

Chapter 17 Problems: Phase Transitions in Pure Substances

1. Prove that the dependence of the freezing point on the pressure for a pure substance for large changes in pressure is given by:

$$T = T_m e^{\Delta P \Delta_{\text{fus}} V_i / \Delta_{\text{fus}} H_i}$$

Answer: The plan is to integrate Eq. 17.1.8 without assuming the temperature on the right side of the equation is constant.

Separating variables in Eq. 17.1.8 and specifying the melting or fusion phase transition:

$$\frac{dP}{dT} = \frac{\Delta_{\text{fus}} H_i}{T \Delta_{\text{fus}} V_i} \quad \text{gives} \quad dP = \frac{\Delta_{\text{fus}} H_i}{T \Delta_{\text{fus}} V_i} dT$$

Integration from an initial pressure of P_o and initial melting point of T_m to a final pressure of P gives:

$$\int_{P_o}^P dP = \int_{T_m}^T \frac{\Delta_{\text{fus}} H_i}{T \Delta_{\text{fus}} V_i} dT$$

Assuming that $\Delta_{\text{fus}} H_i$ and $\Delta_{\text{fus}} V_i$ are constant over the pressure and temperature range gives:

$$\Delta P = \frac{\Delta_{\text{fus}} H_i}{\Delta_{\text{fus}} V_i} \ln T/T_m \quad \text{or} \quad \ln T/T_m = \frac{\Delta P \Delta_{\text{fus}} V_i}{\Delta_{\text{fus}} H_i}$$

Solving for the new melting point, T , gives:

$$T = T_m e^{\Delta P \Delta_{\text{fus}} V_i / \Delta_{\text{fus}} H_i}$$

The temperature change, $\Delta T = T - T_m$, is given by:

$$\Delta T = T_m (e^{\Delta P \Delta_{\text{fus}} V_i / \Delta_{\text{fus}} H_i} - 1)$$

Note that for small pressure changes, the exponential term can be approximated using a Taylor expansion, $e^x \approx 1 + x$, and the last equation reduces to Eq. 17.1.24.

2. Calculate the change in the melting point for water ice for an increase in pressure of 10.00 bar starting from the melting point at 1.00 bar. The densities of water and ice at 0.00°C are 1.000 g cm⁻³ and 0.917 g cm⁻³, respectively. The enthalpy of fusion is 6.008 kJ mol⁻¹ at 273.15 K.

Answer: The change in molar volume on melting is:

$$\begin{aligned} \Delta_{\text{fus}} V_m &= 18.02 \text{ g mol}^{-1} \left(\frac{1}{1.000 \text{ g cm}^{-3}} - \frac{1}{0.917 \text{ g cm}^{-3}} \right) = -1.63 \text{ cm}^3 \text{ mol}^{-1} \\ &= -1.63 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1} \end{aligned}$$

Note that 10.00 bar = 1.000 × 10⁶ Pa. The change in melting point is then:

$$\Delta T = \frac{T_m^* \Delta_{\text{fus}} V_m}{\Delta_{\text{fus}} H_m} \Delta P = \frac{273.15 \text{ K} (-1.63 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1})}{6.008 \times 10^3 \text{ J mol}^{-1}} (1.000 \times 10^6 \text{ Pa})$$

$$= -0.074 \text{ K}$$

3. The vapor pressure of acetone is 0.377 bar at 30.0°C and 0.817 bar at 50.0°C. Calculate (a) the enthalpy of vaporization of acetone and (b) the normal boiling point.

Answer: The plan is to use the Clausius-Clapeyron equation to find the enthalpy of the phase transition and then again to find the temperature at which the vapor pressure is 1.00 atm.

(a). The Clausius-Clapeyron equation is:

$$\ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta_{\text{vap}} H_m}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad \text{or} \quad \ln\left(\frac{0.817}{0.377}\right) = -\frac{\Delta_{\text{vap}} H_m}{R} \left(\frac{1}{323.15} - \frac{1}{303.15}\right)$$

Giving: $0.7734 = -\frac{\Delta_{\text{vap}} H_m}{R} (-2.042 \times 10^{-4} \text{ K}^{-1})$

Make sure to keep sufficient significant figures for the temperature dependent term. Solving for the enthalpy change:

$$\Delta_{\text{vap}} H_m = -\frac{0.7734}{-2.042 \times 10^{-4} \text{ K}^{-1}} (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) = 3.149 \times 10^4 \text{ J mol}^{-1} = 31.5 \text{ kJ mol}^{-1}$$

(b). The normal boiling point is the temperature where the vapor pressure is equal to 1.00 atm = 1.0132 bar. We can use either of the data points given in the problem and the Clausius-Clapeyron equation. Using the given vapor pressure at the warmer temperature, since it is closest to the normal boiling point:

$$\ln\left(\frac{1.0132}{0.817}\right) = -\frac{\Delta_{\text{vap}} H_m}{R} \left(\frac{1}{T_2} - \frac{1}{323.15}\right) = -\frac{3.149 \times 10^4 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \left(\frac{1}{T_2} - \frac{1}{323.15}\right)$$

which gives:

$$0.2152 = -3.788 \times 10^3 \text{ K}^{-1} \left(\frac{1}{T_2} - 3.0945 \times 10^{-3} \text{ K}^{-1}\right)$$

$$1/T_2 = 3.0378 \times 10^{-3} \text{ K}^{-1}$$

Solving for the boiling point gives: $T_2 = 329.20 \text{ K} = 56.0^\circ\text{C}$

4. The normal boiling point of methanol is 64.05°C. The vapor pressure of methanol at 20.00°C is 0.1530 bar. Calculate the enthalpy of vaporization of methanol.

Answer: The plan is to use the Clausius-Clapeyron equation to find the enthalpy of the phase transition, given that the normal boiling point is the temperature that gives a vapor pressure of 1.000 atm (1.01325 bar).

