Key points of the last lecture

- U and H (like P, V & T) are state functions
- U and H can be calculated from any path, even one involving changing chemical species from one form to another.

\[ C_p = C_v + nR \] for an ideal gas, and are given otherwise. \( C_v \) is independent of V and depends weakly on T. (Usually a power series expansion in powers of T (or T/K) is sufficient.)
A quick review (I):

- Two state functions:
  \[ \Delta U = q + w \]
  \[ H = U + PV \]

- Pressure-Volume work, (rev. and irrev.)

\[ w = -P_{ext} dV \]

\[ w_{rev} = -\int_{V_i}^{V_f} P(V) dV \]
\[ w_{irrev} = -P_{final} \Delta V \]
## Heat Capacity Summary

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<th>Heat capacity</th>
<th>Definition</th>
<th>For P-V work</th>
<th>For ideal gases</th>
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<td>$C_V$</td>
<td>$\frac{dq_V}{dT}$</td>
<td>$\left( \frac{\partial U}{\partial T} \right)_V$</td>
<td>$\frac{dU}{dT}$</td>
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<tr>
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<td>$\frac{dH}{dT}$</td>
</tr>
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For an ideal gas, $C_P = C_V + nR$
Phase transitions

\[ \Delta H_{\text{melting}} = -\Delta H_{\text{fusion}} \]

\[ \Delta H_{\text{vaporization}} = -\Delta H_{\text{condensation}} \]

\[ \Delta H_{\text{sublimation}} = -\Delta H_{\text{condensation}} \]

Most phase transitions in everyday life occur at constant pressure. Therefore we want to measure \( \Delta H \). These are heats that change a substance from one phase to another but there is no change in temperature.

\[ \Delta H_P = q_P \]
Phase transitions are a good way to store energy.

\[ \Delta H_{\text{vaporization}} \text{ of steam at } 100^\circ C = 40660 \text{ J/mole} \]

Think of the industrial revolution!

Example

Calculate the enthalpy used to convert 5 moles (100 grams) of water from ice at 250 K to steam at 450 K by adding heat at constant pressure of 1 atm.

\[ \Delta H_{\text{melting}} = 6007 \text{ J/mole } @ \text{ } 273 K \quad C_{P,\text{ice}} = 38.1 \text{ JK}^{-1}\text{mole}^{-1} \]

\[ \Delta H_{\text{vaporization}} = 40660 \text{ J/mole } @ \text{ } 373 K \quad C_{P,\text{water}} = 75.4 \text{ JK}^{-1}\text{mole}^{-1} \]

\[ C_{P,\text{steam}} = 33.8 \text{ JK}^{-1}\text{mole}^{-1} \]
\[ \Delta H = \Delta H_I + \Delta H_{II} + \Delta H_{III} + \Delta H_{IV} + \Delta H_{V} \]

\( \Delta H_I = \Delta H \) of heating ice from 250 K to 273 K

\( \Delta H_{II} = \Delta H \) of melting at 273 K

\( \Delta H_{III} = \Delta H \) of heating water from 273 K to 373 K

\( \Delta H_{IV} = \Delta H \) of vaporization at 373 K

\( \Delta H_{V} = \Delta H \) of heating steam from 373 K to 450 K

\[ \Delta H = \int_{T_1}^{T_2} C_p(T) \, dT \approx C_p(\bar{T}) \Delta T \quad (\text{no phase change}) \]

\( \Delta H_I = n \bar{C}_{P,\text{ice}} \Delta T = 4.38 \times 10^3 \, J \)

\( \Delta H_{II} = n H_{\text{melting}} = 3.00 \times 10^4 \, J \)

\( \Delta H_{III} = n \bar{C}_{P,\text{water}} \Delta T = 3.77 \times 10^4 \, J \)

\( \Delta H_{IV} = n \bar{H}_{\text{vaporization}} = 2.03 \times 10^5 \, J \)

\( \Delta H_{V} = n \bar{C}_{P,\text{steam}} \Delta T = 1.30 \times 10^4 \, J \)

\[ \Delta H_{\text{TOTAL}} = \sum_{j=1}^{5} \Delta H_j = 2.88 \times 10^5 \, J \]

N.B.: The heat of vaporization is 70% of the total. The heat from melting is 10% Ice is much better at cooling a soda (and the earth) than water at 0°C.
Heat required or given off during a chemical reaction occurring at constant pressure (and constant Temperature).

