Accurate Calculation of Very Low Vapor Pressures: Ice, Benzene, and Carbon Tetrachloride

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THE TEMPERATURE dependence of the vapor pressure of a pure substance is expressed by the Clapeyron equation. Exact integration of this equation is, however, tedious since the terms ΔH and ΔV for the process of vaporization are functions of both temperature and pressure. An exact vapor pressure equation of very convenient form has been derived by Gottschal and Korvezee (*9*) by a somewhat different thermodynamic approach. Their equation is applied below to the extrapolation of vapor pressures to low temperatures for three substances for which the relevant thermodynamic properties are very well known. The resulting tables of vapor pressures should provide an independent method of calibrating vacuum gages in the micron and submicron region of pressure.

VAPOR PRESSURE EQUATION

The basic equation for the vaporization process may be written as

$$R \ln f/a = -\Delta G^{\circ}/T \qquad (1)$$

The standard state of the vapor is the hypothetical ideal gas at 1 atm. of pressure. The standard state of the condensed phase is chosen to be the solid or liquid under its equilibrium (saturation) vapor pressure. Thus the value of a is unity. By utilizing Equation 1 at two temperatures, the vapor pressure equation may be deduced readily in final form,

$$R \ln P_2/P_1 = \Delta H_2^{\circ} (1/T_1 - 1/T_2) - I + J - K + L \qquad (2)$$

$$I = (1/T_1) \int_{T_1}^{T_2} (C_p^{\circ} - C_{\text{sat}}) dT$$

$$J = \int_{T_1}^{T_2} (C_p^{\circ} - C_{\text{sat}}) d \ln T$$

$$K = R \ln f_2/P_2 - R \ln f_1/P_1$$

$$L = (1/T_1) \int_{P_1}^{P_2} V_{\text{sat}} dP$$

$$\Delta H^{\circ} = \Delta H_v + (H^{\circ} - H_p)$$

with the condition that no phase change, other than the vaporization process, occur between T_1 and T_2. An approximate value of P_1, the pressure to be calculated, is required to evaluate the relatively small terms K and L. This may be obtained by solving Equation 2 with $K = L = 0$. A reiterative procedure is in general unnecessary.

The actual information required to calculate the vapor pressure of a substance with Equation 2 is (a) the vapor pressure and very accurate, calorimetrically determined heat of vaporization at T_2, (b) the equation of state of the vapor, (c) the heat capacity of the condensed phase and heats of transition and fusion in the region between T_1 and T_2, (d) the normal vibrational frequencies of the molecule, and (e) the density of the condensed phase. For this article, the following requirements have been added: that the substance in question be common, readily purified, noncorrosive, and have a vapor pressure below 1 micron at −100°. The only three compounds that appear to meet the above requirements are water, benzene, and carbon tetrachloride. The calculated vapor pressures of these compounds are presented in Table I as log P *vs.* $1000/T$ for the range of about 1 mm. to 10^{-6} mm. For interpolation between two adjacent points, sufficient accuracy may be attained by assuming a linear relationship between these two quantities.

The estimation of the error in the calculated vapor pressures was based upon the estimated error in the data employed to evaluate the terms in Equation 2. Estimates quoted by the original authors were used when available. To establish a degree of confidence in the data which could be said to be independent of the claims made by the original authors, vapor pressures were calculated above 25° and compared with the well known, experimental values (Table II). This provided a test mainly of data from categories (a), (b), and (d) in so far as their use for the calculation of low pressures was concerned.

Data sources used in all the calculations are listed in Table III.

WATER, ICE

Calculation of standard heats of vaporization and sublimation used in Equation 2

$$\begin{aligned}
\Delta H_v(25^{\circ}) &= 10{,}513 \pm 1 \text{ cal./mole} \\
H^{\circ} - H_p &= \underline{5 \pm 0} \\
\Delta H_{298}^{\circ} &= 10{,}518 \\
-\int_{273.16}^{298.15} (C_p^{\circ} - C_{\text{sat}}) dT &= \underline{250 \pm 0} \\
\Delta H_{273}^{\circ}(\text{vap.}) &= 10{,}768 \\
\Delta H_f &= \underline{1{,}436 \pm 1} \\
\Delta H_{273}^{\circ}(\text{subl.}) &= 12{,}204 \text{ cal./mole}
\end{aligned}$$