(a). The Clausius-Clapeyron equation is:

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$$\ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta_{\text{vap}}H_m}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad \text{or} \quad \ln\left(\frac{1.01325}{0.153}\right) = -\frac{\Delta_{\text{vap}}H_m}{R}\left(\frac{1}{337.20} - \frac{1}{293.15}\right)$$

Giving: $1.8904 = -\frac{\Delta_{\text{vap}}H_m}{R}(-4.45624 \times 10^{-4} \text{ K}^{-1})$

Make sure to keep sufficient significant figures for the temperature dependent term. Solving for the enthalpy change:

$$\Delta_{\text{vap}}H_m = -\frac{1.8904}{-4.45624 \times 10^{-4} \text{ K}^{-1}} (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) = 3.5269 \times 10^4 \text{ J mol}^{-1} = 35.27 \text{ kJ mol}^{-1}$$

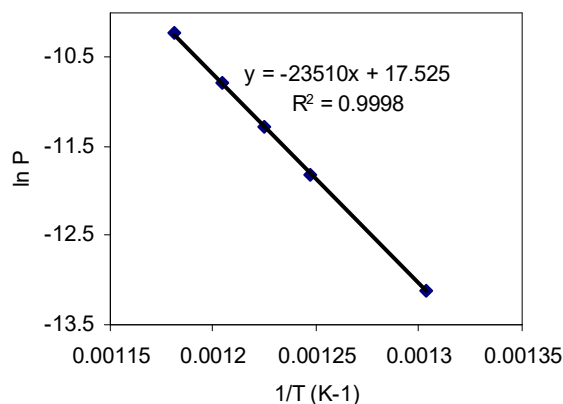
5. The vapor pressure of solid CsI at several temperatures is given in the following table. Calculate the enthalpy of sublimation of CsI.

T (K)	767.2	801.8	816.3	830.3	846.8
P/10 ⁻⁶ (bar)	2.03	7.45	12.5	20.5	36.4

Answer: Sublimation follows the Clausius-Clapeyron equation using the molar enthalpy of sublimation. The following spreadsheet and plot were constructed:

T (K)	P/10 ⁻⁶ (bar)	1/T (K ⁻¹)	ln P
767.2	2.03	0.001303	-13.1075
801.8	7.45	0.001247	-11.8073
816.3	12.5	0.001225	-11.2898
830.3	20.5	0.001204	-10.7951
846.8	36.4	0.001181	-10.2209

slope	-23509.9	17.52472	intercept
±	171.5568	0.211513	±
r ²	0.99984	0.016052	st.dev. y
F	18779.64	3	df
SS _{reg}	4.839104	0.000773	SS _{resid}



The slope has three significant figures, and slope = $-\Delta_{\text{sub}}H_m/R$, giving:

$$\Delta_{\text{sub}}H_m = -(-23509.9 \text{ K})(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) = 1.95 \times 10^5 \text{ J mol}^{-1} = 195. \text{ kJ mol}^{-1}$$

This result is very large compared to moderate molar mass organic compounds.

6. The vapor pressure of ethanol as a function of temperature is given in the table below. Determine the enthalpy of vaporization of ethanol. Calculate the standard boiling point of ethanol.

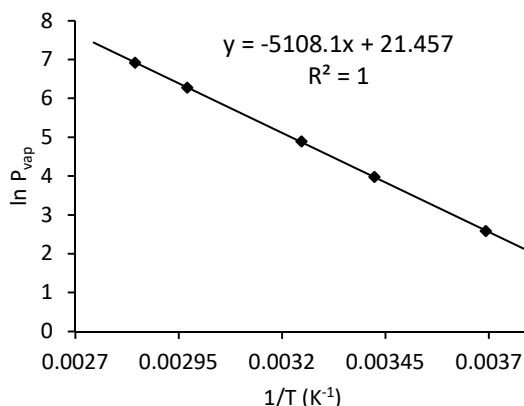
T (°C)	-2.3	19.0	34.9	63.5	78.4
P _{vap} (mbar)	13.3	53.3	133.3	533.3	1013.
P _{vap} (mm Hg)	10.0	40.0	100.0	400.0	760.0

Answer: The plan is to use the Clausius-Clapeyron equation in its linear form to find the enthalpy of vaporization from a plot of $\ln P$ vs. $1/T$. The enthalpy of vaporization is then used to find the vapor pressure at 1.00 bar to give the standard boiling point.

Any units may be used for the pressure. The following spreadsheet was developed.

T (°C)	T (K)	P _{vap} (mbar)	1/T (K ⁻¹)	ln P _{vap}
-2.3	270.85	13.3	0.003692	2.5878
19	292.15	53.3	0.003423	3.9759
34.9	308.05	133.3	0.003246	4.8926
63.5	336.65	533.3	0.00297	6.2791
78.4	351.55	1013	0.002845	6.9207

slope	-5108.1	21.45713	intercept
±	18.43946	0.059922	±
r ²	0.999961	0.012598	st.dev. y
F	76740.03	3	df
SS _{reg}	12.18002	0.000476	SS _{resid}



The slope has three significant figures, and slope = $-\Delta_{\text{sub}}H_m/R$, giving:

$$\Delta_{\text{vap}}H_m = -(-5108.1 \text{ K})(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) = 4.247 \times 10^4 \text{ J mol}^{-1} = 42.47 \text{ kJ mol}^{-1}$$

The Clausius-Clapeyron equation for two data points is:

$$\ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta_{\text{vap}}H_m}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

The normal boiling point, which corresponds to 1.01325 bar, is 351.55 K. Applying the Clausius-Clapeyron equation from 351.55 K and 1.01325 bar to a final pressure of 1.000 bar gives:

$$\ln\left(\frac{1.000}{1.01325}\right) = -\frac{4.247 \times 10^4 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} \left(\frac{1}{T_b^*} - \frac{1}{351.55 \text{ K}}\right)$$

$$-0.013163/-5108.1 = \left(\frac{1}{T_b^*} - 2.84455 \times 10^{-3} \text{ K}^{-1}\right) \quad T_b^* = 351.52 \text{ K} = 78.4^\circ\text{C}$$

The difference between the normal boiling point and standard boiling point is within experimental error for ethanol.

7. The vapor pressure of benzoic acid is 0.133 bar at 186.2°C and 0.533 bar at 227.0°C. Calculate the standard boiling point.

Answer: The plan is to calculate the enthalpy of vaporization using the Clausius-Clapeyron equation, and then use the same equation to calculate the temperature for which the vapor pressure is 1.000 bar.

