Announcement

• Exam 2 this Friday. Please be well prepared!

• HW average 80-85.
• You will probably have one drop for the home work. So don’t worry if you did not do very well in one HW.
How does $\mu$ in three phases depend on $T$?

$$d\mu(T, P) = -S_m dT + V_m dP = -S_m dT$$

$$0 < S_{m, \text{solid}}(T) < S_{m, \text{liquid}}(T) < S_{m, \text{gas}}(T)$$

Assuming $S_m$ is constant,

$$\mu(T, P) = \mu(0, P) - S_m T$$

Q1. Where is the melting point?

Q2. Which line represents $\mu_{\text{solid}}(T)$?

Q3. How do you explain the phase transition from solid to liquid using the figure?

$\mu(T)$ plot when $P$ is increased
- How are $T_m$ and $T_b$ affected by $P$?

$$\mu(T, P + \Delta P) = \{\mu(0, P) + V_m \Delta P\} - S_m T$$

$V_m \text{ Gas} > [\text{Q1}]$

Figure: 07-02
7.2 The Pressure-Temperature Phase Diagram

L-G coexists above critical point
\((T \geq T_c, P \geq P_c)\)

**Isobar T Increases**

a) \(S \rightarrow L \rightarrow G\)
(P higher than triple point Pressure)
b) \(S \rightarrow G\)
(P lower than triple point P)

**Isotherm; P Increases**
c) \(G \rightarrow L \rightarrow S\)
(T higher than triple point T)

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**P-T Phase Diagram \(V_{m}^{\text{Solid}} < V_{m}^{\text{Liquid}}\)**

What is the difference from the previous graph for \(V_{m}^{\text{Solid}} < V_{m}^{\text{Liquid}}\)?

**Isobar T Increases**

c) \(G \rightarrow S \rightarrow L\)

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Water

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Figure: 07-04
P7.3) Within what range can you restrict the values of $P$ and $T$ if the following information is known about CO$_2$? Use Figure 7.8 to answer this problem.

a. As the temperature is increased, the solid is first converted to the liquid and subsequently to the gaseous state.

b. As the pressure on a cylinder containing pure CO$_2$ is increased from 65 to 80 atm, no interface delineating liquid and gaseous phases is observed.

c. Solid, liquid, and gas phases coexist at equilibrium.

a. $5.11 \text{ atm} < P < 73.75 \text{ atm}$

7.4 Providing a Theoretical Basis for the P-T Phase Diagram

When two phase $\alpha$ and $\beta$ are in equilibrium at a constant $P$ and $T$,

$$\mu_\alpha(P, T) = \mu_\beta(P, T)$$

When $(P, T)$ is changed by $(dP, dT)$ while keeping the equilibrium,

$$\mu_\alpha(P, T) + d\mu_\alpha = \mu_\beta(P, T) + d\mu_\beta$$

Thus,

$$d\mu_\alpha = d\mu_\beta$$

$$\rightarrow -S_{m_\alpha}dT + V_{m_\alpha}dP = -S_{m_\beta}dT + V_{m_\beta}dP$$

$$\rightarrow 0 = (S_{m_\beta} - S_{m_\alpha})dT - (V_{m_\beta} - V_{m_\alpha})dP = \Delta S_m dT - \Delta V_m dP$$

Clapeyron equation

$$\frac{dP}{dT} = \frac{\Delta S_m}{\Delta V_m}$$
\( \frac{dP}{dT} \) for fusion and vaporization

**For Fusion**

\[
\left( \frac{dP}{dT} \right)_{\text{fusion}} = \frac{\Delta S_{\text{fusion}}}{\Delta V_{\text{fusion}}} \approx 22 \text{ Jmol}^{-1} \text{K}^{-1}
\]

\[
= \pm 5.5 \times 10^6 \text{ PaK}^{-1} = \pm 55 \text{ bar K}^{-1}
\]

\( (dT/dP)_{\text{fusion}} \approx 0.05 \text{ K bar}^{-1} \) Negative sign only for H\(_2\)O

**For Vaporization**

\[
\left( \frac{dP}{dT} \right)_{\text{vap}} = \frac{\Delta S_{\text{vap}}}{\Delta V_{\text{vap}}} \approx 95 \text{ Jmol}^{-1} \text{K}^{-1}
\]

\[
= 5.0 \times 10^3 \text{ PaK}^{-1} = 5 \times 10^{-2} \text{ bar K}^{-1}
\]

