Recap…

- $\frac{1}{2} mv^2 = \frac{3}{2} K_B T$

- $\Delta \overline{U} \sim \Delta \overline{H}.$ (Liquid/Solid phase)

- $\Delta \overline{U} \neq \Delta \overline{H}.$ (if Gas is involved. CAREFUL)

- Measure Heat (q) of a process and assign the value of $\Delta \overline{U}$ and $\Delta \overline{H}$

  $\Delta \overline{U} = q_v$

  $\Delta \overline{H} = q_p$

We know how to measure heat (Calorimetry)

$$q = C\ m_w\ \Delta T \qquad \text{Water}$$

$$\mathbf{q = C\ n\ \Delta T} \qquad \mathbf{n = number\ of\ moles,\ GAS}$$

$$\mathbf{C = \dfrac{q}{n\ \Delta T}}$$

HEAT CAPACITY IS A PATH FUNCTION

The *amount of energy required to raise the temperature of a substance by one degree* is different if done at constant V or constant P:

- At constant V, the energy added as heat is q_V, $\left(\Delta U = q_V\right)$

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

- At constant P, the energy added as heat is q_P, $\left(\Delta H = q_P\right)$

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

Heat Capacities of Ideal Gas

For an ideal gas:
$$H = U + PV$$
$$= U + nRT$$

Differentiating:
$$\frac{dH}{dT} = \frac{dU}{dT} + nR$$

For an ideal gas, U and H depend only on T, not P or V

So:
$$\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V + nR$$
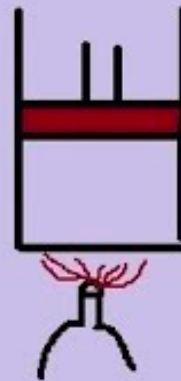
Or:
$$C_P = C_V + nR$$

Home work

Recall that for a monatomic ideal gas, $\overline{C}_V = (3/2)R$, so the difference between $\overline{C}_P$ and $\overline{C}_V$ is 67% of $\overline{C}_V$

Determining Enthalpy

The difference in enthalpy at two different temperatures is determined from integration of C_P over the temperature range:

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \rightarrow dH = C_P dT \rightarrow H(T_2) - H(T_1) = \int_{T_1}^{T_2} C_P(T)\, dT$$

This is true *only if* there is no phase transition occurring between T_1 and T_2. At a phase transition, there is no change in the temperature as you add heat ($C_P \rightarrow \infty$), so one must also add any enthalpy associated with a phase change where needed:
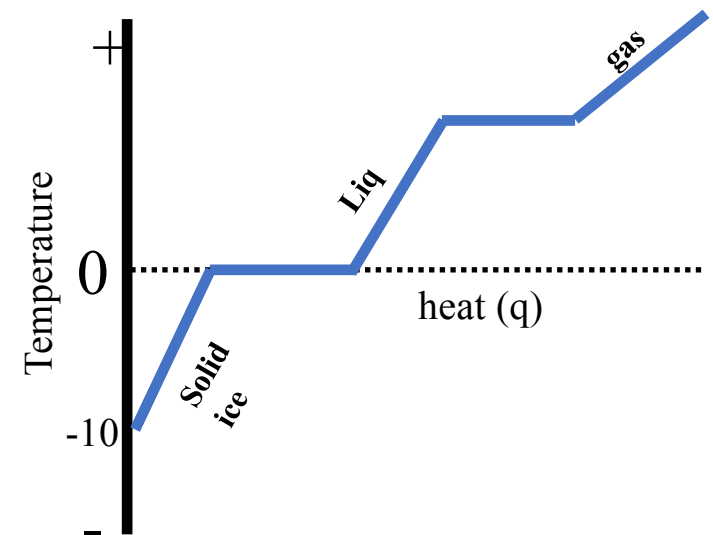
Example: $H(T) - H(0) = \int_0^{T_{\text{fus}}} C_P^{\text{S}}(T')\, dT' + \Delta_{\text{fus}} H + \int_{T_{\text{fus}}}^{T} C_P^{\text{l}}(T')\, dT'$