Why would we want to know the heat given off (or consumed) during a particular chemical reaction?

a) Maximize the heat (i.e. find the best fuel)
b) Minimize the heat (i.e. batteries)
c) Compare efficiencies (metabolism, exercise, etc.)

If $\Delta H$ of some reactions are known then we can combine them to calculate unknown $\Delta H$s
Example: It is not practical to measure the heat given off when C burns to CO in a limited amount of O₂ because the product will be a mixture of CO₂ and CO. But we can measure the following at 25 °C:

(1) \[ C + O₂ \rightarrow CO₂ \quad \Delta H_1 = -393.5 \text{ kJ/mole} \]

(2) \[ CO + \frac{1}{2} O₂ \rightarrow CO₂ \quad \Delta H_2 = -282.9 \text{ kJ/mole} \]

To find \[ C + \frac{1}{2} O₂ \rightarrow CO \quad \Delta H = ? \]
\[(1) \quad C + O_2 \rightarrow CO_2 \quad \Delta H_1 = -393.5 \text{ kJ/mole} \]

\[-(2) \quad CO_2 \rightarrow CO + \frac{1}{2} O_2 \quad \Delta H_2 = 282.9 \text{ kJ/mole} \]

\[C + \frac{1}{2} O_2 \rightarrow CO \quad \Delta H = -110.62 \text{ kJ/mole} \]

In general, if we know \(A \rightarrow B\) and \(C \rightarrow B\), we can rearrange the equations to get \(A \rightarrow C\).
Method of Alternate Paths

\[
\Delta H_{\text{rxn}} = \Delta H_A + \Delta H^\circ_{\text{rxn}} + \Delta H_B
\]
Example 1: Calculating phase change at a different temperature using an alternate path

Find $\Delta H_{\text{vap}}$ of one mole of water at 60 °C.

$\Delta H_{\text{melting}} = 6007 \text{ J/mole @ 273 K}$  \hspace{1cm} $C_{P,\text{ice}} = 38.1 \text{ JK}^{-1}\text{mole}^{-1}$

$\Delta H_{\text{vaporization}} = 40660 \text{ J/mole @ 373 K}$  \hspace{1cm} $C_{P,\text{water}} = 75.4 \text{ JK}^{-1}\text{mole}^{-1}$

$C_{P,\text{steam}} = 33.8 \text{ JK}^{-1}\text{mole}^{-1}$

\[\begin{align*}
\Delta H_{\text{rxn}} & = \Delta H_A + \Delta H_B \\
\Delta H_A & = nC_{P,\text{water}}\Delta T = (1 \text{ mole})(75.4\text{ JK}^{-1}\text{mole}^{-1})(40 \text{ K}) \\
& = 3.02 \times 10^3 \text{ J} \\
\Delta H_{\text{vap}} & = nC_{P,\text{steam}}\Delta T = (1 \text{ mole})(33.8\text{ JK}^{-1}\text{mole}^{-1})(-40 \text{ K}) \\
& = -1.35 \times 10^3 \text{ J} \\
\Delta H & = \Delta H_A + \Delta H_{\text{vap}} + \Delta H_B \\
& = 4.24 \times 10^4 \text{ J}
\end{align*}\]
Example 1: Finding the enthalpy of solution

Conversion of glycine to urea in aqueous solution as opposed to solids.

\[ \text{Gly}(s) + \infty \text{H}_2\text{O}(l) \rightarrow \text{Gly}(aq) \quad \Delta H_{\text{diss gly}} = 15.69 \text{kJ/mole of Gly} \]

\[ \text{Urea}(s) + \infty \text{H}_2\text{O}(l) \rightarrow \text{Urea}(aq) \quad \Delta H_{\text{diss urea}} = 13.93 \text{kJ/mole of Urea} \]

\[ 3\text{O}_2 + 2\text{Gly}(s) \rightarrow \text{Urea}(s) + 3\text{CO}_2(g) \quad \Delta H = -1296.8 \text{kJ/mole} \]

We want to find:

\[ 3\text{O}_2 + 2\text{Gly}(aq) \rightarrow \text{Urea}(aq) + 3\text{CO}_2(g) \quad \Delta H = ? \]
\[ \Delta H = -2\Delta H_{\text{diss gly}} + \Delta H_{\text{solid, oxidation}} + \Delta H_{\text{diss urea}} \]

\[ = -2(15.69 \text{ kJ/mole}) - 1296.8 \text{ kJ/mole} + 13.93 \text{ kJ/mole} \]

\[ = -1314.2 \text{ kJ/mole} \]