\( (dT/dP)_{\text{vap}} \approx 20 \text{ K bar}^{-1} \)
7.5 Using the Clapeyron Equation to Calculate Vapor Pressure as a Function of $T$

**For Vaporization**

\[
\left(\frac{dP}{dT}\right)_{vap} = \frac{\Delta S^\text{vap}}{\Delta V^\text{vap}} = \frac{\Delta H^\text{vap}}{\Delta V^\text{vap}T} = \frac{\Delta H^\text{vap}}{V^\text{gas}T} = \frac{P\Delta H^\text{vap}}{RT^2}
\]

\[
\frac{1}{P} dP = \frac{\Delta H^\text{vap}}{nR} \frac{1}{T^2} dT
\]

**Clausius-Clapeyron equation**

\[
\int_{P_\text{ini}}^{P_\text{fin}} \frac{1}{P} dP = \int_{T_\text{ini}}^{T_\text{fin}} \frac{\Delta H^\text{vap}}{R} \frac{1}{T^2} dT
\]

\[
\ln\left(\frac{P_\text{fin}}{P_\text{ini}}\right) = -\frac{\Delta H^\text{vap}}{R} \left(\frac{1}{T_\text{fin}} - \frac{1}{T_\text{ini}}\right)
\]

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- HW 8 P7.5) The vapor pressure of liquid SO\textsubscript{2} is 2232 Pa at 201 K, and $\Delta H^\text{vaporization} = 24.94 \text{ kJ mol}^{-1}$. Calculate the normal and standard boiling points. Does your result for the normal boiling point agree with that in Table 7.1? If not, suggest a possible cause.

Q. Which equation should we use?

\[
\ln\left(\frac{P_\text{fin}}{P_\text{ini}}\right) = [Q1]
\]

$T_{\text{ini}} = 201 \text{ K}$  $P_{\text{ini}} = 2232 \text{ Pa}$

- For normal BP, $P_{\text{fin}} = [Q2]$
- For standard BP, $P_{\text{fin}} = [Q3]$
• HW 8 P7.6) For water, $\Delta H_{\text{vaporization}}$ is 40.65 kJ mol$^{-1}$, and the normal boiling point is 373.15 K. Calculate the boiling point for water on the top of a mountain of height 5500 m, where the normal barometric pressure is 380 Torr.

$$\ln \frac{P_{\text{fin}}}{P_{\text{ini}}} = - \frac{\Delta H_{\text{vap}}}{R} \left( \frac{1}{T_{\text{fin}}} - \frac{1}{T_{\text{ini}}} \right)$$

$P_{\text{ini}} = 1$ atm & $T_{\text{ini}} = 373.15$ K

Review Q. How much is $\Delta S_{\text{vap}}$ at normal BP?

$\Delta S_{\text{vap}} = [Q1]$

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Review Q

• HW 8 P7.7) Use the values for $\Delta G_f$(ethanol, l) and $\Delta G_f$(ethanol, g) from Appendix B to calculate the vapor pressure of ethanol at 298.15 K.

For the transformation $\text{C}_2\text{H}_5\text{OH}$ (l) $\rightarrow$ $\text{C}_2\text{H}_5\text{OH}$ (g), what is $K_p$?

$K_p = [Q1]$

$K_p = \exp(-[Q2])$
7.5 Using the Clapeyron Equation to Calculate Vapor Pressure as a Function of $T$

For Fusion

$$
\int_{P_i}^{P_f} dP = \int_{T_i}^{T_f} \frac{\Delta S_m^{\text{fusion}}}{\Delta V_m^{\text{fusion}}} dT = \int_{T_i}^{T_f} \frac{\Delta H_m^{\text{fusion}}}{\Delta V_m^{\text{fusion}}} \frac{dT}{T} \sim \int_{T_i}^{T_f} \frac{\Delta H_m^{\text{fusion}}}{\Delta V_m^{\text{fusion}}} \frac{dT}{T}
$$

$$
P_f - P_i \sim \frac{\Delta H_m^{\text{fusion}}}{\Delta V_m^{\text{fusion}}} \ln \frac{T_{\text{fin}}}{T_{\text{ini}}} \sim \frac{\Delta H_m^{\text{fusion}}}{\Delta V_m^{\text{fusion}}} \frac{\Delta T}{T_{\text{ini}}}
$$