Solid, from $T=0$ to $T=T_{\text{fus}}$

Enthalpy of fusion $\Delta_{\text{fus}} H = H^{\text{l}}(T_{\text{fus}}) - H^{\text{s}}(T_{\text{fus}})$
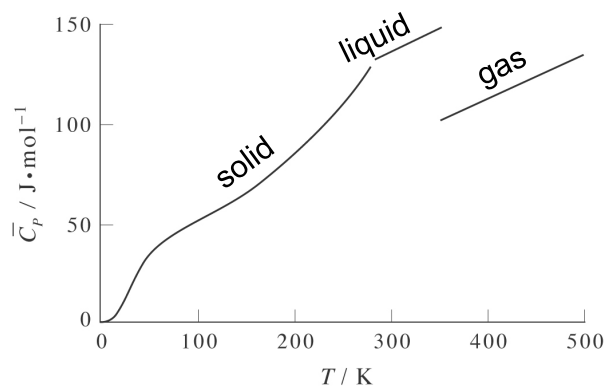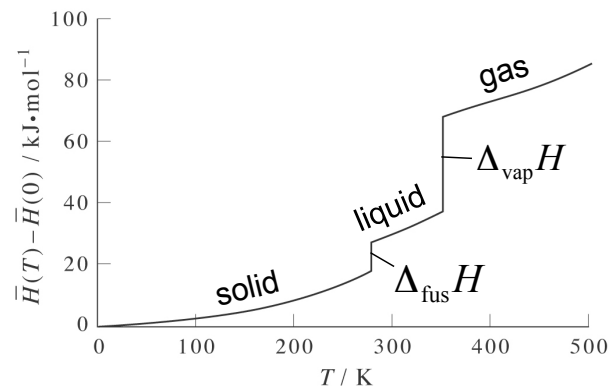
Liquid, from $T=T_{\text{fus}}$ to $T=T$

Enthalpy of Benzene

Benzene: $T_{\text{fus}}=278.7$ K, $T_{\text{vap}}=353.2$ K

*Measuring the heat capacity,
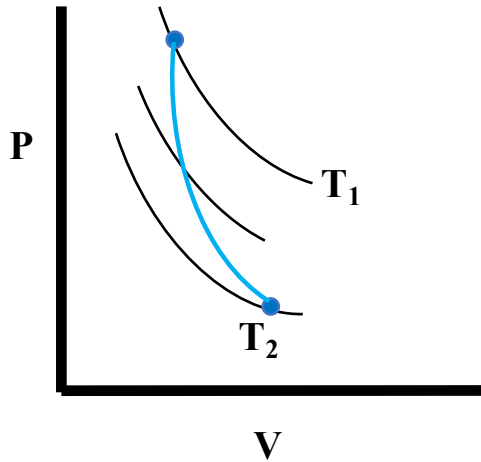temperature by temperature*

*Integrating the heat capacity,
adding phase changes*

For $T > T_{\text{vap}}$,

$$H(T) - H(0) = \int_0^{T_{\text{fus}}} C_P^{\text{s}}(T')\,dT' + \Delta_{\text{fus}}H + \int_{T_{\text{fus}}}^{T_{\text{vap}}} C_P^{\text{l}}(T')\,dT' + \Delta_{\text{vap}}H + \int_{T_{\text{vap}}}^{T} C_P^{\text{g}}(T')\,dT'$$

Lets calculate the work done (Adiabatic Processes)

$$w = -\int_{V_1}^{V_2} P \, dV$$

(Ideal gas, $PV = nRT$, ISOTHERM)

I do not know how "P" vary with "V" along the **blue line** ?