The Clausius-Clapeyron equation is:

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$$\ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta_{\text{vap}}H_m}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad \text{or} \quad \ln\left(\frac{0.533}{0.133}\right) = -\frac{\Delta_{\text{vap}}H_m}{R}\left(\frac{1}{500.2 \text{ K}} - \frac{1}{459.4 \text{ K}}\right)$$

Giving: $1.388 = -\frac{\Delta_{\text{vap}}H_m}{R}(-1.7775 \times 10^{-4} \text{ K}^{-1})$

Make sure to keep sufficient significant figures for the temperature dependent term. Solving for the enthalpy change:

$$\Delta_{\text{vap}}H_m = -\frac{0.7651}{-1.7775 \times 10^{-4} \text{ K}^{-1}} (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) = 6.493 \times 10^4 \text{ J mol}^{-1} = 64.93 \text{ kJ mol}^{-1}$$

Applying the Clausius-Clapeyron equation from 227.0°C and 0.533 bar to a final pressure of 1.000 bar gives:

$$\ln\left(\frac{1.000}{0.533}\right) = -\frac{6.493 \times 10^4 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} \left(\frac{1}{T_b^*} - \frac{1}{500.2 \text{ K}}\right)$$

$$-0.6292/7809.7 = \left(\frac{1}{T_b^*} - 1.9992 \times 10^{-3} \text{ K}^{-1}\right) \quad T_b^* = 521.1 \text{ K} = 247.9^\circ\text{C}$$

8. For methanol, the enthalpy of fusion is 3.215 kJ mol⁻¹ and the volume change on melting is 2.75 mL mol⁻¹ at the standard melting point of 175.59 K.¹ The enthalpy of vaporization is 35.21 kJ mol⁻¹ at the standard boiling point of 337.8 K. Estimate the triple point temperature and pressure for methanol. Assume constant transition enthalpies over the temperature range. [Hint: you may use the Goal Seek option in Excel.]

Answer: The triple point is at the intersection of the melting curve and the vapor pressure curve. The plan is to find the temperature that gives the same equilibrium phase transition pressures for melting and vaporization. The Clausius-Clapeyron equation, Eq. 17.1.14°, is used to find the vapor pressure at the given temperature. Eq. 17.1.24 is used to find the pressure necessary for the melting temperature to equal the given temperature.

Note that P° = 1.00 bar = 1.000 × 10⁵ Pa with the corresponding standard melting point, T_m[°], and standard boiling point T_b[°]. The change in melting point is then:

$$\Delta T = \frac{T_m^\circ \Delta_{\text{fus}}V_i}{\Delta_{\text{fus}}H_i} \Delta P \quad \text{or} \quad P = P^\circ + (T - T_m^\circ)/\mathcal{K} \quad 1$$

with the constant \mathcal{K} given by:

$$\mathcal{K} = \frac{T_m^\circ \Delta_{\text{fus}}V_i}{\Delta_{\text{fus}}H_i} = \frac{175.59 \text{ K} (2.75 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1})}{3.215 \times 10^3 \text{ J mol}^{-1}} = 1.502 \times 10^{-7} \text{ K Pa}^{-1} \quad 2$$

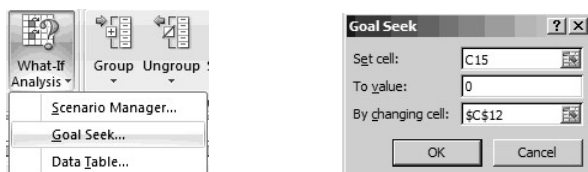
The Clausius-Clapeyron equation, with the reference pressure at P°, is given by Eq. 17.1.14°:

$$P = P^\circ e^{-\frac{\Delta_{\text{tr}}H_i}{R}\left(\frac{1}{T} - \frac{1}{T_b^\circ}\right)} = 1 \times 10^5 \text{ Pa} e^{-\frac{35.31 \times 10^3 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}}\left(\frac{1}{T} - \frac{1}{337.8 \text{ K}}\right)} \quad 3$$

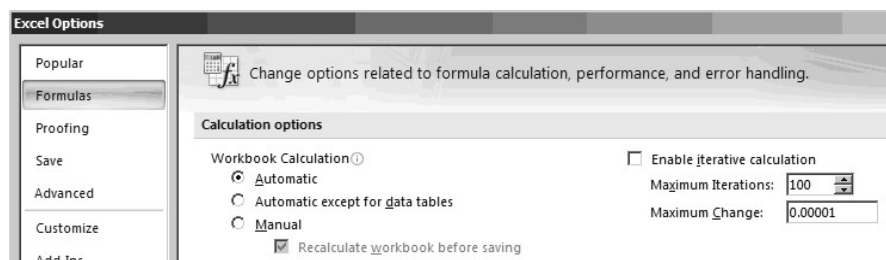
A spreadsheet was written to do these two calculations at a variable input temperature (in cell C12). This temperature was changed until the calculated vapor pressure and equilibrium melting pressure were equal.

A1	B	C	D	E
2				
3	$\Delta_{\text{fus}}H$	3.215	kJ mol ⁻¹	
4	$\Delta_{\text{fus}}V$	2.75	mL mol ⁻¹	
5	T_{melt}°	175.59	K	
6	\mathcal{K}	1.50194E-07	K Pa ⁻¹	
7				
8	$\Delta_{\text{vap}}H$	35.21	kJ mol ⁻¹	
9	T_b°	337.8	K	
10	R	8.3145	J K ⁻¹ mol ⁻¹	
11				
12	T	175.5749808	K	← change this value
13	P_{melt}	0.93221509	Pa	
14	P_{vap}	0.932215156	Pa	
15	ΔP	-6.6131E-08	Pa	← to get a small pressure difference

The equation for the melting constant, \mathcal{K} , in cell C6 is “=C5*C4*1E-6/(C3*1000)”. In cell C13 is Eq. 1 for the equilibrium melting pressure: “=1E5+(C12-C5)/C6”. In cell C14 is Eq. 3 for the vapor pressure: “=1E5*exp(-C8*1000/C10*(1/C12-1/C9))”. The search for the triple point can be easily implemented using the Goal Seek option. The Goal Seek option is accessed from the Data tab and “What If Analysis”:



The Goal Seek option uses linear iteration to find the best value. You must be careful, however, to ensure that the calculation has converged. The convergence criteria are given in the Excel options window, which is accessed by clicking on the “Office button”. For this calculation, the maximum change was decreased from the default value of 0.001 to a more precise setting of 0.00001, as shown below:



The final result is at 0.923 Pa and 175.57 K, only slightly less than the standard melting point. The literature value for the triple point is 175.5 K. The triple point is only slightly different than the standard melting point because the P vs. T curve for the melting transition is very steep. That is, the curve has a large slope of $1/\mathcal{K} = 6.7 \times 10^6$ Pa K⁻¹ resulting in small melting point changes even for large changes in pressure.

