



# Thermodynamics and Equilibrium

# Overview



- First Law of Thermodynamics
- Spontaneous Processes and Entropy
  - Entropy and the Second Law of Thermodynamics
  - Standard Entropies and the Third Law of Thermodynamics
- Free Energy Concept
  - Free Energy and Spontaneity
  - Interpretation of Free Energy
- Free Energy and Equilibrium Constants
  - Relating  $\Delta G^\circ$  to the Equilibrium Constant
  - Change of Free Energy with Temperature

# First Law of Thermodynamics



- First law can be written as:

$$\Delta E = q + w$$

where  $q$  = heat involved in the process and  $w$  = work done by or to the system.

- Work can be electrical or pressure –volume
- **Work** = force acting over some distance:  $w = - d \times F$  (referenced to the system).
  - During reactions often there is an expansion of gases against some pressure where pressure is equal to the force per unit area:

$$P = \frac{F}{A} \text{ or } F = P \times A$$

- Work is obtained by substitution:
  - $w = - d \times F = - d \times (P \times A)$  or
  - $w = - P \Delta V$ .
- The first law can be restated as  $\Delta E = q - P \Delta V$ .

# Energy and Enthalpy



- From the first law:  $q = \Delta E + P\Delta V$ .
- With no change in volume the equation simplifies to  $q_V = \Delta E$ .
- At constant pressure:  $q_P = \Delta E + P\Delta V$ .
- There are times when both volume and pressure can change; the heat involved in the reaction is then a more complicated function of  $\Delta E$ .
- **Enthalpy:** the heat output at constant pressure.  $H = E + PV$ .
- In general,  $\Delta H = \Delta E + P\Delta V + V\Delta P$ .
- At constant pressure, a change in enthalpy is given by:
$$\Delta H = \Delta E + P\Delta V = q_P.$$
- Normally,  $\Delta H$  and  $\Delta E$  are fairly close to each other in magnitude. In the combustion of propane (see book),  $\Delta E = -2043$  kJ,  $\Delta H = -2041$  kJ and  $w = -P\Delta V = -2$  kJ.

# ENTROPY



- **Entropy:** thermodynamic quantity that is measure of randomness of system.
- All changes tend to increase in randomness (second law of thermodynamics).

$$\Delta S_{\text{total}} = S_{\text{final}} - S_{\text{initial}}$$

$$\Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \geq 0.$$

- $\Delta S_{\text{sys}}$  is sometimes negative, but is more than offset by  $\Delta S_{\text{surr}}$ .
- $\Delta S$  is positive for a transition from ordered to less ordered system (such as with melting and vaporization) and negative for the reverse.

# Entropy and the Second Law



- **Second Law:** all systems tend towards an increase in the randomness of the system. In terms of entropy, the total entropy of the universe always increases.
  - $\Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \geq 0.$
  - $\Delta S_{\text{rev}} = -\Delta S_{\text{fwd}}.$
  - $\Delta S_{\text{surr}} = \frac{-\Delta H}{T}$
- $\Delta S$  of phase change determined from heat of phase change.  $\Delta S = \Delta H/T.$

# Entropy and Probability



- Randomness is related to the probability of finding a molecule in a particular microstate;  
E.g. determine the probability of having perfectly order system (HH) when:
- Two microstates (heads, H, and tails,T) of same exact energy (same likelihood of existing).
- Two particles. Then the possible states are: HH, TT, TH, HT.  
Probability, P, of perfectly order system 25% ( $P_{HH} = 2^{-2} \cdot 100\%$ ).  
E.g.2 determine  $P_{HHH}$  for 3 particles.
- Possible states: HHH, TTT, HHT, HTH, THH, HTT,THT, TTH. ( $P_{HHH} = 2^{-3} \cdot 100\%$ ).
- Ludwig Boltzmann = statistical approach to entropy, S, given by  $S = k \cdot \ln W$  where  $k = \text{Boltzmann's const.} = R/N = 1.38 \times 10^{-23} \text{ J/K}$ .
- $W = \text{total \# of ways that all atoms in a sample can be arranged and still have same energy.}$

E.g. Determine molar entropy of CO (2 states) and HCl (1 state) molecules in a crystal.

# Entropy and Probability



- **Third Law** = perfectly ordered crystal has zero entropy.
- entropy change when molecules filling a container after expansion is related probability of this expansion and is given by the relationship (constant T and n):

$$\begin{aligned}\Delta S &= R \ln \frac{V_{\text{final}}}{V_{\text{initial}}} \\ &= R \ln \frac{P_{\text{initial}}}{P_{\text{final}}}\end{aligned}$$