Target : Find the PV relation

Adiabatic process, q= 0
1st Law,

$\Delta U = q + w$

=) $\Delta U = 0 + w$

=) $C_v \, dT = - P \, dV$

=) $C_v \, dT = - (nRT/V) \, dV$

=) $C_v \, (dT/T) = -nR \, (dV/V)$

=) $C_v \ln(T_2/T_1) = -nR \ln(V_2/V_1)$

=) $\ln (T_2/T_1) = -(nR/C_v) \ln(V_2/V_1)$

=) $\ln(T_2/T_1) = \ln(V_1/V_2)^{nR/C_v}$

=) $T_2/T_1 = (V_1/V_2)^{nR/C_v}$

$TV^{(nR/Cv)} = \text{constant}$

$P V^{(1+ nR/Cv)} = \text{constant}$

$$\boxed{\begin{array}{l} \mathbf{P\ V^{(1+\ nR/Cv)} = constant} \\ \mathbf{PV^{\gamma} = K} \end{array}}$$

$$w = -\int_{V_1}^{V_2} P\ dV = -\int_{V_1}^{V_2} (K/V^{\gamma})\ dV$$

$$\gamma = 1 + nR/C_v$$
$$= [C_v + nR]\ /C_v$$
$$= \quad C_p\ /C_v$$

The adiabatic condition

$$PV^{\gamma} = constant = K$$

leads to the work expression

$$W = \frac{K(V_f^{1-\gamma} - V_i^{1-\gamma})}{1-\gamma}$$

$$\gamma = \frac{C_P}{C_V}$$

The ratio of specific heats for the gas.

Pressure

Volume

Adiabatic

Derivation

Calculation

Other Processes
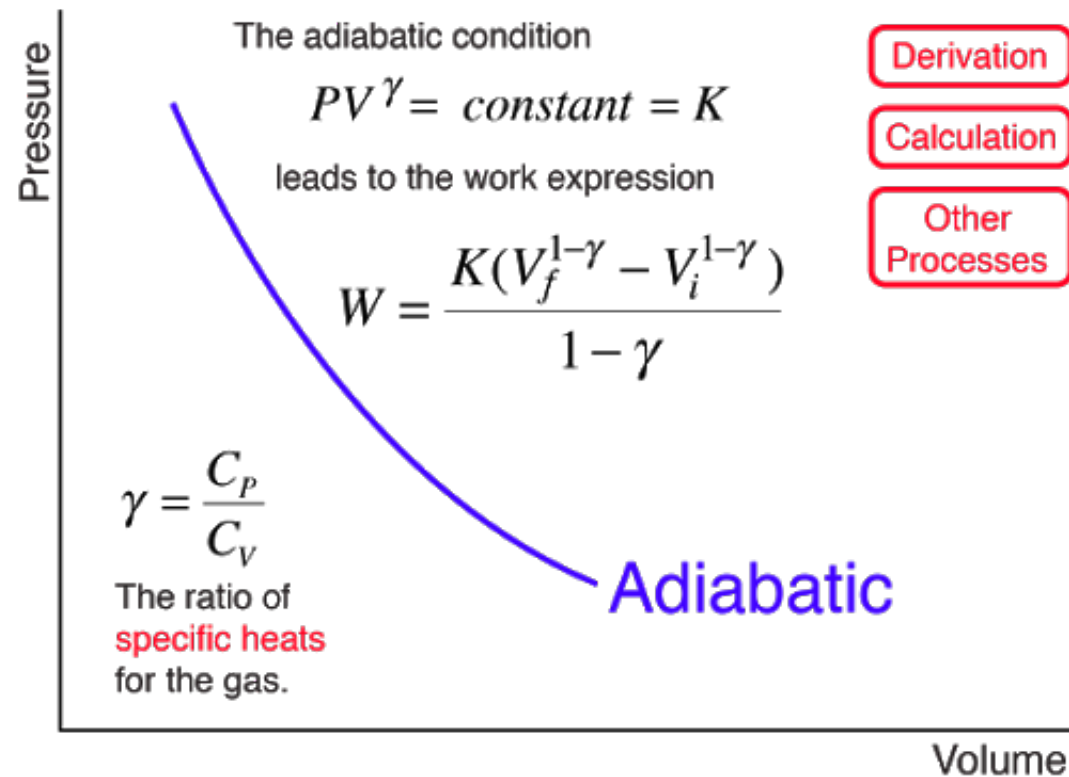
-Thermochemistry
-Standard Enthalpy