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9. The sublimation pressure versus temperature of ammonia is $\ln P = 23.03 - 3754./T$. The vapor pressure of liquid ammonia is $\ln P = 19.49 - 3063./T$. (a) Find the enthalpy of sublimation and the enthalpy of vaporization. (b). Calculate the triple point for ammonia. (c). Find the enthalpy of fusion at the triple point.²

Answer: (a). The Clausius-Clapeyron equation, Eq. 17.1.16°, is:

$$\ln P = -\Delta_{tr}H_i/R (1/T) + b.$$

giving for sublimation: $-\Delta_{sub}H_i/R = -3754.$ or $\Delta_{sub}H_i = 31.21 \text{ kJ mol}^{-1}$

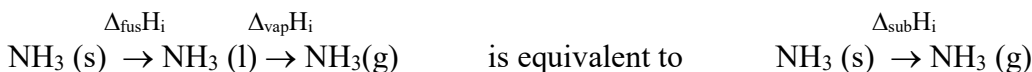
and for vaporization: $-\Delta_{vap}H_i/R = -3063.$ or $\Delta_{vap}H_i = 25.47 \text{ kJ mol}^{-1}$

(b). At the triple point solid, liquid, and vapor are in equilibrium. The sublimation pressure and the vapor pressure of the liquid are equal:

$$\begin{aligned} 23.03 - 3754./T_{tp} &= 19.49 - 3063./T_{tp} \\ 3.54 &= 691./T_{tp} \end{aligned}$$

Solving for the triple point gives: $T_{tp} = 195. \text{ K}$.

(c). At the triple point the solid, liquid, and vapor are in equilibrium. The enthalpies of the phase transitions are state functions and independent of the path:



giving: $\Delta_{sub}H_i = \Delta_{fus}H_i + \Delta_{vap}H_i$

$$31.21 \text{ kJ mol}^{-1} = \Delta_{fus}H_i + 25.47 \text{ kJ mol}^{-1}$$

$$\Delta_{fus}H_i = 31.21 \text{ kJ mol}^{-1} - 25.47 \text{ kJ mol}^{-1} = 5.74 \text{ kJ mol}^{-1} \quad \text{at } 195. \text{ K}$$

10. Integrate the differential form of the Clausius-Clapeyron equation:

$$d \ln P = \frac{\Delta_{tr}H_i}{RT^2} dT$$

from an initial temperature of T_o to a final temperature of T . In this equation T is the equilibrium phase transition temperature at the given pressure. Assume the phase transition has a molar enthalpy change given by:

$$\Delta_{tr}H_{i,T} = \Delta_{tr}H_{i,T_o} + \Delta_{tr}C_{p,i} (T - T_o)$$

where $\Delta_{tr}C_{p,m}$ is the change in heat capacity for the phase transition, which is assumed to be a constant. Show that the result is:

$$\ln\left(\frac{P}{P_o}\right) = -\frac{\Delta_{tr}H_{i,T_o}}{R} \left(\frac{1}{T} - \frac{1}{T_o}\right) + \frac{\Delta_{tr}C_{p,i}}{R} \ln\left(\frac{T}{T_o}\right) + \frac{\Delta_{tr}C_{p,i}T_o}{R} \left(\frac{1}{T} - \frac{1}{T_o}\right)$$

Answer: Substituting the temperature dependent enthalpy change into the Clausius-Clapeyron equation gives:

$$d \ln P = \frac{\Delta_{tr}H_{i,T_0}}{RT^2} dT + \frac{\Delta_{tr}C_{p,i}}{RT} dT - \frac{\Delta_{tr}C_{p,i}T_0}{RT^2} dT$$

Applying the integration limits:

$$\int_{T_0}^T d \ln P = \int_{T_0}^T \frac{\Delta_{tr}H_{i,T_0}}{RT^2} dT + \int_{T_0}^T \frac{\Delta_{tr}C_{p,i}}{RT} dT - \int_{T_0}^T \frac{\Delta_{tr}C_{p,i}T_0}{RT^2} dT$$

Factoring out the constants gives:

$$\ln\left(\frac{P}{P_0}\right) = \frac{\Delta_{tr}H_{i,T_0}}{R} \int_{T_0}^T \frac{1}{T^2} dT + \frac{\Delta_{tr}C_{p,i}}{R} \int_{T_0}^T \frac{1}{T} dT - \frac{\Delta_{tr}C_{p,i}T_0}{R} \int_{T_0}^T \frac{1}{T^2} dT$$

The integrals are then:

$$\ln\left(\frac{P}{P_0}\right) = -\frac{\Delta_{tr}H_{i,T_0}}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right) + \frac{\Delta_{tr}C_{p,i}}{R} \ln\left(\frac{T}{T_0}\right) + \frac{\Delta_{tr}C_{p,i}T_0}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right)$$

Note that the first and last terms may be combined:

$$\ln\left(\frac{P}{P_0}\right) = -\frac{(\Delta_{tr}H_{i,T_0} - T_0 \Delta_{tr}C_{p,i})}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right) + \frac{\Delta_{tr}C_{p,i}}{R} \ln\left(\frac{T}{T_0}\right)$$

Grouping all the terms in P_0 and T_0 together into a constant, a , gives:

$$\ln P = a - \frac{b}{T} - c \ln T$$

where $b = (\Delta_{tr}H_{i,T_0} - T_0 \Delta_{tr}C_{p,m})/R$ and $c = -\Delta_{tr}C_{p,i}/R$. Reference handbooks sometimes list the vapor pressure of liquids in this form.

11. Reference handbooks sometimes list the vapor pressure of liquids in the form:

$$\ln P = A - \frac{B}{T} - C \ln T + D T$$

Show that the result from the last problem can be rewritten in this form. Use *General Pattern 4: Exponential Temperature Dependence* as a guide.

