

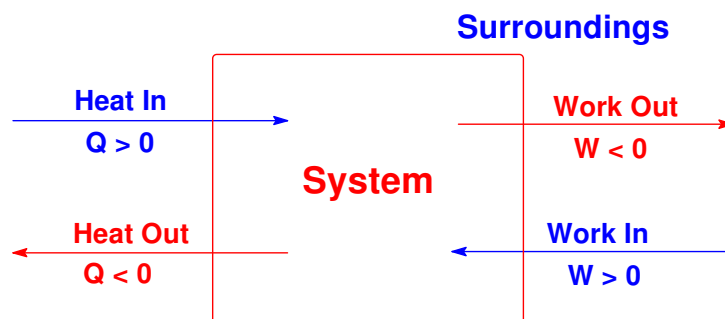
Chemical Thermodynamics -- Chapter 18 (and 6.1 - 6.5)

Energy Changes in Chemical Reactions

1. First Law of Thermodynamics (conservation of energy)

$$\Delta E = q + w \quad \text{where, } q = \text{heat absorbed by system} \\ w = \text{work done on system}$$

Sign Conventions: $q (+)$ \rightarrow system absorbs heat
 $w (+)$ \rightarrow work done on system



$E = \text{internal energy}$ = sum of all potential and kinetic energy of the system

$$\Delta E = E_{\text{final}} - E_{\text{initial}}$$

E is a "state function" - independent of pathway
but, q and w are not! (they do depend on pathway)

2. Pressure - Volume Work

in general:

q (heat) is "easy" to measure (by calorimetry), but
w (work) is not, except for reactions that involve gases

for *gaseous* systems:

$$w = -P\Delta V \quad \text{where } \Delta V = V_{\text{final}} - V_{\text{initial}} \\ \text{and } P = \text{opposing pressure}$$

e. g., for a gas expanding against a piston:

ΔV is (+) since $V_{\text{final}} > V_{\text{initial}}$

and w is (-) so the system does work on surroundings

3. Heats of Reaction

(a) *at constant volume*

$$\Delta V = 0 \quad \text{thus, } w = -P\Delta V = 0$$

$$\text{and, } \Delta E = q + w = q$$

$$\Delta E = q_v \quad (\text{heat change at constant volume})$$

(b) *at constant pressure*

define a new state function called **enthalpy (H)**

$$H = E + PV$$

$$\text{or, } \Delta H = \Delta E + P(\Delta V)$$

substituting, $\Delta E = q - P(\Delta V)$ yields:

$$\Delta H = q_p \quad (\text{heat change at constant pressure})$$

(c) conversions between ΔE and ΔH

from above, $\Delta H - \Delta E = P\Delta V$

difference is the $P\Delta V$ term, the P-V work
usually small, unless gases are involved

when combined with ideal gas law ($PV = nRT$),

$$\Delta H = \Delta E + \Delta nRT$$

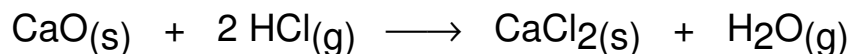
where, $\Delta n = n_{\text{final}} - n_{\text{initial}}$
(change in total # moles of gas)

be careful with units !

$$R = 0.0821 \text{ L}\cdot\text{atm}\cdot\text{mole}^{-1}\text{K}^{-1} = 8.314 \text{ J}\cdot\text{mole}^{-1}\text{K}^{-1}$$

Problem:

Calculate ΔE° for the following reaction, for which
 $\Delta H^\circ = -217.1 \text{ kJ}$.



$$\Delta n = 1 - 2 = -1 \text{ mole}$$

$$\Delta H^\circ = \Delta E^\circ + \Delta nRT$$

$$-217.1 \text{ kJ} = \Delta E^\circ + (-1 \text{ mole})(8.314 \times 10^{-3} \text{ kJ / mole K})(298 \text{ K})$$

$$\Delta E^\circ = -214.6 \text{ kJ} \text{ (difference of only about 1\%)}$$

Entropy and Spontaneity

1. Two factors effect any change or reaction

(a) Enthalpy (H)

exothermic processes (negative ΔH)
tend to be spontaneous, but not always

(b) Entropy (S) ~ degree of disorder or randomness

higher entropy ~ greater energy dispersal

change in entropy: $\Delta S = S_{\text{final}} - S_{\text{initial}}$

for a reaction: $\Delta S = S_{\text{products}} - S_{\text{reactants}}$

positive ΔS means:

an increase in disorder as reaction proceeds
products more disordered (random) than reactants

in general: $S_{\text{gas}} \gg S_{\text{liquid}} > S_{\text{solid}}$

for a reaction, **positive ΔS favors spontaneity**

2. Second Law of Thermodynamics

"...for any spontaneous process, the overall entropy of the universe increases..."