Heat of Reaction

Heat may be absorbed or evolved in a chemical reaction. When that occurs at constant pressure $\Delta H = q_P$ and we define:
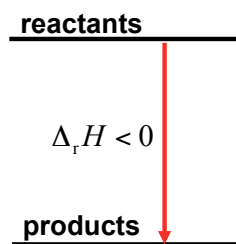
$$\Delta_r H = H_{products} - H_{reactants}$$

(reaction)

(*exo*=out)

exothermic

$$\boxed{q_P = \Delta_r H < 0}$$

Releases (evolves) energy as heat, 'downhill'. Heat is produced.

reactants

$\Delta_r H < 0$

products

enthalpy
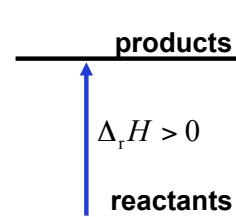
(*endo*=in)

endothermic
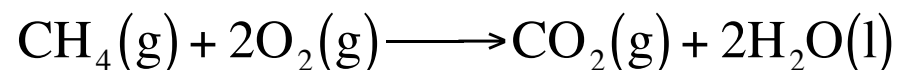
$$\boxed{q_P = \Delta_r H > 0}$$

products

$\Delta_r H > 0$

reactants

Absorbs energy as heat, 'uphill'. Heat must be supplied to drive the reaction.
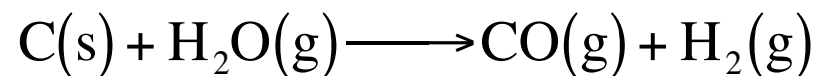
Thermochemistry Examples

Exothermic: combustion of methane,

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

$$\Delta_r H = -890.36 \text{ kJ} \quad \text{at } 298 \text{ K} \qquad \text{(heat is evolved)}$$

(also referred to as a "heat of combustion" when O_2 is a reactant)
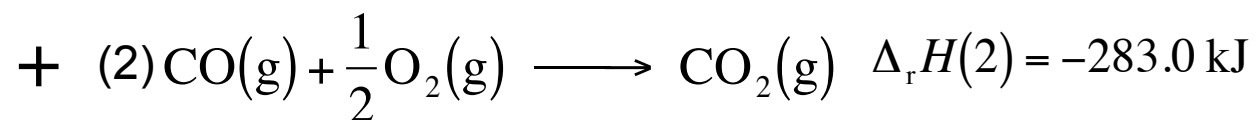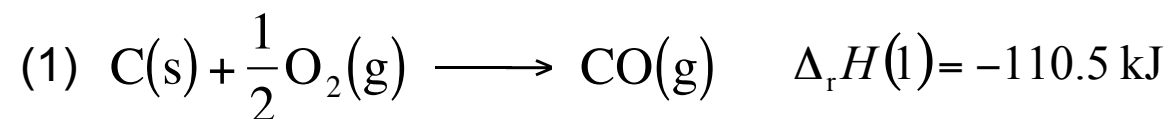
Endothermic: water-gas reaction,

$$C(s) + H_2O(g) \longrightarrow CO(g) + H_2(g)$$

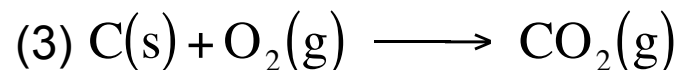$$\Delta_r H = 131 \text{ kJ} \quad \text{at } 298 \text{ K} \qquad \text{(heat is required to drive the reaction)}$$

Enthalpy Is Additive

ΔH is a state function, which means it is an additive property

Given $\Delta_r H$ values for (1) and (2)

(1) $C(s) + \dfrac{1}{2}O_2(g) \longrightarrow CO(g) \qquad \Delta_r H(1) = -110.5 \text{ kJ}$

$+$ (2) $CO(g) + \dfrac{1}{2}O_2(g) \longrightarrow CO_2(g) \qquad \Delta_r H(2) = -283.0 \text{ kJ}$