For the calculation of the vapor pressure of water, the starting point was 25° (i.e., T_2 = 298.150° K., P_2 = 23.756 mm., ΔH_2° = 10,518 cal./mole). Values of C_p rather than C_{sat} are available for liquid water (*23*). The difference between these two quantities has a small, but not negligible, effect on the integrals I and J. However, the effect is partially canceled out in Equation 2 to the extent that the following expression is negligible.

$$-(1/T_1) \int_{T_1}^{T_2} (C_p - C_{\text{sat}}) dT + \int_{T_1}^{T_2} (C_p - C_{\text{sat}}) d \ln T$$

Thus, even to the high accuracy of the present calculation, C_p could be substituted for C_{sat}. A conversion factor of 1.00064 defined cal./*IT* cal. was applied to the C_p data. Comparison of the calculated values of the vapor pressure of water with the experimental values bears out the reliability of the data used in Equation 2, in particular the high accuracy of the value of the heat of vaporization.

For the calculation of the vapor pressure of ice, the starting point was the triple point (T_2 = 273.16° K., P_2 = 4.579 mm., ΔH_2° = 12,204 cal./mole).

BENZENE

Equation 2 has been applied previously to benzene between the melting and boiling points (*10*). Any disagreement between the calculated and measured values of the vapor pressure in this range could be expressed as an uncertainty of no more than 5 cal./mole in the value of the heat of vaporization at 25°.

Table I. Calculation of Vapor Pressures, Micron Range

T°, K.	Terms in Equation 2				Log P, Mm.	1000/T	Estd. % Error in P
	ΔH°	$-I$	$-J$	$-K$			
			Ice				
273.16	0	0	0	0	(0.6608)	3.661	
260	2.261	0.043	0.042	0.001	0.1660	3.846	±0.05
240	6.172	0.075	0.069	0.001	0.3102 − 1	4.167	±0.1
220	10.795	0.057	0.044	0.001	0.299 − 2	4.545	±0.2
200	16.342	−0.028	−0.043	0.001	0.086 − 3	5.000	±0.3
180	23.123	−0.201	−0.205	0.001	0.607 − 5	5.556	±0.4
160	31.597	−0.491	−0.455	0.001	0.763 − 7	6.250	±0.5
			Solid Benzene				
278.68	0	0	0	0	(1.555)	3.588	
260	2.767	0.847	0.817	0.008	0.942	3.846	±0.2
240	6.203	1.769	1.636	0.008	0.169	4.167	±0.4
220	10.266	2.744	2.412	0.008	0.237 − 1	4.545	±0.7
200	15.142	3.799	3.156	0.008	0.104 − 2	5.000	±1
180	21.100	4.987	3.882	0.008	0.700 − 4	5.556	±1.5
160	28.548	6.373	4.600	0.008	0.927 − 6	6.250	±2
			Solid Carbon Tetrachloride				
	(Step 1, ΔH°_2 = 7765 cal./mole)						
298.15	0	0	0	0	(2.058)	3.354	
250.30	4.979	2.270	2.080	0.018	0.925	3.995	±0.3
	(Step 2, ΔH°_2 = 8934 cal./mole)						
250.30	0	0	0	0	(0.925)		
225.35	3.951	1.147	1.086	0.000	0.048	4.438	±0.6
	(Step 3, ΔH°_2 = 10,287 cal./mole)						
225.35	0	0	0	0	(0.048)		
220	1.110	0.238	0.235	0.000	0.805 − 1	4.545	±0.9
200	5.786	1.123	1.054	0.000	0.769 − 2	5.000	±1.3
180	11.501	2.074	1.838	0.000	0.485 − 3	5.556	±1.7
160	18.644	3.153	2.608	0.000	0.857 − 5	6.250	±2
140	27.289	4.437	3.387	0.000	0.737 − 7	7.143	±3

The gas imperfection terms required for the low temperature extrapolation were obtained by averaging values based on three equations of state, reported independently in the literature. These values are $(H^\circ - H_p)_{298}$ (cal./mole) = 28.8, 12.9, 17.0, and $K(T_2 = 278.68,\ T_1 \leqq 260°\text{K.})$ (cal./deg. mole) = −0.010, −0.006, −0.008. The spread in values serves as an indication of the error associated with these terms.

