

**Basic Concepts in Chemical Thermodynamics**  
 (Chapter 19, Chemistry The Central Science, 13<sup>th</sup> ed., Brown et al.)  
 Excerpts for BIOC 221 by D-Y Suh

(1) How fast is the reaction? (depends on energy barrier and temperature)

The Arrhenius equation:  $k = A \cdot \exp(-E_a/RT)$

$A$  : frequency factor for productive collision

$E_a$  : activation energy (minimum energy required to initiate a chemical reaction)

$T$  : temperature

$k$  increases as  $T$  increases (approx. doubles for each 10°C increase)

as  $E_a$  decreases (The lower energy barrier to overcome, the faster a reaction proceeds)

(2) How far does the reaction proceed to one direction?

(till equilibrium reaches when the opposing reactions occur at equal rates.)

(3) In which direction a reaction will proceed spontaneously and release (free) energy?

To what extent (how much energy is released)?

**[1] The First Law of Thermodynamics (p. 170)**

$E$ : Internal energy of a system; the sum of all the kinetic and potential energies of all its components.

Energy transfer between systems and surroundings in two general ways, as work or heat

$$\Delta E = q + w \quad \text{--- ①}$$

$\Delta E$  : change in internal energy of a system

$q$  : heat added to a system

$w$  : work done on a system

$\Delta E > 0$ , when heat is added to the system ( $q > 0$ , endothermic), or work is done on the system ( $w > 0$ ).

A system loses its internal energy ( $\Delta E < 0$ ) by losing heat to the surroundings ( $q < 0$ , exothermic) or doing work on the surroundings ( $w < 0$ ).

However, it is difficult to measure  $\Delta E$ . We'd like to have another thermodynamic quantity, which is similar to  $\Delta E$  but can be measured.

Lucky for us chemists, many chemical reactions occur at constant pressure ( $P$ ).

Can we then have a thermodynamic variable that makes it easy to measure energy change ( $\Delta E$ ) at constant  $P$ ?

Often, the only kind of work produced by chemical changes is pressure-volume work ( $P \updownarrow, V \updownarrow$ ) and at constant  $P$ ,

$$w = -P\Delta V \text{ (negative as the system does work on the surroundings, losing energy) --- ②}$$

Now, let us define a thermodynamic quantity, enthalpy ( $H$ ) as:

$$H = E + PV$$

where  $H$  is the sum of internal energy plus the product of the pressure and volume.

$$\Delta H = \Delta E + \Delta(PV)$$

$$\Delta H = \Delta E + P\Delta V \text{ (at constant } P, \Delta P = 0) \text{ --- ③}$$

# Chapter 19 Chemical Thermodynamics Test Bank

**F Rizvi**



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