equilibrium with the solid at the melting point, 14°A. The pressure, as extrapolated beyond the last value of Onnes at 14.2°A. , is 55.27 mm. We obtain $S_{\text{gas}} = 17.29$. From the vapor-pressure curve the entropy of vaporization is 15.34 at 14°A. If the entropy of solid hydrogen at the melting point is 0.6, then the entropy of fusion is $17.29 - (0.6 + 15.34) = 1.35$, and the heat of fusion is 18.9 cal./mole.

It will be noted that the calculated values are as accurate as the specific-heat data used in the formulas, and in the case of the best known vapor-pressure measurements, namely, those of mercury, the agreement between the observed and calculated values is best. Unfortunately, the values of the specific heats in the neighborhood of the boiling points are extrapolated over a long range, so that accurate values of the heats and entropies of vaporization at the boiling points cannot be calculated.

¹⁵ Cath and Onnes, *Comm. Phys. Lab. Leiden*, 152a (1917).

Of course the same method can be used to calculate the partial pressure at a series of temperatures of a monatomic gas in equilibrium with any solid or liquid phase of constant composition for which the specific-heat curve and entropy are known, providing one value of the partial pressure is known.

TABLE I							
CALCULATED AND OBSERVED VALUES OF VAPOR PRESSURE IN MILLIMETERS							
Equation	<i>t</i>	<i>T</i>	<i>p</i> (calc.) Millar	<i>p</i> (calc.) others	<i>p</i> (obs.)	Observer or calculator	
MERCURY							
4	458	731	3582.5	3611.7	} Smith and Men- zies ⁸	
	444	717	2969	2990		
	434.7	707.8	2611.5	2624.3		
	417.2	690.3	2036.6	2037.2		
	404.3	677.4	1670.7	1675.3		
	372.7	645.8	1001.2	1002.5		
	357	630.1	(760)	760		
	254	527	82.4	82.08		
	191.5	464.6	13.08	13.02		
	150.0	423.1	2.812	2.802		} Menzies ¹⁸
	121.8	394.9	0.822	0.829		
	5	30	303	.00290	0.00299		0.00278
25		298	.001955	.001995	S. and M.	
20		293	.00126	.00131	.00188	Observations	
0		273	.0 ₂ 2033	.0 ₂ 207	.0 ₂ 184	Knudson ¹⁷	
- 39		234.1	.0 ₂ 228	
6	-183	m. p. 90	10 ⁻⁸⁰				
SODIUM							
7	861	1134	760	760	} Gebhardt ¹¹ Kröner ¹⁸	
	858	1131	740		
	857	1130	731		
	727	1000	217		
	570	843	29.0	80.0		
	560	833	25.4	33.2		
	550	823	21.4	23.0		
	540	813	(18.5)	18.5		
	520	793	13.2	12.4		
	500	773	9.0	8.6		
	480	753	6.2	6.1		
	460	733	4.2	4.2		
	440	713	2.8	2.9		
360	633	0.39	0.32			
97.5	370.6	14×10 ⁻⁷			
8	25	m. p. 298	17×10 ⁻⁹	
ZINC							
9	1510	1783	42.7 atm.	53 atm.	} Greenwood ¹⁹	
	1280	1553	14.2	21.5		
	1230	1503	10.7	14.2		
	1120	1393	5.3	6.3		

	920	1193	(760 mm.)	(760 mm.)	} Johnston ²⁰
	750	1023	106	100	
	500	773	1.06	1	
	419	692	0.121	
		m. p.				
10	363	636	0.0174	0.018	} Edgerton ²¹
	331	604	.004760052	
	312	585	.002060021	
	280	553	.0004400042	
	257	530	.00013000012	
	25	298	1.25×10^{-14}	
			HYDROGEN			
11	...	33.18	6.8 atm.	12.9 atm.	} Cath and Onnes ¹⁶
	...	20.39	(760 mm.)	760 mm.	
	...	14.2	88	61.80	
12	...	33.18	12.1 atm.	12.9 atm.	
	...	31.36	(7484.2 mm.)	7484.2 mm.	
	...	20.39	(760 mm.)	760 mm.	
	...	14.2	43.8	61.80	

Summary

A formula has been derived by means of which the pressure of a monatomic gas in equilibrium with the liquid or solid element can be calculated from specific-heat data and one vapor-pressure measurement.

Sample calculations have been made for mercury, sodium, zinc and hydrogen.

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¹⁶ Menzies, *THIS JOURNAL*, **41**, 1783 (1919).

¹⁷ Knudson, *Ann. Physik*, **29**, 179 (1909). Hill, [*Phys. Rev.*, **20**, 259 (1922)] gives 0.000350 mm. at 0°C., and 0.00273 mm. at 25°C.

¹⁸ Kröner, *Ann. Physik*, [3] **40**, 138 (1913).

¹⁹ Greenwood, *Proc. Roy. Soc. London*, **83A**, 483 (1910).

²⁰ Johnston, *J. Ind. Eng. Chem.*, **9**, 873 (1917).

²¹ Edgerton, *Phil. Mag.*, **33**, 33 (1917).