Answer: Note that taking a common denominator in the temperature dependent portion of the last term from Problem 6 and approximating $TT_0 \approx T_0^2$ gives:

$$\frac{\Delta_{tr}C_{p,m}T_0}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right) = \frac{\Delta_{tr}C_{p,m}T_0}{R} \left(\frac{T_0 - T}{TT_0}\right) \approx \frac{\Delta_{tr}C_{p,m}T_0}{R} \left(\frac{T_0 - T}{T_0^2}\right) \approx -\frac{\Delta_{tr}C_{p,m}}{RT_0} (T - T_0)$$

The last term from Problem 6 can then be rewritten as:

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$$\ln\left(\frac{P}{P_0}\right) = -\frac{\Delta_{\text{tr}}H_{\text{m},T_0}}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right) + \frac{\Delta_{\text{tr}}C_{\text{p},\text{m}}}{R}\ln\left(\frac{T}{T_0}\right) - \frac{\Delta_{\text{tr}}C_{\text{p},\text{m}}}{RT_0}(T - T_0)$$

Grouping all the terms in P_0 and T_0 together into a constant A gives:

$$\ln P = A - \frac{\Delta_{\text{tr}}H_{\text{m},T_0}}{RT} + \frac{\Delta_{\text{tr}}C_{\text{p},\text{m}}}{R}\ln T - \frac{\Delta_{\text{tr}}C_{\text{p},\text{m}}}{RT_0}T$$

Comparing the reference handbook form with this last equation gives:

$$\ln P = A - \frac{B}{T} - C \ln T + D T$$

Comparison shows that $B = \frac{\Delta_{\text{tr}}H_{\text{m},T_0}}{R}$, $C = -\frac{\Delta_{\text{tr}}C_{\text{p},\text{m}}}{R}$, and $D = -\frac{\Delta_{\text{tr}}C_{\text{p},\text{m}}}{RT_0}$

12. Long's Peak in the Colorado Rocky Mountains is 3962. m high. What is the boiling point of water at this altitude? Assume a constant temperature of 20.0°C (see Problem 1.15) and the pressure at sea level is 1.00 atm. The enthalpy of vaporization of water is 42.00 kJ mol⁻¹.

Answer: Assuming the atmospheric pressure at sea level is 1 atm and the mole fraction averaged molar mass of air is 28.8 g mol⁻¹ gives the barometric formula as:

$$\left(\frac{-\mathcal{M}_{\text{gas}} g h}{RT}\right) = \frac{-28.8 \times 10^{-3} \text{ kg}(9.807 \text{ m s}^{-2})(3962. \text{ m})}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1}(293.15 \text{ K})} = -0.4591$$

$$P = P_0 e^{\left(\frac{-\mathcal{M}_{\text{gas}} g h}{RT}\right)} = 1.00 \text{ atm } e^{-0.4591} = 0.632 \text{ atm}$$

The enthalpy of vaporization of water at 100°C is $\Delta_{\text{vap}}H^\circ = 42.00 \text{ kJ mol}^{-1}$. The boiling point is the temperature that gives the vapor pressure equal to the ambient pressure. Applying the Clausius-Clapeyron equation from 100.0°C and 1.00 atm to a final pressure of 0.632 atm:

$$\ln\left(\frac{0.632}{1.00}\right) = -\frac{4.200 \times 10^4 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}}\left(\frac{1}{T_b^*} - \frac{1}{373.2 \text{ K}}\right)$$

$$0.4589/5051.4 = \left(\frac{1}{T_b^*} - 2.6799 \times 10^{-3} \text{ K}^{-1}\right) \quad T_b^* = 360.9 \text{ K} = 87.8^\circ\text{C}$$

13. For non-ideal gases, from Eq. 7.5.2, $PV = z nRT$. Find the corresponding integrated form of the Clausius-Clapeyron equation for liquid-vapor or solid-vapor equilibrium. In other words, correct Eq. 17.1.13° for vapor non-ideality. Assume z and $\Delta_{\text{tr}}H_{\text{m}}$ are constant over the temperature range for the integration.

Answer: For non-ideal gases, from Eq. 7.5.2, $PV = z nRT$ and Eq. 17.1.9° is corrected to give:

$$\Delta_{tr}V_m \approx V_m(\text{vapor}) = \frac{zRT}{P} \quad (\text{equilibrium}) \quad 1$$

Substituting this last relationship into the Clapeyron equation gives:

$$\frac{dP}{dT} = \frac{\Delta_{tr}H_m P}{zRT^2} \quad (\text{equilibrium}) \quad 2$$

Separating variables gives:

$$\frac{dP}{P} = \frac{\Delta_{tr}H_m}{zRT^2} dT \quad (\text{equilibrium}) \quad 3$$

Integrating Eq. 3 assuming both $\Delta_{tr}H_m$ and z are constant over the temperature range:

$$\ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta_{tr}H_m}{zR} \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad (\text{equilibrium, cst. } z \text{ \& } \Delta_{tr}H_m) \quad 4$$

or alternatively, a plot of $\ln P$ versus $1/T$ gives a straight line with slope $-\Delta_{tr}H_m/(zR)$.

14. Calculate the vapor pressure of methanol at 20.0°C under a total ambient pressure of 10.0 bar of air. The vapor pressure of methanol at 20.00°C is 0.1530 bar, under its own vapor pressure.

Answer: The plan is to use Eq. 17.1.31° to determine the vapor pressure under the ambient conditions.

The molar volume of pure liquid methanol is $V_{MeOH} = \mathcal{V}/d = 32.04 \text{ g mol}^{-1}/0.791 \text{ g mL}^{-1} = 40.51 \text{ mL mol}^{-1} = 4.051 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$.

$$\ln \frac{P_{\beta,2}}{P_{\beta,1}} = \frac{V_i(\alpha)}{RT} (P_2 - P_1)$$

$$\ln \frac{P_{\beta,2}}{0.1530 \text{ bar}} = \frac{4.051 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1} (293.15 \text{ K})} (10.0 \text{ bar} - 0.1530 \text{ bar}) (1 \times 10^5 \text{ Pa} / 1 \text{ bar})$$

$$= 0.01637$$

$$P_{\beta,2} = 0.1555 \text{ bar}$$

In torr the new pressure is 116.7 torr and the vapor pressure under pure vapor is 114.8 torr, which is roughly a 2% difference.