The following frequency assignment (cm.$^{-1}$) was used to calculate the ideal gaseous heat capacities listed in Table IV (degeneracies indicated in parentheses) 3080 (2), 3062, 3060, 3047 (2), 1596 (2), 1485 (2), 1340, 1310, 1178 (2), 1152, 1037 (2), 1010, 995, 992, 975 (2), 850 (2), 703, 673, 606 (2), 405 (2).

Calculation of standard heat of sublimation to be used in Equation 2.

$$\begin{aligned}
\Delta H_v(25^\circ) &= 8{,}090 \pm 5 \text{ cal./mole}\\
H^\circ - H_p &= \underline{20 \pm 6}\\
\Delta H^\circ_{298} &= 8{,}110\\
-\int_{278.68}^{298.15} (C^\circ_p - C_{\text{sat}})\,dT &= \underline{257 \pm 0}\\
\Delta H^\circ_{278.68}(\text{vap.}) &= 8{,}367\\
\Delta H_f &= \underline{2{,}358 \pm 0.5}\\
\Delta H^\circ_{278.68}(\text{subl.}) &= 10{,}725 \text{ cal./mole}
\end{aligned}$$

For the calculation of the vapor pressure of solid benzene, the starting point was the melting point (T_2 = 278.68° K., P_2 = 35.87 mm., ΔH°_2 = 10,725 cal./mole).

CARBON TETRACHLORIDE

To calculate the vapor pressure of the liquid above 25°, it was necessary to extrapolate the heat capacity data for the liquid from 300° K., the values of Hicks, Hooley, and Stepenson (*13*) being favored for this purpose. The low temperature extrapolation was performed in three steps, since the melting point, 250.30° K., and a transition point, 225.35° K., occur at temperatures above the low pressure region.

The required gas imperfection terms were based on two equations of state. The values of $(H^\circ - H_p)_{298}$ are 22.4, 16.0; and $K(T_2 = 298.15)$ for various values of T_1 are −0.020, −0.017 (T_1 = 250.30); 0.0099, 0.0091 (T_1 = 313,15); 0.0316, 0.0303 (T_1 = 333.15); 0.0573, 0.0577 (T_1 = 353.15).

Calculation of the standard heats of vaporization and sublimation used in Equation 2

$$\begin{aligned}
\Delta H_v(25^\circ) &= 7{,}746 \pm 5 \text{ cal./mole}\\
H^\circ - H_p &= \underline{19 \pm 3}\\
\Delta H^\circ_{298} &= 7{,}765\\
-\int_{250.30}^{298.15} (C^\circ_p - C_{\text{sat}})\,dT &= \underline{568 \pm 3}\\
\Delta H^\circ_{250.30}(\text{vap.}) &= 8{,}333\\
\Delta H_f &= \underline{601 \pm 2}\\
\Delta H^\circ_{250.30}(\text{subl., crystal II}) &= 8{,}934\\
-\int_{225.35}^{250.30} (C^\circ_p - C_{\text{sat}})\,dT &= \underline{258 \pm 2}\\
\Delta H^\circ_{225.35}(\text{subl., crystal II}) &= 9{,}192\\
\Delta H_{tr}(\text{I} \rightarrow \text{II}) &= \underline{1{,}095 \pm 3}\\
\Delta H^\circ_{225.35}(\text{subl., crystal I}) &= 10{,}287 \text{ cal./mole}
\end{aligned}$$

For the calculation of the vapor pressure of the liquid, the starting point was 25° (T_2 = 298.15° K., P_2 = 114.16 mm., ΔH°_2 = 7765 cal./mole). The same starting point served for the calculation of the vapor pressure of the solid. The value of log P (mm.) obtained at the melting point agrees to the third decimal with the extrapolated Antoine equation (*14*).