when $|\Delta T| << T_{\text{ini}}$

7.10 Conformational Transitions of Biological Polymers

$$
N \leftrightarrow D
$$

$$
\Delta G_{\text{den}} = \Delta H_{\text{den}} - T \Delta S_{\text{den}}
$$

$\Delta H_{\text{den}} > 0 \Rightarrow$ At lower $T$, $N$ is stable

$\Delta S_{\text{den}} > 0 \Rightarrow$ At higher $T$, $D$ is stable

At $T_m \Rightarrow K = 1$ & $f_D = 0.5$
7.10 Conformational Transitions of Biological Polymers

\[ N \leftrightarrow D \]

\[ K = \frac{C_D}{C_N} = \frac{f_D C}{f_N C} = \frac{f_D}{1 - f_D} \]

At \( T_m \rightarrow K = 1 \) & \( f_D = 0.5 \)

**Table 7.7** Thermodynamic Parameters for Protein Denaturation

<table>
<thead>
<tr>
<th>Protein (Temperature, pH)</th>
<th>( \Delta G^\circ ) (kJ mol(^{-1}))</th>
<th>( \Delta H^\circ ) (kJ mol(^{-1}))</th>
<th>( \Delta S^\circ ) (J K(^{-1}) mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ribonuclease (303 K, 2.5)</td>
<td>3.8</td>
<td>240</td>
<td>774</td>
</tr>
<tr>
<td>Chymotrypsinogen (298 K, 3)</td>
<td>31</td>
<td>160</td>
<td>439</td>
</tr>
<tr>
<td>Myoglobin (298 K, 9)</td>
<td>56.9</td>
<td>180</td>
<td>400</td>
</tr>
<tr>
<td>( \beta )-Lactoglobulin (298 K, 3, 5 M urea)</td>
<td>3</td>
<td>-88</td>
<td>-300</td>
</tr>
</tbody>
</table>

• $\Delta G_{\text{den}} = \Delta H_{\text{den}} - T\Delta S_{\text{den}}$

• $\Delta G_{\text{den}}^0 = -RT\ln K$

• $\Delta H_{\text{den}}^0 = RT^2(\partial\ln K/\partial T)_P$

• $\Delta S_{\text{den}}^0 = (\Delta H_{\text{den}}^0 - \Delta G_{\text{den}}^0)/T$

• $\Delta C_{\text{den}}^0 = (\partial \Delta H_{\text{den}}^0/\partial T)_P$

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**P7.19** A protein has a melting temperature of $T_m = 335$ K. At $T = 315$ K, UV absorbance determines that the fraction of native protein is $f_N = 0.965$. At $T = 345$ K, $f_N = 0.015$.

(a) Assuming a two-state model and assuming also that the enthalpy is constant between $T = 315$ and $345$ K, determine the enthalpy of denaturation.

$$\ln \{K(T_2)\} - \ln \{K(T_1)\} = (\Delta H/R)(1/T_2-1/T_1)$$

(b) Also, determine the entropy of denaturation at $T = 335$ K.

Obtain $\Delta G_{\text{Den}}(335K)$ using $\Delta G_{\text{Den}}(T_2)=T_2/\Delta G_{\text{Den}}(T_1)+\Delta H(1/T_2-1/T_1)$ $\Rightarrow \Delta G_{\text{Den}}(335K) = [Q2]$

(c) By DSC, the enthalpy of denaturation was determined to be 251 kJ mol$^{-1}$. Is this denaturation accurately described by the two-state model?

$\Rightarrow$ If the answer of (a) $\sim$251 kJmol$^{-1}$, yes
7.6 Surface Tension

- H₂O molecules maximize the number of neighboring molecules for stability
  → A water forms a spherical droplet

*How does the energy of a droplet depend on the surface area σ?*

- The work (in Helmholtz energy A) associated with creating additional surface area dσ at constant V and T is
  \[ dA = \gamma d\sigma, \]
where \( \gamma \) is the surface tension

7.6 Surface Tension (Continued)

\[ dA = \gamma d\sigma, \]  
where \( \sigma \) is a surface area.