15. Particulates released from volcanic eruptions can be a significant source of heavy metals in the environment. The magma under a volcano is at high temperature and total pressure. Under these circumstances, normally non-volatile substances can have a significant vapor pressure. NaCl and heavy metal chlorides are found in the vapor phase at high total pressure as volatile molecular species. The concentration of Pb in the minerals formed from the vapor phase in a volcano is much higher than in the original magma. At high pressure, the vapor above a magma is non-ideal and the fugacity must be used. Eq. 17.1.30 assumes the vapor behaves as an ideal gas. Let $P_{\beta,o}$ be the vapor pressure of the pure liquid under its pure vapor pressure. Assume the

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pure vapor pressure at the given temperature is sufficiently small that the pure vapor is ideal, giving $f_{\beta,o} = P_{\beta,o}$. Show that the fugacity of the vapor, f_{β} , in equilibrium with the pure liquid at the elevated total pressure, P , is then:

$$\ln \frac{f_{\beta}}{P_{\beta,o}} = \frac{V_i(\alpha)}{RT} (P - P_{\beta,o})$$

Answer: The plan is to repeat the derivation of Eqs. 17.1.24-17.1.29°, but with the partial vapor pressure replaced by the fugacity, $\mu_i(g) = \mu_i^{\circ}(g) + RT \ln f_{\beta}/P^{\circ}$.

Consider the partial vapor pressure of a substance, P_{β} , with a total applied pressure of P . At constant temperature, from Eq. 17.1.26:

$$V_i(\alpha) dP = d\mu_i(\beta, P', T) \quad (\text{equilibrium, cst. T}) \quad (17.1.26)$$

The chemical potential of the real vapor is dependent on the fugacity of the vapor above the liquid, Eq. 16.6.20°:

$$\mu_i(g) = \mu_i^{\circ}(g) + RT \ln f_{\beta}/P^{\circ} \quad 1$$

The change in chemical potential is given as:

$$d\mu_i(g) = RT d \ln f_{\beta} \quad 2$$

Substitution of this last equation into Eq. 17.1.26 gives the dependence of the fugacity on applied pressure:

$$RT d \ln f_{\beta} = V_i(\alpha) dP \quad (\text{equilibrium, cst. T}) \quad 3$$

Integration of this last equation from the initial vapor fugacity $f_{\beta,1}$ and applied pressure P_1 to the final vapor fugacity $f_{\beta,2}$ and applied pressure P_2 , assuming that the molar volume of the liquid is constant, gives:

$$\ln \frac{f_{\beta,2}}{f_{\beta,1}} = \frac{V_i(\alpha)}{RT} (P_2 - P_1) \quad (\text{equilibrium, cst. T}) \quad 4$$

Let P_1 be the vapor pressure of the liquid under its pure vapor pressure, $P_1 = P_{\beta,o}$. Assume the pure vapor pressure at the given temperature is sufficiently small that the pure vapor is essentially ideal, then $f_{\beta,o} = P_{\beta,o}$. The fugacity of the vapor, f_{β} , at the elevated total pressure, P , is then:

$$\ln \frac{f_{\beta}}{P_{\beta,o}} = \frac{V_i(\alpha)}{RT} (P - P_{\beta,o}) \quad (\text{equilibrium, } P_{\beta,o} \text{ small, cst. T}) \quad 5$$

The vapor phase above magmas is composed primarily of water vapor and CO_2 . Water at high temperature, and especially above the critical point, is much less polar than at room temperature. The decreased polarity of water decreases the degree of dissociation of electrolytes. The interaction of NaCl and heavy metal molecular chlorides with water vapor is strong, which gives small fugacity coefficients. The fugacity is given by $f_{\beta} = \gamma_{\beta} P_{\beta}$. However, Eq. 5 fixes the value of the fugacity, so that a small fugacity coefficient increases the partial vapor pressure: $P_{\beta} = f_{\beta}/\gamma_{\beta}$. The partial vapor pressure above the liquid is increased by both the increase in total

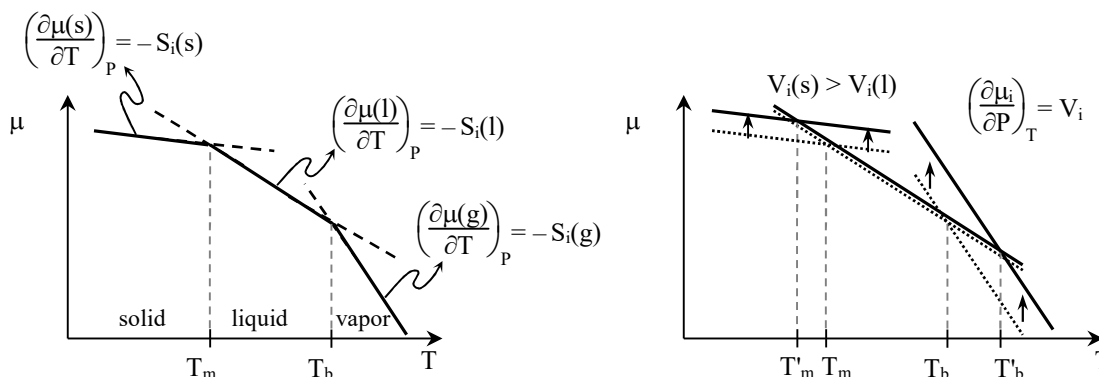
pressure and favorable interactions with the other vapor phase components. Lead is considered a “volatile” element by volcanologists.

16. Redraw Figure 17.1.1 for water.

Answer: The slope of the chemical potential versus temperature at constant pressure is the negative of the entropy for each individual phase. So Figure 17.1.1a is qualitatively correct for water. An increase in pressure increases the chemical potential of each phase, proportional to the pure molar volume of the phase, through the molar thermodynamic force:

$$\left(\frac{\partial \mu_i}{\partial P}\right)_T = V_i$$

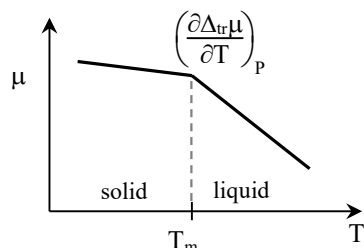
For water, $V_{\text{H}_2\text{O}(s)} > V_{\text{H}_2\text{O}(l)}$, because of the open structure caused by the extensive network of hydrogen bonds in the solid. The increase in chemical potential for solid water is greater than for liquid water. The melting and boiling points are at the intersections of the new chemical potential curves. The result is a decrease in melting point and an increase in boiling point.



