MKS-03409: Effect of Pressure on the Melting Point

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Abstract

A chemical's melting point is typically assumed to be independent of pressure. However, as more processes begin operating at high pressure, it is important to understand just how pressure affects the melting point and how this effect can be estimated.

Effect of Pressure

Figure 1 shows the melting point as a function of pressure for methanol [1], ethanol [1], and acetone [2]. The curves show melting point increases with an increase in pressure. Although there are some common exceptions, e.g., water, this trend is true for the majority of compounds.

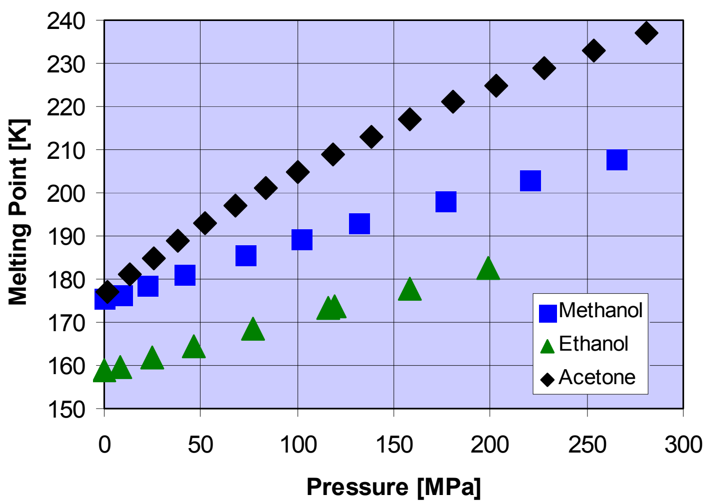

Figure 1: Effect of Pressure on the Melting Point of Various Chemicals

Table 1 compares melting points at atmospheric pressure with those at 98.7 atm (10 MPa) for these three chemicals. The numerical values show that the general assumption of pressure independence is quite valid.

Table 1: Evaluation of Pressure Independence Assumption

Chemical	Tm [K] @ 1 atm	Tm [K] @ 98.7 atm
Methanol	175.47	176.61
Ethanol	159.05	159.79
Acetone	176.35	179.95

Estimating the Effect of Pressure

The Clapeyron equation, shown in Equation 1, describes the effect of pressure on the equilibrium melting point.

$$\frac{dT_m}{dP} = \frac{T_m \Delta V_m}{\Delta H_{fus}} \tag{1}$$

In Equation 1 T_m is the equilibrium melting point, P is the pressure, ΔV_m is equal to the liquid molar volume minus the solid molar volume, and ΔH_{fus} is the enthalpy of fusion.

Integrating Equation 1 requires knowing the liquid volume, solid volume, and the enthalpy of fusion as functions of pressure. Such relationships are seldom available. One possible approach is to assume these properties are independent of pressure. Equation 2 shows the result of using this assumption and using the melting point at atmospheric pressure as a boundary condition to integrate Equation 1.

$$\ln T_m - \ln T_{m,1atm} = \frac{\Delta V_m}{\Delta H_{fus}} (P - 101325) \tag{2}$$

Here $T_{m,1\ atm}$ is the chemical's melting point at 1 atmosphere pressure and P is the pressure in units of Pa.

Table 2 shows values for solid molar volume, liquid molar volume, and enthalpy of fusion all measured at temperatures near the atmospheric melting temperature [3].

Table 2: Properties Needed for Equation 2

Chemical	V_s [m3/kmol]	V_l [m3/kmol]	ΔHfus [J/kmol]
Methanol	0.03270	0.03616	3.2049E6
Ethanol	0.04367	0.05115	4.9310E6
Acetone	0.05996	0.06361	5.6912E6

Figure 2 compares estimates from Equation 2 with data for methanol. Similar results for ethanol and acetone indicate that the "pressure independent" assumption does not produce good results.

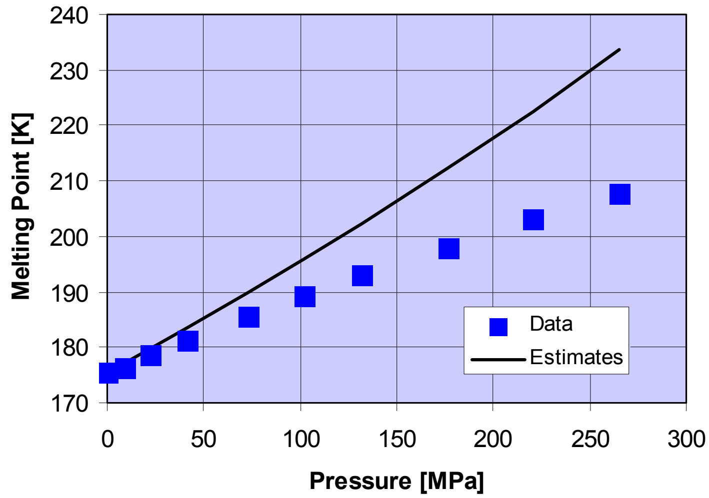

Figure 2: "Pressure Independent" Clapeyron Equation Estimates and Data for Methanol

