The Heat of Vaporization as a Function of Pressure and Temperature

BY J. E. HAGGENMACHER

From an analytic expression of the line of saturation of liquids and vapors the heat of vaporization is deduced as a function of pressure and temperature.

The behavior of a two phase system consisting of a liquid and its vapor at equilibrium may be represented by the equation[1]

$$P = \frac{RT}{M(v + B)} - \frac{A}{T(v + B)^2} \qquad (1)$$

where

$$A = \frac{R^2T_c^3}{4M^2P_c}, \quad B = \frac{RT_c}{2MP_c} - v_c$$

For unit mass, p is the pressure; T, the absolute temperature; v, the specific volume; M, the molecular weight; R, the perfect gas constant; and A and B are constants. Subscripts, c, indicate critical values.

Denoting by v_g and v_L the specific volume of saturated liquid and saturated vapor, respectively, there is obtained for the difference of the roots of equation (1)

$$v_g - v_L = \frac{RT}{Mp}\sqrt{1 - \frac{DP}{T^3}} \qquad (2)$$

where

$$D = T_c^3/P_c$$

Introducing this expression into the Clapeyron–Clausius equation

$$L = \frac{dp}{dT}\,T(v_g - v_L)$$

the heat of vaporization, per unit mass, becomes

$$L = \frac{RT^2}{MP}\frac{dp}{dT}\sqrt{1 - \frac{DP}{T^3}} \qquad (3)$$

Equation (3) is compared with some calorimetrically measured heats of vaporization.

The vapor pressure and heat of vaporization have been measured for propylene by Powell and Giauque,[2] for methyl mercaptan by Russell, Osborne and Yost,[3] for 1,1,1-trifluoroethane by Russell, Golding and Yost[4] and for dimethyl sulfide by Osborne, Doescher and Yost.[5] These authors correlate their vapor pressure data by a relationship of the form

$$\log P_{\text{mm}} = -\frac{a}{T} - b\log T + c$$

Then

$$\frac{dp}{dT} = \frac{P}{T^2}(2.303a - bT)$$

Taking p in atmospheres, T in °K. (ice-point 273.16), $R = 0.08206$, and 1 liter-atm. = 24.206 g-cal., the heat of vaporization from equation (3), becomes

$$L = (4.5737a - 1.9863bT)\sqrt{1 - \frac{Dp}{T^3}}\ \text{g. cal./mole} \qquad (4)$$

The vapor pressure and heat of vaporization of dimethyl ether have been measured by Kennedy, Sagenkahn and Aston.[6] Their vapor pressure equation is of the form

$$\log P_{\text{mm}} = -\frac{a}{T} + b\log T - cT + d$$

Then

$$\frac{dp}{dT} = 2.303\frac{P}{T^2}\left(a + \frac{bT}{2.303} - cT^2\right)$$

and from equation (3)

$$L = 4.5737\left(a + \frac{bT}{2.303} - cT^2\right)\sqrt{1 - \frac{Dp}{T^3}}\ \text{g. cal/mole} \qquad (5)$$

Inserting for the constants a, b and c the numerical values given by the authors cited the heats of vaporization have been calculated and are compared with the measured ones in Table I.

TABLE I

Substance	T, °C.	p, atm.	L, g-cal./mole meas.	eq. (4)
Propylene	−47.75	1.0000	4402	4346
Methylmercaptan	5.96	1.0000	5872	5833
1,1,1-Trifluoroethane	−48.76	0.9339	4583	4607
Dimethyl sulfide	17.90	0.4809	6688	6664
				eq. (5)
Dimethyl ether	−24.80	1.0000	5141	5101
				eq. (6)
Benzene	20	0.0982	(8123)[a]	8146
	50	.3539	7756	7729
	80	.9916	7355	7306
	110	2.300	6914	6841
	130	3.717	(6594)	6497

[a] Values in parentheses are extrapolated.

For benzene the vapor pressure data of E. R. Smith[7] and the measurements of the heat of vaporization of Fiock, Ginnings and Holton[8] have been used.

The Smith formulation of the vapor pressure is of the form

$$\log P_{\text{mm}} = -\frac{a}{b + t} + c$$

Then, changing from °C. to °K.

$$\frac{dP}{dT} = \frac{2.303\,aP}{(T + b - 273.16)^2}$$

and from equation (3), upon inserting for a and b the values given by Smith,

$$L = \frac{70.923T^2}{(T - 52.29)^2}\sqrt{1 - \frac{Dp}{T^3}}\ \text{g-cal./mole} \qquad (6)$$

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[1] Haggenmacher, THIS JOURNAL, **66**, 313 (1944); **68**, 1123 (1946); *Phys. Rev.*, **69**, 242 (1946).

[2] Powell and Giauque, *ibid.*, **61**, 2366 (1939).

[3] Russell, Osborne and Yost, *ibid.*, **64**, 165 (1942).

[4] Russell, Golding and Yost, *ibid.*, **66**, 16 (1944).

[5] Osborne, Doescher and Yost, *ibid.*, **64**, 169 (1942).

[6] Kennedy, Sagenkahn and Aston, *ibid.*, **63**, 2267 (1941).

[7] E. R. Smith, *J. Research Natl. Bur. Standards*, **26**, 129 (1941).

[8] Fiock, Ginnings and Holton, *ibid.*, **6**, 881 (1931).