17. Some property needs to be discontinuous to observe a phase transition. What property is discontinuous in a pure Ehrenfest second-order phase transition?

Answer: The heat capacity curve as a function of temperature is discontinuous for a second-order phase transition. For a first-order phase transition, the entropy as a function of temperature is discontinuous.

18. Find the difference in slope across the melting transition for the chemical potential versus temperature curve, $(\partial \Delta_{\text{tr}} \mu / \partial T)_P$, at standard pressure.



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Answer: The plan is to use Eq. 17.2.3 and reference tabulations.

Rearranging Eq. 17.2.3 to find the difference in slope across the phase transition gives:

$$\left(\frac{\partial \Delta_{tr}\mu}{\partial T}\right)_P = -\Delta_{tr}S_i$$

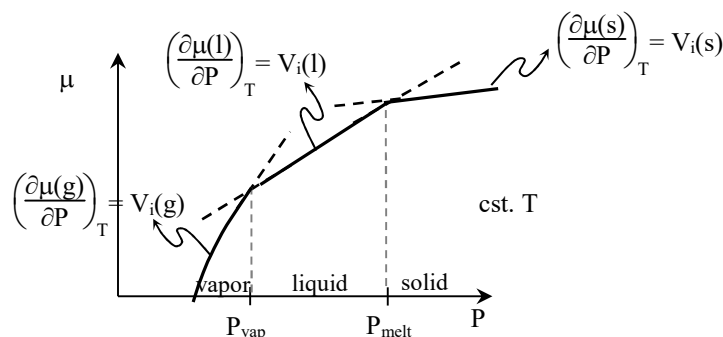
The standard transition temperature is 273.15 K for water, where $\Delta_{tr}S_{H_2O} = S_{H_2O}^{\circ}(l) - S_{H_2O}^{\circ}(s) = 22.00 \text{ J K}^{-1} \text{ mol}^{-1}$ and the corresponding difference in slope is $-22.00 \text{ J K}^{-1} \text{ mol}^{-1}$. Liquid water has higher entropy than solid water and then a more negative slope.

19. Draw the chemical potential versus pressure curves for the solid, liquid, and vapor phases of a pure substance, at constant temperature. Assume that $V_i(s) < V_i(l)$. Describe the process that occurs at the intersection of the chemical potential curves.

Answer: The slope of the chemical potential versus pressure is given by the molar thermodynamic force:

$$\left(\frac{\partial \mu_i}{\partial P}\right)_T = V_i$$

The chemical potential of a substance increases with pressure. The assumption that $V_i(s) < V_i(l)$, which corresponds to a “normal” substance, shows that the slope of the liquid curve is greater than the solid. The solid phase is the stable phase at high pressure:



Starting at low pressure, as the pressure is increased, when the pressure exceeds the equilibrium vapor pressure at the chosen temperature, the liquid phase is more stable. The chosen constant temperature is the equilibrium melting point at a specific pressure, P_{melt} . When the pressure exceeds P_{melt} , the solid phase is the stable phase. The intersection of the vapor and liquid curves is the equilibrium boiling point at applied pressure P_{vap} . The intersection of the liquid and solid curves is the equilibrium melting point at applied pressure P_{melt} .

20. (a). Sketch the chemical potential curves versus temperature for the solid, liquid, and vapor phases of substance at a constant pressure below the triple point and (b) for a substance at the triple point pressure.

Answer: The plan is to redraw Figure 17.1.1a for (a) the direct transition from the solid to the vapor phase with no intersection with the liquid line, and (b) for a system where the chemical potential of all three phases is equal at the triple point temperature, T_{tp} .

The slope of the chemical potential versus temperature at constant pressure is the negative of the entropy for each individual phase. So the slopes in Figure 17.1.1a are qualitatively correct. However, for pressures below the triple point pressure, the chemical potential of the liquid phase must be higher than either the solid or the vapor throughout the temperature range, otherwise the liquid phase will form. The equilibrium sublimation temperature, T_{sub} , and triple points are at the intersections of the new chemical potential curves, Figure P17.1.

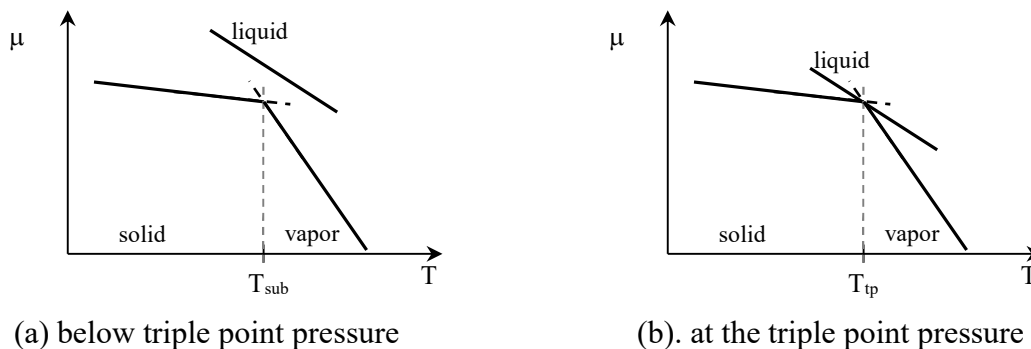


Figure P17.1: The chemical potential versus temperature for a substance (a). below the triple point pressure, and (b). at the triple point pressure.

21. If first-order phase transitions are “completely cooperative,” how can two-phase systems exist at equilibrium? For example, how can ice and liquid water coexist at equilibrium at the equilibrium phase transition temperature?

Answer: First-order phase transitions are completely cooperative. The molecules cooperate with each other in gaining new motional freedom; when one molecule gains motional energy then other nearby molecules find it easier to add motional energy. The motions of the molecules are correlated throughout the phase at the phase transition temperature. However, first-order phase transitions have a finite enthalpy for the phase transition (or so-called latent heat). Energy transfer from the surroundings is necessary for the phase transition to occur. Thermal energy is the “limiting reagent” for the phase transition. Once energy is transferred into the two-phase system from the surroundings, additional molecules can make the phase transition, without an increase in temperature. In a first-order phase transition, all the molecules undergo the phase transition together, subject only to the availability of thermal energy.