- The **surface tension** \( \gamma \) (>0) has the units of energy/area or J m⁻².
- For a natural process, Helmholtz \( dA < 0 \)
  → \( d\sigma < 0 \) for a natural process
- For a sphere of a radius \( r \),
  \( \sigma = 4\pi r^2 \)  
  \( d\sigma = 8\pi r \, dr \)  
(2)
(1) & (2) yield
  \[ dA = \gamma (8\pi r \, dr) = (8\pi r \, \gamma) \, dr = F_{surf} \, dr \]

\[ P_{surf} = F_{surf}/4\pi r^2 = (2\gamma/r) \]
γ is dependent on compound!

Sample Question

• There large and small bubbles of H₂O. Assume that \( P_{\text{outer}} \) (~1 atm) + \( P_{\text{sur}} \) is in equilibrium with the internal pressure \( P_{\text{inner}} \). Which bubble has a higher \( P_{\text{inner}} \)?

\[
P_{\text{inner}} = P_{\text{out}} + P_{\text{sur}} = 1 \text{ atm} + (2\gamma/r)
\]

Q. Is “\( P_{\text{inner \ large}} > P_{\text{inner \ small}} \)” correct?
How two bubbles fuse into one.

\[ P_{\text{inner large}} < P_{\text{inner small}} \]

P7.40

- Calculate the difference in pressure across the liquid-air interface for a water droplet of radius 150 nm.

\[ P_{\text{outer}} + P_{\text{sur}} = P_{\text{inner}} \]

\[ P_{\text{inner}} - P_{\text{outer}} = P_{\text{sur}} = \frac{2\gamma}{r} \approx 10 \text{ bar} \]

*Laplace’s equation*

<table>
<thead>
<tr>
<th>Surface Tension of Selected Liquid</th>
<th>Formula</th>
<th>Name</th>
<th>( \gamma ) (mN m(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Br(_2)</td>
<td>Bromine</td>
<td>40.95</td>
</tr>
<tr>
<td></td>
<td>H(_2)O</td>
<td>Water</td>
<td>71.99</td>
</tr>
</tbody>
</table>
Vapor Pressure of a Droplet (Derivation)

- \( dP_{\text{liq}} - dP_{\text{vap}} = d(2\gamma/r) = 2\gamma d(1/r) \) \[1\]
- Chemical potential of two phase should be same
  \( 0 = d\mu_{\text{liq}} - d\mu_{\text{vap}} \)
  \( 0 = V_{m,\text{liq}} dP_{\text{liq}} - V_{m,\text{vap}} dP_{\text{vap}} \) \[2\]

- By combining [1, 2]
  \( (V_{m,\text{vap}}/V_{m,\text{liq}} - 1)dP_{\text{vap}} = 2\gamma d(1/r) \)
  \( V_{m,\text{vap}}/V_{m,\text{liq}} \sim 2\gamma d(1/r) \)
  \( V_{m,\text{vap}} dP_{\text{vap}} = 2\gamma V_{m,\text{liq}} d(1/r) \)
  \( RT/P_{\text{vap}} = 2\gamma V_{m,\text{liq}}/\rho_{\text{liq}}RT \)

P(r) and \( P_{\text{bulk}} \) are \( P_{\text{vap}} \) for a droplet of a radius \( r \) and bulk liquid (\( r = \infty \))

\[\begin{align*}
\ln \frac{P(r)}{P_{\text{bulk}}} &= \frac{2\gamma V_{m,\text{liq}}}{RT} (1/r) = \frac{2\gamma M}{\rho_{\text{liq}}RT} (1/r)
\end{align*}\]

\[\begin{align*}
\ln \left[ \frac{P(T)}{P_\text{atm}} \right] &= A(1) - \frac{A(2)}{T} + A(3) = 23.593 - \frac{3.6971 \times 10^3}{325 - 31.317} \Rightarrow \text{Calculate} \ P_\text{atm}(T)
\end{align*}\]

Then, use

\[\ln \frac{P(r)}{P(r = \infty)} = \frac{2\gamma V_{m,\text{liq}}}{RT} (1/r) = \frac{2\gamma M}{\rho_{\text{liq}}RT} (1/r) \]

\[\text{P7.41} \) Calculate the factor by which the vapor pressure of a droplet of methanol of radius \( 1.00 \times 10^{-4} \) m at \( 45.0^\circ C \) in equilibrium with its vapor is increased with respect to a very large droplet. Use the tabulated value of the density and the surface tension at 298 K from Appendix B (table 2.3 & table 7.5) for this problem. (Hint: You need to calculate the vapor pressure of methanol at this temperature.)