The heats of vaporization calculated from equation (6) are compared with the measurements of Fiock, Ginnings and Holton in Table I.

For water the data of Smith, Keyes and Gerry[9] for the vapor pressure, and the values of Osborn and Meyers[10] for the rate of change of the vapor pressure, have been used. The heats of vaporization calculated from equation (3) are compared with the values given by Osborn, Stimson and Ginnings[11] in Table II.

TABLE II

HEAT OF VAPORIZATION OF WATER

T, °C.	L, g. cal./g. O.S.G.	L, g. cal./g. eq. (3)	T, °C.	L, g. cal./g. O.S.G.	L, g. cal./g. eq. (3)	T, °C.	L, g. cal./g. O.S.G.	L, g. cal./g. eq. (3)
0	596.5	596.7	140	512.0	515.6	280	368.2	372.2
20	585.6	586.5	160	497.1	500.9	300	335.1	338.7
40	574.5	575.8	180	480.9	485.3	320	295.5	298.1
60	563.1	564.7	200	463.1	467.5	340	245.1	245.5
80	551.2	553.3	220	443.5	448.0	350	212.8	211.4
100	538.9	541.5	240	421.5	425.9	360	171.3	166.5
120	525.9	529.0	260	396.6	400.9	370	107.0	93.3
						374.11	0	0

Heats of vaporization may also be determined from equation (3) in the absence of an analytic correlation of the vapor pressure data. Given a sufficient number of experimental points an approximation for dp/dT is obtained from

$$\left|\frac{dP}{dT}\right|_{T_2} \cong \left|\frac{\Delta P}{\Delta T}\right|_{T_2} = \frac{P_3 - P_1}{T_3 - T_1}$$

where, geometrically, the slope of the chord between the points p_1,T_1 and p_3,T_3 is taken for the slope of the tangent line at p_2,T_2. The accuracy of the method, clearly, depends upon the narrowness of the spacing of the experimental points. A very useful method of evaluating dp/dT has been proposed by Rutledge.[12] His formulations permit simple application but require equal intervals of either p or T. Both methods are suitable for calculating the rate of change of the vapor pressure since in its entire range the vapor pressure curve is devoid of abrupt directional changes and points of inflection.

Summary

A function of pressure and temperature is derived for the heat of vaporization.

The equation is applicable to all substances whose critical pressure and critical temperature are known and for which vapor pressure data are available.

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[9] Smith, Keyes and Gerry, *Proc. Am. Acad. Arts Sci.*, **69**, 137 (1934).

[10] Osborn and Meyers, *J. Research Natl. Bur. Standards*, **1**, 1 (1934).

[11] Osborn, Stimson and Ginnings, *Mech. Eng.*, **57**, 162 (1935).

[12] Rutledge, *Phys. Rev.*, **40**, 262 (1932), and Margenau and Murphy, "The Mathematics of Physics and Chemistry," D. Van Nostrand Co., New York, N. Y., 1943, p. 456.

[CONTRIBUTION FROM THE PACIFIC EXPERIMENT STATION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

Heat Capacities at Low Temperatures of Na_2TiO_3, $Na_2Ti_2O_5$ and $Na_2Ti_3O_7$[1]

BY C. HOWARD SHOMATE[2]

The thermodynamic properties of certain titanates are of interest in connection with experimental studies of methods of treatment and utilization of titaniferous iron ores. Data for the sodium titanates are particularly pertinent to the smelting of such ores under a slag rich in sodium carbonate.

A recent paper[3] from the Pacific Experiment Station of the Bureau of Mines presented low temperature heat capacity and entropy data for ferrous, calcium, and magnesium metatitanates. This paper reports similar data for three titanates of sodium. No previous low-temperature values exist for these substances, but Naylor[4] has determined their high-temperature heat contents.

Materials

The titanates were prepared in this Laboratory by R. J. O'Dea[2] by repeated heating of stoichiometric amounts of sodium carbonate and titanium dioxide at 900 to 1,100° for several hours with continuous pumping to remove carbon dioxide.

Analyses of the final products for titanium and carbon dioxide, and the known silica impurity of the original titanium dioxide, indicated the following proximate compositions: 98.4% Na_2TiO_3, 1.1% Na_2SiO_3 and 0.5% Na_2CO_3; 98.7% $Na_2Ti_2O_5$, 1.0% Na_2SiO_3 and 0.3% Na_2CO_3; 98.6% $Na_2Ti_3O_7$, 1.1% Na_2SiO_3 and 0.3% Na_2CO_3.

X-Ray examinations of the samples were made by Dr. E. V. Potter.[5] The crystalline character of the substances was proved, but there were no previous data with which to check the diffraction patterns.

Heat Capacities

The method and apparatus used in the low-temperature heat capacity measurements were described previously.[6,7] The experimental results, expressed in defined calories (1 calorie =

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[2] Chemist, Pacific Experiment Station, Bureau of Mines.

[3] Shomate, THIS JOURNAL, **68**, 964 (1946).

[4] Naylor, *ibid.*, **67**, 2120 (1945).

[5] Physicist, Salt Lake City Station, Bureau of Mines.

[6] Kelley, THIS JOURNAL, **63**, 1137 (1941).

[7] Shomate and Kelley, *ibid.*, **66**, 1490 (1944).