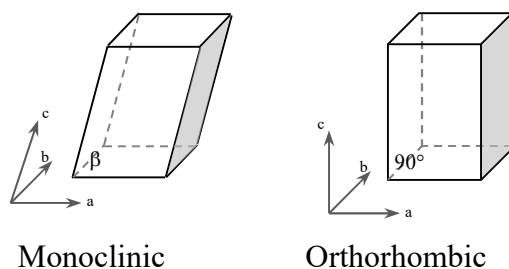
22. Use the concept of correlation length and domain size to explain why the heat capacity of a substance increases as the temperature increases to the critical point.

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Answer: The plan is to note that thermally activating motional degrees of freedom increases the heat capacity of a substance.

As the temperature increases near the critical point, the correlation length of the intermolecular cooperation increases. As the correlation length increases, the domain size increases, which increases the fraction of the substance in the more mobile, higher entropy phase. The increase in motion corresponds to activating motional degrees of freedom, for example segmental torsions in the fatty acid chains in a phospholipid. The larger fraction of molecules in the more mobile domains increases the heat capacity of the sample.

23. The monoclinic and orthorhombic unit cells are illustrated, below. The unit cell lengths for both unit cells are all different, $a \neq b \neq c$. The orthorhombic unit cell has all 90° angles between the unit cell directions, $\alpha = \beta = \gamma = 90^\circ$. The monoclinic unit cell has one angle not equal to 90° , $\alpha = \gamma = 90^\circ$, β .



Methanol crystallizes into long hydrogen-bonded chains. There are two crystalline forms. Crystal II has a monoclinic unit cell and is the low temperature form. Crystal I has an orthorhombic unit cell and is the high temperature form. The difference is a small displacement of the hydrogen-bonded chains in the direction perpendicular to the direction of the chains. The solid-solid phase transition temperature is 157.4 K at 1 atm. The transition was reported to be second-order. Carlson and Westrum redetermined the heat capacity of very pure methanol samples to determine the thermodynamic parameters for the phase transition, Figure P17.1.¹ Crystal I readily super-cools, so heat capacity data for this phase is available below the equilibrium phase transition temperature. Is the transition first or second order?

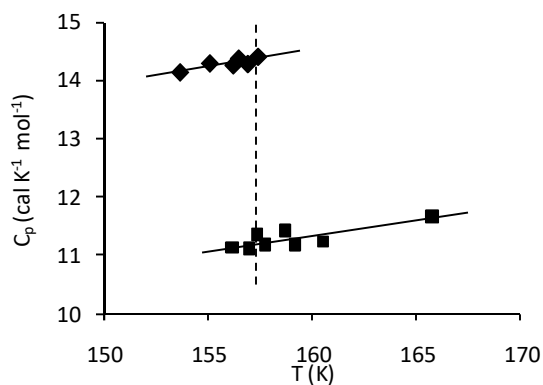
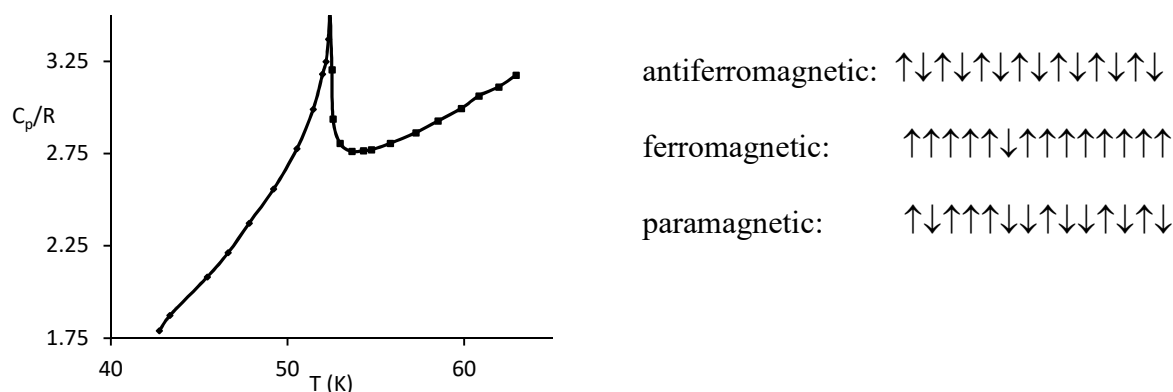


Figure P17.1: Heat capacity data for 99.98 mol% methanol near the solid-solid phase transition at 157.4 K.

Answer: The heat capacity is discontinuous and slowly varying at temperatures less than and greater than the solid-solid phase transition temperature. In other words, there are no pre-transition effects. The transition is first-order.

24. NiCl_2 has a solid-state magnetic phase transition at 52 K. The low temperature phase is antiferromagnetic, and the high temperature phase is paramagnetic. Antiferromagnetic phases are an ordered lattice of unpaired electrons that alternate spin-up and spin-down. In the absence of an external magnetic field, paramagnetic phases also have an equal, or nearly equal, number of electrons spin-up and spin-down, distributed at random. The paramagnetic phase is at higher entropy at a given finite temperature. A plot of the heat capacity as a function of temperature is shown below.³ Characterize this solid-state phase transition.



Answer: The transition is lambda-type, second-order. Extensive pre-transition effects are seen approaching the critical temperature from both the high and low temperature side of the transition. Experimental uncertainty prevents the determination of the heat capacity at the critical temperature. Therefore, it is usually impossible to determine if the heat capacity is finite or if the heat capacity diverges to infinity at the critical temperature. Refrigerator magnets are ferromagnetic. The degree of ordering for ferro- and antiferromagnetic substances decreases with increasing temperature. Increasing the temperature provides thermal energy that increases the probability of a spin flip that decreases the order compared to the perfect zero-Kelvin phase.

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2. F. C. Andrews, *Thermodynamics: Principles and Applications*, Wiley-Interscience, New York, NY, 1971. Problem 25.13.

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3. R. H. Busey, W. F. Giaque, "The Heat Capacity of Anhydrous NiCl_2 from 15 to 300 K. The Antiferromagnetic Anomaly near 52 K. Entropy and Free Energy," *J. Am. Chem. Soc.*, **1953**, 75, 4443.