The calculated vapor pressure at 80° is seen to be in error by +0.28%. It is estimated that the uncertainty in $-I + J$ arising from the extrapolated C_{sat} data is ±0.0012. A consideration of the other errors contributing to the terms

Table II. Calculation of Vapor Pressures, Micron Range

	Terms in Equation 2					Log P, Mm.		% Error in Calcd. P
t, ° C.	$-\Delta H^\circ$	I	J	K	$-L$	Calcd.	Exptl.	
				Liquid Water				
25	0	0	0	0	0	(1.37577)	1.37577	
40	1.6898	0.4771	0.4890	0.0023	0.0001	1.74298	1.74291	+0.02
60	3.7062	1.0457	1.1050	0.0071	0.0002	2.17436	2.17429	+0.02
80	5.4942	1.5504	1.6856	0.0150	0.0005	2.55031	2.55023	+0.02
100	7.0905	2.0028	2.2360	0.0267	0.0011	2.88044	2.88081	−0.09
				Liquid Carbon Tetrachloride				
25	0	0	0	0	0	(2.0575)	2.0575	
40	1.2475	0.5432	0.5567	0.0095	0.0010	2.3295	2.3292	+0.07
60	2.7362	1.1757	1.2428	0.0310	0.0031	2.6483	2.6470	+0.30
80	4.0561	1.7228	1.8746	0.0575	0.0066	2.9248	2.9236	+0.28

Table III. References to Data Used in Calculating Very Low Vapor Pressures by Equation 2

Types of Data	H_2O	C_6H_6	CCl_4
Vapor pressure, mm. range	(*12*)	(*2*)	(*14*)
Heat of vaporization	(*22*)	(*2, 22*)	(*14*)
Equation of state of vapor	(*11, 16*)	(*3, 17, 25*)	(*5, 17*)
Heat capacity of solid, liquid	(*7, 23*)	(*21*)	(*13, 26*)
Heats of fusion, transition	(*7*)	(*21*)	(*13*)
Frequency assignment or heat capacity of vapor	(*6*)	(*19*)	(*1, 8*)
Density of liquid	(*12*)	...	(*15*)

Table IV. Ideal Gaseous Heat Capacity of Benzene

	C_p°, Cal./Deg. Mole	
T, ° K.	Calcd.	Exptl.
160	10.509	
180	11.527	
200	12.699	
220	13.975	
240	15.355	
278.68	18.148	
400	26.951	26.89[a]

[a] Based on C_p(1 atm.) = 27.38; anharmonicity correction = 0.13; gas imperfection correction = 0.36 (*25, 28*).

Table V. Previously Reported Vapor Pressure Data

	Ice (*4, 20*)		Benzene (*2*)		Benzene (*18*)	
T°, K.	Log P, mm.	% deviation[a]	Log P, mm.	% deviation	Log P, mm.	% deviation
260	0.1670	+0.4	0.944	+0.5	0.949	+2
240	0.3115 − 1	+0.3	(0.170)	+0.2	0.178	+2
220	0.299 − 2	0	(0.235 − 1)	−0.5	0.242 − 1	+1
200	0.079 − 3	−2	(0.081 − 2)	−5	0.081 − 2	−5
180	0.58 − 5	−7			(0.603 − 4)	−22

[a] Deviation from values calculated in this article.

in Equation 2 shows that the value of ΔH_v must be adjusted down by 5 to 16 cal./mole, depending on whether the errors add favorably or not, in order to bring the calculated vapor pressure into agreement with the experimental value. Thus one might anticipate that the error in ΔH_v is a few calories greater than the ±5 cal./mole assigned. Therefore, the estimated errors given in Table I are to be taken with caution.

PREVIOUSLY REPORTED VAPOR PRESSURE DATA

The vapor pressure of ice has been extrapolated to low temperatures (*4, 20*) with an equation of the form

$$\log P = -a/T + b \log T - cT + dT^2 - e$$

The constants a and b were theoretically related in the usual way to the heat of sublimation at 0° and the heat capacities of solid and gaseous H_2O at 0°; c and d were obtained by fitting the equation to the experimental values of the vapor pressure at −50° (*24*) and −100° (*27*); and e was fixed by the experimental vapor pressure at 0°.

The measured vapor pressure of solid benzene in the mm. range has been fitted to the Antoine equation (*2*). Also, one set of low pressure measurements has been reported in the form of the Antoine equation (*18*).

