Lecture 14: Enthalpy

Enthalpy, C_P, γ, $q_{in} = -q_{out}$, Non-standard enthalpy

Enthalpy

Motivation

- Many chemical processes occur at constant pressure
- Measuring heat is annoying because it is a path function
- What if we could have a state function for constant pressure processes?

Internal energy works for constant volume processes:

$$dU = dq + dw \implies dU = dq_V$$

We define enthalpy to be the constant pressure analog:

Enthalpy

$$H = U + PV$$

$$\Delta H = \Delta U + P\Delta V$$

Change in enthalpy is the heat transferred in a constant pressure process

Enthalpy Derivation

Starting from First Law:

$$\Delta U = q + w$$

Consider constant pressure:

$$\Delta U = q_P - P\Delta V$$

Rearrange:

$$\begin{aligned} \Delta U + P\Delta V &= q_P \\ \Delta U + \Delta(PV) &= q_P \\ \Delta H &= \Delta(U + PV) = q_P \end{aligned}$$

Heat Capacity

Constant Volume Heat Capacity

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

Constant volume heat capacity

$$dU = dq + dw = dq - \cancel{PdV}$$

At constant volume:

$$dU = dq_V$$

Constant Pressure Heat Capacity

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P$$

Constant pressure heat capacity

$$dH = dU + d(PV)$$

$$dH = dq + dw + PdV + \cancel{VdP}$$

At constant pressure:

$$dH = dq_P$$

Evaluating Heat Capacity

Conceptually: $C_P > C_V$

- Constant Volume - heat increases the internal energy
- Constant Pressure - Volume increases, expansion work, extra energy needed

Mathematical Derivation:

$$H = U + PV$$

Substitute Ideal Gas Law:

$$H = U + nRT$$

Take Partial:

$$\frac{dH}{dT} = \frac{dU}{dT} + nR$$
$$C_P = C_V + nR$$

Relating Heat Capacities

$$\overline{C_P} = \overline{C_V} + R$$

Get $\overline{C_V}$ from equipartition, always at high T limit

Adiabatic Expansion of Ideal Gas

Another way to relate heat capacities is to use a ratio, recall last lecture:

$$n\overline{C_V}dT = -PdV$$

Substitute ideal gas law $PV = nRT$:

$$n\overline{C_V}dT = -\frac{nRT}{V}dV$$

Group similar terms and integrate:

$$\int_{T_1}^{T_2} \frac{1}{T}dT = -\frac{R}{\overline{C_V}} \int_{V_1}^{V_2} \frac{1}{V}dV$$

$$\ln\left(\frac{T_2}{T_1}\right) = -\frac{R}{\overline{C_V}} \ln\left(\frac{V_2}{V_1}\right)$$

Adiabatic Expansion of Ideal Gas

Define γ:

$$\gamma = \frac{\overline{C_P}}{\overline{C_V}} \qquad \overline{C_P} - \overline{C_V} = R$$

Therefore:

$$\frac{R}{\overline{C_V}} = \frac{\overline{C_P} - \overline{C_V}}{\overline{C_V}} = \gamma - 1$$

Substituting back:

$$\ln\left(\frac{T_2}{T_1}\right) = -(\gamma - 1)\ln\left(\frac{V_2}{V_1}\right)$$

$$\boxed{\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}}$$

Conservation of Energy: $q_{in} = -q_{out}$

Conservation of Energy

$$q_{in} = -q_{out}$$

Energy released from one object
gets absorbed by the other

A steel rod (10 g, heat capacity 0.5 $\frac{\text{J}}{\text{g}^\circ\text{C}}$) is heated to 75°C. The rod is set on a concrete block (20 g, heat capacity 0.1 $\frac{\text{J}}{\text{g}^\circ\text{C}}$) that is at 25°C. When the two materials come to thermal equilibrium, what is their final temperature?

$$q_{\text{steel}} = -q_{\text{concrete}}$$

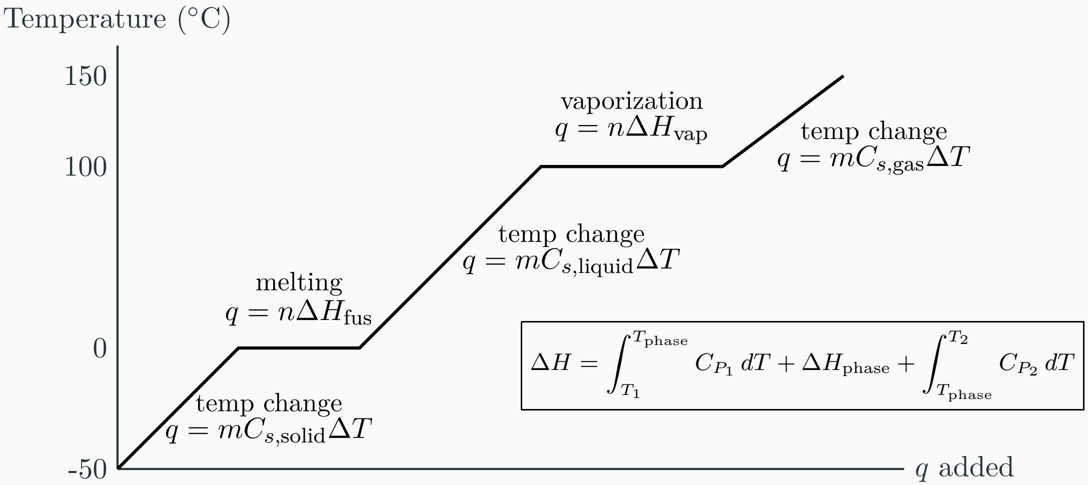
$$m_{\text{steel}}C_{s,\text{steel}}(T_f - 75^\circ\text{C}) = -m_{\text{concrete}}C_{s,\text{concrete}}(T_f - 25^\circ\text{C})$$

