$\Delta G$ & phase changes

$\Delta G$ & phase changes:

Example: $\text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{O}(g)$

- For $P = 1 \text{ atm}$; $T < 373 \text{ K}$ (100 °C) $\Delta G > 0$
  (we know water doesn’t boil below 100 °C)
- For $P = 1 \text{ atm}$; $T > 373 \text{ K}$ $\Delta G < 0$
- For $P = 1 \text{ atm}$; $T = 373 \text{ K}$ $\Delta G = 0$

At the boiling point, the liquid and vapor are in equilibrium. The boiling point is defined as the temp. at which the liquid and vapor phases are at equilibrium at 1 atm.
\[ \Delta G : H_2O(l) \rightleftharpoons H_2O(g) \quad - \text{more} \]

- From Appendix E:
  \begin{align*}
  &|H_2O(g)| \quad |H_2O(l)| \quad |\Delta H_f^\circ (kJ/mol)| \quad |S^\circ (J/mol K)| \\
  &-241.8 \quad -285.8 \quad 188.8 \quad 69.9
  
  
  \end{align*}

- For the vaporization process at 298 K:
  \begin{align*}
  \Delta H_{298} &= \Delta H_f^\circ \text{(gas)} - \Delta H_f^\circ \text{(liq.)} \\
  &= -241.8 - (-285.8) = +44.8 \text{ kJ}
  
  \Delta S_{298} &= S^\circ \text{(gas)} - S^\circ \text{(liq.)} \\
  &= 188.8 - 69.9 = 118.9 \text{ J/K} = 0.119 \text{ kJ/K}
  
  \Delta G_{298} &= \Delta H_{298} - (298 \text{ K}) \Delta S_{298} = +8.9 \text{ kJ}
  
  \end{align*}

\[ \Delta G : H_2O(l) \rightleftharpoons H_2O(g) \quad - \text{more} \]

- We saw that at 298 K, \( \Delta G > 0 \)
- \((\Delta H_{298}/\Delta S_{298}) = (44.8/0.119) \text{ K} = 376 \text{ K}\) this is close to 373 K, the boiling point! Why?
  
  rearrange: \( \Delta H_{298} = (376 \text{ K}) \Delta S_{298} \)
  
  \( \Delta H_{298} - (376 \text{ K}) \Delta S_{298} = 0 \)
  
  recall: \( \Delta H_{373} -(373 \text{ K})\Delta S_{373} = \Delta G_{373} = 0 \) (why?)
  
  if \( \Delta H_{373} \approx \Delta H_{298} \) and \( \Delta S_{373} \approx \Delta S_{298} \)
  
  then \( \Delta G_{373} = 0 \approx \Delta H_{298} - (373 \text{ K})\Delta S_{298} \)
Generalization

- $\Delta H$ and $\Delta S$ often don’t change much for a process or reaction from $\Delta H_{298}$ and $\Delta S_{298}$
- Often, can estimate for $\Delta G$ at other temps.:
  \[
  \Delta G(T) \approx \Delta H_{298} - T \Delta S_{298}
  \]

P-T Phase diagram for H$_2$O
Phase diagram for CO\(_2\)

**Note:** boiling and freezing points are not defined for CO\(_2\).

Free Energies and Phase Diagrams
**Phase Diagrams**

- All phase changes are determined by $\Delta G$, phases are in equilibrium when $\Delta G = 0$.
- P-T phase diagrams tell us what phases are stable at various values of T and P.
- A line separating two regions of a phase diagram represents the temperatures and pressures where $\Delta G = 0$ for the change from one phase to another.

**Example: recent exam**

Aluminum metal has a melting point of 660.3 °C.

Use the table below to calculate an estimate for the boiling point of aluminum in °C

<table>
<thead>
<tr>
<th>Substance</th>
<th>$\Delta H_f^\circ$ (kJ mol$^{-1}$)</th>
<th>$\Delta G_f^\circ$ (kJ mol$^{-1}$)</th>
<th>$S^\circ$ (J mol$^{-1}$ K$^{-1}$)</th>
<th>$C_p^\circ$ (J mol$^{-1}$ K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(s)</td>
<td></td>
<td>28.33</td>
<td></td>
<td>24.35</td>
</tr>
<tr>
<td>Al(l)</td>
<td>10.56</td>
<td>7.20</td>
<td>39.55</td>
<td>24.21</td>
</tr>
<tr>
<td>Al(g)</td>
<td>326.4</td>
<td>285.7</td>
<td>164.54</td>
<td>21.38</td>
</tr>
</tbody>
</table>

Explain why this is just an estimate. A one- or two-sentence explanation is all that is necessary.


**Example - from old exam**

Solid tin exists in two common forms (allotropes), “white” and “gray” tin. The standard molar enthalpy and molar free energy for the transformation between these two allotropes are given below.

\[ \text{Sn}_{\text{white}} \rightarrow \text{Sn}_{\text{gray}} \]
\[ \Delta H^\circ = -2.090 \text{ kJ/mol}; \quad \Delta G^\circ = 0.130 \text{ kJ/mol} \]

(a) Under standard conditions (298 K, 1 atm), which allotrope is thermodynamically stable?

(b) The standard molar entropy, \( S^\circ \), of gray tin is 44.14 J mol\(^{-1}\) K\(^{-1}\). What is the standard molar entropy of white tin?

(c) The melting point of tin is 505 K. For temperatures below 505 K, give the temperature ranges (if any) over which white and gray tin are the most stable allotropes.