For the sake of completeness, values of the vapor pressures from the above sources are given in Table V at temperatures appropriate for comparison with the present calculations. Values in parentheses fall outside the stated temperature range for the corresponding Antoine equation. These data are not sufficiently accurate to provide a check on the present calculations.

NOMENCLATURE

a = activity of condensed phase at equilibrium (saturation) pressure
C_p° = heat capacity of hypothetical, ideal gas at constant pressure
C_p = heat capacity of condensed phase at 1 atm. pressure
C_{sat} = heat capacity of condensed phase at saturation pressure
f = fugacity of real vapor at saturation pressure
f_1, f_2 = values of f at T_1 and T_2, respectively
ΔG° = standard Gibbs free energy of vaporization
$H^\circ - H_p$ = real gas correction to enthalpy at saturation pressure
ΔH_2° = standard enthalpy of vaporization or sublimation at T_2
ΔH_f = heat of fusion
ΔH_{tr} = heat of transition
ΔH_v = heat of vaporization to real vapor at saturation pressure
P_1 = vapor pressure at T_1, to be calculated
P_2 = known vapor pressure at T_2
R = gas constant, 1.98726 cal./deg. mole
T = absolute temperature
V_{sat} = molar volume of condensed phase at saturation pressure

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Densities and Refractive Indices of Aqueous Solutions

Diethylenetriamine, Triethylenetetramine, and Tetraethylenepentamine

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CONTINUING AN INVESTIGATION of the effect of chemical structure on density and refractive index, data have been obtained for aqueous solutions of diethylenetriamine, triethylenetetramine, and tetraethylenepentamine. The purification procedures and methods of analysis described by Chu and Thompson (*4*) were employed.

Refractive index and density data were determined at 25° C. Data on these properties have been reported (*1*) for commercially available compounds but no values have been given for aqueous solutions.

PURIFICATION AND PREPARATION

Following purification by distillation (*4*), the water contents by weight were determined by Karl Fischer reagent to be as follows: diethylenetriamine 0.009%, triethylenetetramine 0.008% and tetraethylenepentamine 0.011%. Within the limits of the experimental measurements, these purified materials gave the same values for density and refractive index as those for pure compounds determined by extrapolation to 100% in each case.

Data for the pure amines are compared in Table I with those reported earlier (*1*) for commercial products.

Solutions covering the entire composition range at approximately 10 weight % increments were prepared according to the established procedure (*4*). Based on amounts of material and the precision possible, compositions were known to within ±0.003%.

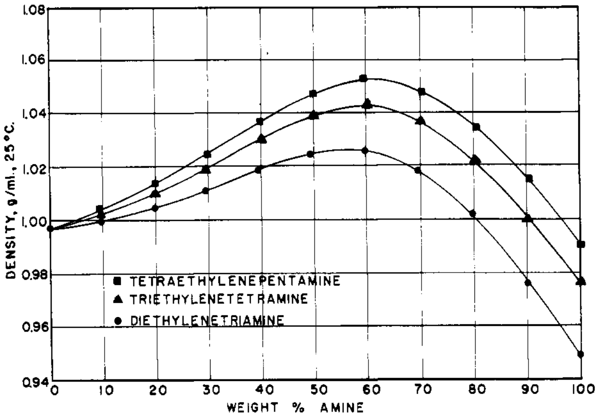

Figure 1. Densities of aqueous amine solutions at 25° C.

DENSITY MEASUREMENTS

Densities of all solutions were determined at 25.00° ±0.01° C. in a constant temperature bath using calibrated 10-ml. Weld-type, capped specific gravity bottles. A precision of ±0.0001 gram per ml. was possible by this procedure. The experimental data for the densities of the three amines are presented in Table II.

The density-composition curves for diethylenetriamine, triethylenetetramine, and tetraethylenepentamine are shown in Figure 1. All three curves show pronounced maxima in the midcomposition range similar to those for many compounds, including aqueous solutions of propylene glycol (*7*), dipropylene glycol (*2*), ethylene glycol monomethyl ether (*4*), diethylene glycol monomethyl ether (*3*) and diethylene glycol monoethyl ether (*3*).

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