$$10\,\text{g}\,(0.5\,\frac{\text{J}}{\text{g}^\circ\text{C}})(T_f - 75^\circ\text{C}) = -20\,\text{g}\,(0.1\,\frac{\text{J}}{\text{g}^\circ\text{C}})(T_f - 25^\circ\text{C})$$

$$5T_f - 375 = -2T_f + 50$$

$$T_f = 60.7^\circ\text{C}$$

Heating Curve



temp change
$q = mC_{s,\text{solid}}\Delta T$

melting
$q = n\Delta H_{\text{fus}}$

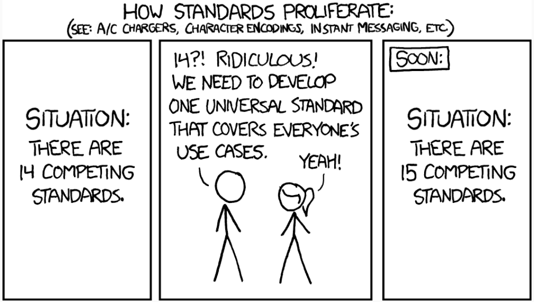
temp change
$q = mC_{s,\text{liquid}}\Delta T$

vaporization
$q = n\Delta H_{\text{vap}}$

temp change
$q = mC_{s,\text{gas}}\Delta T$

$$\boxed{\Delta H = \int_{T_1}^{T_{\text{phase}}} C_{P_1}\,dT + \Delta H_{\text{phase}} + \int_{T_{\text{phase}}}^{T_2} C_{P_2}\,dT}$$

Standard Conditions



2 Standard Conditions

Thermodynamics
SATP: 298 K, 1 bar or 1 atm

Gases
STP: 273 K, 1 bar or 1 atm

SATP States of Matter

Liquid: Br_2, Hg
Gas: H_2, O_2, N_2, F_2, Cl_2, He, Ne, Ar, Kr, Xe, Rn
Diatomic: H_2, O_2, N_2, F_2, Cl_2, Br_2, I_2
Otherwise, mono-atomic solid

Non-Standard Enthalpies

Gen Chem: Heat capacities independent of temperature, always use same $\Delta H^\circ_{\text{rxn}}$
PChem: Heat capacities can be temperature dependant, calculate ΔH_{rxn} at diff T

Calculating $\Delta H_{\text{rxn}}(T_2)$

For a reaction aA + bB → yY + zZ

$$\Delta H_{\text{rxn}}(T_2) = \Delta H_{\text{rxn}}(T_1) + \int_{T_1}^{T_2} \Delta C_P(T)dT$$

$$\Delta C_P(T) = yC_{P,Y}(T) + zC_{P,Z}(T) - aC_{P,A}(T) - bC_{P,B}(T)$$

Example: Non-Standard Enthalpies

Given NH_3 $\Delta H_f^\circ = -46.11\,\text{kJ/mol}$, determine NH_3 $\Delta H_f(1000\,\text{K})$

$$\tfrac{1}{2}\,N_2 + \tfrac{3}{2}\,H_2 \longrightarrow NH_3$$

$$\begin{aligned}
C_P^\circ(H_2)/\tfrac{\text{J}}{\text{K}\cdot\text{mol}} &= 29.07 - 0.837\times10^{-3}T + 2.012\times10^{-6}T^2\\
C_P^\circ(N_2)/\tfrac{\text{J}}{\text{K}\cdot\text{mol}} &= 26.98 + 5.912\times10^{-3}T - 0.3376\times10^{-6}T^2\\
C_P^\circ(NH_3)/\tfrac{\text{J}}{\text{K}\cdot\text{mol}} &= 25.89 + 32.58\times10^{-3}T - 3.046\times10^{-6}T^2
\end{aligned}$$

$$\begin{aligned}
\Delta H_f^\circ(1000\,\text{K}) &= \Delta H_f^\circ(298\,\text{K}) + \int_{298\,\text{K}}^{1000\,\text{K}} \Delta C_P^\circ(T)\,dT\\
\Delta C_P^\circ(T)/\tfrac{\text{J}}{\text{K}\cdot\text{mol}} &= C_P^\circ(NH_3) - \tfrac{1}{2}C_P^\circ(N_2) - \tfrac{3}{2}C_P^\circ(H_2)\\
&= -31.21 + 30.88\times10^{-3}T - 5.895\times10^{-6}T^2\\
\int_{298\,\text{K}}^{1000\,\text{K}} &\left[-31.21 + 30.88\times10^{-3}T - 5.895\times10^{-6}T^2\right] dT\\
&= (-21.91 + 14.07 - 1.913)\,\text{kJ/mol}\\
&= -9.75\,\text{kJ/mol} \implies \Delta H_f(1000\,\text{K}) = \boxed{-55.86\,\text{kJ/mol}}
\end{aligned}$$