

# ***AP Chemistry***

## **Thermodynamics Summary**

### **Terminology:**

**Spontaneity:** The notion of whether or not a process can take place unassisted.

**Entropy:** A measure of how energy is spread out among the atoms and molecules of a system.

**Free Energy:** A thermodynamic function that relates enthalpy and entropy to spontaneity.

### **Thermodynamics:**

-Determines if a process is possible and spontaneous and the equilibrium state of the system (how far the reaction will proceed)

-Kinetics determines the rate of the process.

### **Review of Thermochemistry**

For Pressure-Volume Work

$\Delta U = q + P\Delta V$                        $\Delta U$  is the internal energy change of the system

$q_p = \Delta U - P\Delta V$                       (at constant pressure)

$q_p = \text{Enthalpy change} = \Delta H$     (negative = exothermic; positive = endothermic)

### **Reaction spontaneity: Driven by two factors**

**Enthalpy  $\Delta H$**  (heat of the reaction)

**Spontaneity is favored by exothermic ( $-\Delta H$ )**

**Entropy,  $S$**     related to energy distribution within a system (the availability and occupation of energy states that is usually akin to the measure of “disorder” in a system).

**Spontaneity favored by increase in entropy ( $+\Delta S$ )**

*Reversible processes are in equilibrium*

*Spontaneous processes are not reversible*

*Enthalpy and entropy are both “state functions”*

*Entropy is the basis for the second law of thermodynamics (Sadi Carnot – 1820’s)*

### **Factors that increase the entropy of a system:**

Phase change Solid < Liquid < Gas (Randomness of particles and separation)

Nonelectrolyte solutions of solids or liquids in a solvent (random mixing of particles)

A reaction that increases the molecules of a gas

A substance is heated

The number of atoms in a substance (greater vibrational modes)

The molar mass of a substance.

### **Laws of Thermodynamics:**

1<sup>st</sup> Law: The energy of the universe is constant (conservation law)

2<sup>nd</sup> Law: The entropy of the universe is always increasing

3<sup>rd</sup> Law: The entropy of a perfect, pure crystal at 0K is zero.

## Equation for Entropy

$$\Delta S = q_{\text{rev}}/T \quad (\text{Constant Temperature})$$

Where:

$q_{\text{rev}}$  = heat involved in a reversible process (such as (approximately) the melting and freezing of water at 298K and 1atm). Adding heat,  $q$ , to a system increases atomic and molecular motion.

T is in the denominator because at higher temperatures the addition of heat has less of an effect on the entropy. (The proportional increase with temperature in the number of energy levels is greater at lower temperatures)

Absolute entropy is determined by cooling a pure crystal to near absolute zero and then adding small increments of heat while monitoring the temperature. The summation of the small increments gives the absolute entropy of the substance.

Since  $\Delta U$  and  $\Delta H$  are state functions, but  $q$  &  $w$  are not; to be reversible, the system must be an infinitesimal amount away from equilibrium.

## Derivation of the Gibb's Free Energy Equation:

Free energy is the "free energy" a system possesses to drive a spontaneous reaction or it is the minimum energy required to drive a reaction in a nonspontaneous direction.

**For the 2<sup>nd</sup> Law of Thermodynamics:**

$$\Delta S_{\text{univ}} = \Delta S_{\text{surr}} + \Delta S_{\text{sys}} \quad >0$$

$$\Delta S_{\text{sys}} = q_{\text{rev}}/T = \Delta H_{\text{sys}}/T$$

Since the system exchanges energy with its surroundings:

$$\Delta S_{\text{surr}} = -\Delta H_{\text{sys}}/T$$

Substituting:

$$\Delta S_{\text{univ}} = -\Delta H_{\text{sys}}/T + \Delta S_{\text{sys}} \quad \text{multiplying through by } T$$

$$T\Delta S_{\text{univ}} = -\Delta H_{\text{sys}} + T\Delta S_{\text{sys}} \quad \text{multiplying through by } -1$$

$$-T\Delta S_{\text{univ}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}}$$

$-T\Delta S_{\text{univ}}$  is given the special symbol  $\Delta G$  and is known as **Gibb's Free Energy**

The final form of the equation is:

$$\Delta G = \Delta H - T\Delta S \quad \text{This equation is written totally in terms of the system, not the surroundings.}$$