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

a spontaneous process can have a negative ΔS_{sys} for the system
only if the surroundings have a larger positive ΔS_{surr}

3. Third Law of Thermodynamics

"...the entropy of a pure crystalline substance equals zero at absolute zero..."

$$S = 0 \text{ at } T = 0^\circ \text{ K}$$

(a) **Standard Entropy (at 25°C) = S°** [see Table 18.2]

Entropy change for a reaction:

$$\Delta S^\circ = \sum S^\circ(\text{products}) - \sum S^\circ(\text{reactants})$$

(b) **Gibbs Free Energy = G**

defined as: $G = H - TS$

- a combination of enthalpy and entropy effects
- related to maximum useful work that system can do

for a process (e.g., a reaction),

$$\Delta G = \Delta H - T\Delta S$$

for any spontaneous change, ΔG is negative
(the free energy decreases)

4. **Standard Free Energy**

ΔG° (at STP) generally used to decide if a reaction is spontaneous (Yes, if negative)

Two ways to obtain ΔG° for a reaction

(a) **from ΔH° and ΔS°** requires ΔH°_f and S° data for all reactants and products

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta H^\circ = \sum \Delta H^\circ_f(\text{products}) - \sum \Delta H^\circ_f(\text{reactants})$$

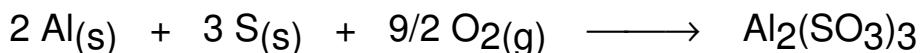
$$\Delta S^\circ = \sum S^\circ(\text{products}) - \sum S^\circ(\text{reactants})$$

(b) from standard “Free Energies of Formation” ΔG°_f

$$\Delta G^\circ = \sum \Delta G^\circ_f (\text{products}) - \sum \Delta G^\circ_f (\text{reactants})$$

where ΔG°_f is the free energy change for the formation of one mole of the compound from its elements, e.g.,

ΔG°_f for $\text{Al}_2(\text{SO}_3)_3$ equals ΔG° for the following reaction



5. Free energy and Equilibrium

(a) for a system at equilibrium:

$$G_{\text{products}} = G_{\text{reactants}} \quad \text{and} \quad \Delta G = 0$$

since, $\Delta G = \Delta H - T\Delta S = 0$

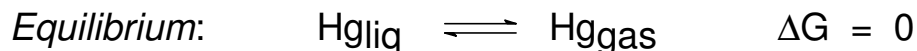
$$\Delta H = T\Delta S \quad \text{or} \quad T = \Delta H / \Delta S$$

Problem:

Given the following, determine the normal boiling point of mercury (Hg).

$$\Delta H_{\text{vaporization of Hg}} = 60.7 \text{ kJ / mole}$$

entropies:	liquid Hg:	$S^\circ = 76.1 \text{ J / mole K}$
	gaseous Hg:	$S^\circ = 175 \text{ J / mole K}$



$$\text{so, } \Delta H - T\Delta S = 0 \quad \text{or} \quad T = \Delta H / \Delta S$$

$$T = [60.7 \times 10^3 \text{ J / mole}] \div [(175 - 76.1) \text{ J / mole K}]$$

$$T = 614 \text{ K}$$

(b) Effect of Temperature on ΔG

ΔG depends on ΔH and ΔS : $\Delta G = \Delta H - T\Delta S$

but ΔH and ΔS are relatively independent of temperature,
so ΔG at some temperature T can be estimated:

$$\Delta G^\circ_T \approx \Delta H^\circ_{298} - T\Delta S^\circ_{298}$$

(c) Relationship between ΔG° and Equilibrium Constant (K)

For any chemical system:

$$\Delta G = \Delta G^\circ + (RT) \ln Q$$

**if ΔG is not zero, then the system is not at equilibrium
it will spontaneously shift toward the equilibrium state**

At Equilibrium: $\Delta G = 0$ and $Q = K$

$$\therefore \Delta G^\circ = -RT \ln K$$

for gaseous reactions: $K = K_p$

for solution reactions: $K = K_c$

{ units of ΔG must match those of R value }

K values can be determined from thermodynamic data !

Note: when $K > 1$ ΔG° is negative

**\therefore spontaneous reactions have
large K and negative ΔG° values**