Summation provides $\Delta_r H$ for (3)

(3) $C(s) + O_2(g) \longrightarrow CO_2(g)$

$$\Delta_r H(3) = (-110.5 \text{ kJ}) + (-283.0 \text{ kJ}) = -393.5 \text{ kJ}$$

THERMITE REACTION

$$Fe_2O_3\ (s)\ +\ 2\ Al\ (s)\ \longrightarrow\ Al_2O_3\ (s)\ +\ 2\ Fe\ (s)$$

rust

or

alumina (Al source)

$$Al_2O_3\ (s)\ +\ 2\ Fe\ (s)\ \longrightarrow\ Fe_2O_3\ (s)\ +\ 2\ Al\ (s)$$
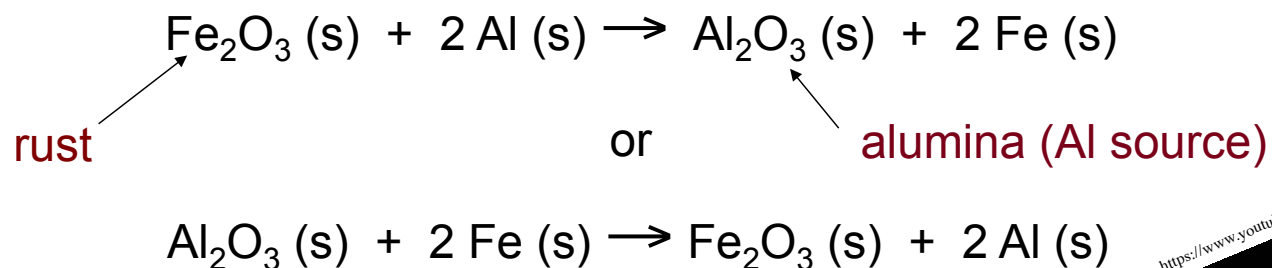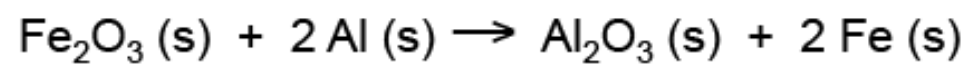
Which way does this reaction go? Why?

Will the metal that is produced melt? How do you know?

The energetics of reactions are important for all chemical processes! For example: H_2SO_4, polyethylene, pharmaceuticals, soaps, food products, petroleum cracking, biochemical processes, etc.
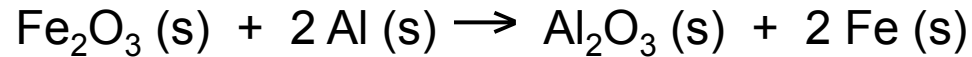
Thermit Welding on Railway Track

Lecture 0

Heat Suitable for Welding

$$Fe_2O_3 \text{ (s)} + 2\,Al \text{ (s)} \longrightarrow Al_2O_3 \text{ (s)} + 2\,Fe \text{ (s)}$$

THERMITE REACTION — EXOTHERMIC

$$Fe_2O_3\ (s)\ +\ 2\ Al\ (s)\ \longrightarrow\ Al_2O_3\ (s)\ +\ 2\ Fe\ (s)$$

assess change in *enthalpy* for a given direction

$$\Delta H_{rxn} \approx -850\ kJ/mol = -850,000\ J/mol$$

Released heat can *raise temperature* and *melt solids*

$$\Delta H_{fus}(Fe) \approx 14\ kJ/mol \qquad \Delta H_{fus}(Al) \approx 11\ kJ/mol$$

$$C_p\ (Fe) \approx 25\ J/mol\bullet °C \qquad C_p\ (Al_2O_3) \approx 128\ J/mol\bullet °C$$

Adiabatic temperature rise? T > 2,500 °C!   *MP* (Fe) = 1530 °C

Home work

Next: 1. How to tabulate Enthalpy of a reaction ?

2"Standard Enthalpy"

3. Tutorial