The Simon Equation

Equation 3 shows the relationship proposed by Simon and Glatzel [4].

$$\frac{P - P_{tp}}{a} = \left(\frac{T_m}{T_{m,1atm}} \right)^b - 1 \qquad (3)$$

In Equation 3, P is the pressure, P_{tp} is the triple point pressure, T_m is the equilibrium melting point at pressure P, $T_{m,1atm}$ is the melting point at 1 atmosphere pressure, and a and b are regression constants. P_{tp} can often be neglected because it is much smaller than P in value.

Babb [5] compiled parameters for the Simon equation for over 200 chemicals. Table 3 lists parameters for several of these chemicals. These parameters, accompanying data, and additional parameters regressed from data, have been added to various Molecular Knowledge Systems® [6] knowledge bases and can be accessed by Cranium® [6] version 2 and later.

Table 3: Parameters for the Simon Equation for Several Chemicals

Chemical	a [MPa]	b [- - -]	Source
Methanol	412.2	2.937	Note 1
Ethanol	931.1	1.398	Note 1
Acetone	119.7	4.137	Note 2
n-Octadecane	345	3.39	Ref 5
Acetonitrile	525	2.06	Ref 5
Ethyl acetate	760	2.20	Ref 5

Note 1: Regressed from the data of reference 1. Note 2: Regressed from the data of reference 2.

Figure 3 compares the parameter fits to the experimental data for methanol, ethanol, and acetone. A legend is not shown on the graph but the symbols and colors are the same as those used in Figure 1. The Simon equation reproduces the data very well.

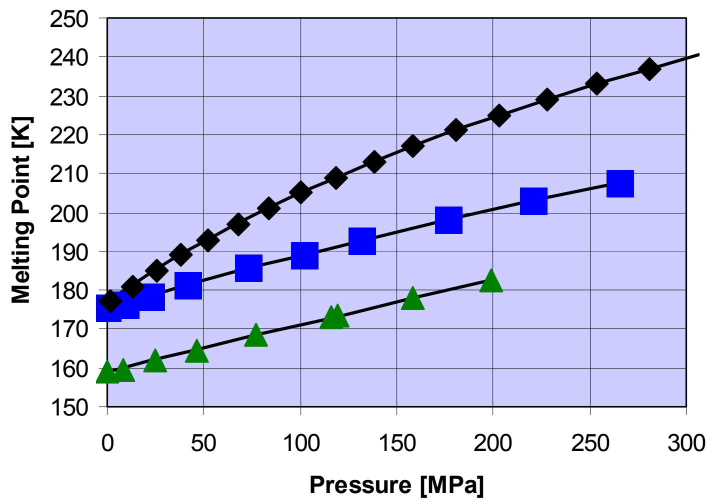

Figure 3: Comparison of the Simon Equation Estimates to Experimental Data. (See Figure 1 for graph's legend.)

Conclusion

The Simon equation fits experimental data very well. Caution must be taken to ensure solid-solid transitions do not occur over the range of values being regressed. Care must also be taken when using published parameters. For example, the published parameters for ethanol [5] fit the experimental data [1] very poorly. Molecular Knowledge Systems, Inc. is reexamining these published parameter values. We are also investigating how to predict parameters from knowledge of only the chemical's molecular structure.

References

1) T. F. Sun, J. A. Schouten, N. J. Trappeniers, and S. N. Biswas. "Accurate Measurement of the Melting Line of Methanol and Ethanol at Pressures up to 270 MPa." Berichte der Bunsen-Gesellschaft für Physikalische Chemie, volume 92, pages 652-655, 1988. MKS-03407.

2) P. W. Richter and Carl W. F. T. Pistorius. "The Effect of Pressure on the Melting Point of Acetone." Zeitschrift für Physikalische Chemie Neue Foge, volume 85, pages S. 82-85, 1973. MKS-03408.

3) NIST Chemistry Website. http://webbook.nist.gov/chemistry/.

4) F. E. Simon and G. Glatzel. Z. Anorg. u. Allgem. Chem., volume 178, number 309, 1929.

5) S. E. Babb, Jr. "Parameters in the Simon Equation Relating Pressure and Melting Temperature." Reviews of Modern Physics, volume 35, number 2, April 1963. MKS-03340.

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