## Sign of $\Delta G$ and Spontaneity

$$\Delta G < 0 \quad \text{Spontaneous}$$

$$\Delta G > 0 \quad \text{Nonspontaneous (Spontaneous in reverse direction)}$$

$$\Delta G = 0 \quad \text{Equilibrium}$$

Sign of Enthalpy	Sign of Entropy	Spontaneous?
-	+	Yes
+	-	No
+	+	Depends on T (Entropy driven)
-	-	Depends on T (Enthalpy driven)

## Calculating $\Delta G^\circ$ , $\Delta H^\circ$ , $\Delta S^\circ$ from Tabulated Data for a Reaction ( $^\circ$ = standard state):

### Standard State

- Solid or liquid = Pure substance at 1atm pressure (actually 1bar =  $1 \times 10^5$ Pa) at the temperature of interest.
- Gases = Pure gas behaving ideally at 1atm pressure at the temperature of interest.

$$\Delta G^\circ = \sum m \Delta G_{f, \text{prod}}^\circ - \sum n \Delta G_{f, \text{react}}^\circ$$

$$\Delta S^\circ = \sum m S_{\text{prod}}^\circ - \sum n S_{\text{react}}^\circ$$

$$\Delta H^\circ = \sum m \Delta H_{f, \text{prod}}^\circ - \sum n \Delta H_{f, \text{react}}^\circ$$

where m and n are the coefficients of the balanced equation.

**Watch Units!** Enthalpy is usually given in kJ/mol, free energy in kJ/mol and entropy in J/molK

## Free Energy Change and Equilibrium

At equilibrium  $\Delta G = 0$

$$\Delta H = T\Delta S$$

At *normal* boiling point  $\cong$  standard states (1atm)

$$\Delta S_{\text{vapn}}^\circ = \Delta H_{\text{vapn}}^\circ / T_{\text{bp}} \cong \mathbf{87 \text{ J/molK}} \quad \mathbf{\text{Trouton's rule}}$$

This molar enthalpy change is approximately the same for all nonpolar substances (i.e. those without strong intermolecular attractions like hydrogen bonding)

## Reassessing Raoult's Law

$$P_{\text{solv}} = x_{\text{solv}} P_{\text{solv}}^\circ \quad (x = \text{mole fraction of solvent})$$

### Assumptions

Enthalpy of vaporization is the same for pure solvent and solution

Entropy of solution is higher than that of the pure liquid

Entropy of vaporization is approximately the same given  $\Delta S_{\text{vapn}} = \Delta H_{\text{vapn}} / T$

Therefore: The vapor above the liquid must be at higher entropy.

This is achieved through decreasing the pressure giving molecules more room to move around.

## $\Delta G^\circ$ and $K_{eq}$

$\Delta G^\circ = 0$  is for equilibrium at a single temperature in which reactants and products are in their standard states.

Given:

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

At equilibrium (nonstandard)  $\Delta G = 0$ ,  $Q = K_{eq}$

$$\Delta G^\circ = -RT \ln K_{eq} \quad \text{Important Equation} \quad \text{Watch Units!}$$

Conditions:

$$R = 8.314 \text{ J/molK}$$

T is in kelvins, K

$K_{eq}$  is written in terms of dimensionless "activities"

Conventions for "activities"

Pure solid and liquid phases: Activity "a" = 1

Gases: Numerical partial pressure in atm (ideal)

Solutes and aqueous solutions: Numerical value of solute molarity (dilute, ideal)

Note that  $K_{eq}$  may not necessarily equal  $K_c$  or  $K_p$ .

## Temperature effects on $\Delta G^\circ$ and $K_{eq}$

Determining  $K_{eq}$  at different temperatures

Assumption:  $\Delta H$  and  $\Delta S$  don't change much with temperature ( $\Delta H^\circ_f$  and  $S^\circ$  for reactants and products change in the same way with temperature)

Therefore, standard values may be used.

$$\Delta H^\circ - T\Delta S^\circ = \Delta G^\circ = -RT \ln K_{eq}$$

$$\ln K_{eq} = -\Delta H^\circ/RT + \Delta S^\circ/R \quad y = mx + b \text{ form}$$

**van't Hoff Equation** (Using rules of logarithms)

$$\ln(K_2/K_1) = \Delta H^\circ/R (1/T_1 - 1/T_2) \quad (\text{for calculating } K \text{ at different } T)$$

Other versions of the equation

## Clausius-Clapeyron Equation

$$\ln(P_2/P_1) = \Delta H^\circ_{vapn}/R (1/T_1 - 1/T_2) \quad (\text{vapor pressure calculation})$$

or

$$\ln(P_2/P_1) = \Delta H^\circ_{subl}/R (1/T_1 - 1/T_2)$$