Ch 18 – Thermodynamics and Equilibrium

Thermodynamics is the study of the relationship between heat and
other forms of energy that are involved in a chemical reaction.

Internal Energy (U)
− Internal energy is the sum of the kinetic and potential energies of the individual molecules.
− Both internal energy (U) and enthalpy (H) are state functions.
  That is, they depend only on the present state, not on their history.
− A state function is completely determined by other state functions.
  For example, U is determined by T and P.

1st Law of Thermodynamics
− ΔU can be used to describe thermodynamic changes to a system due to a reaction.
  $\Delta U = U_f - U_i = q + w$ where q is heat and w is work
− q is positive when heat is added to system, negative when heat is released
− w is positive when work is done to system, negative when work is done by the system
− For constant force, work is force times distance. $w = F(\Delta x)$
− In a gravitational field, $F = mg$ where m is mass and g is the gravitational constant, 9.8 m/s^2.
− Work done by gravity is found by $w = F(\Delta h) = mg(\Delta h)$, where (Δh) is change in height.
− For an expanding gas that is doing work by making a gas piston move upwards: $w = - F(\Delta h)$
− Volume of a cylinder is area times height. $V = A \times h$ $\Delta V = A(\Delta h)$

  So, work is a function of ΔV for the gas. $w = - F(\Delta h) = - F\left(\dfrac{\Delta V}{A}\right) = -\left(\dfrac{F}{A}\right)(\Delta V)$

− Pressure is force over area: $P = F/A$. This gives us $w = - P(\Delta V)$ for an expanding gas piston.
− Suppose a 1.0 kg weight pushes a gas piston downwards by 1.5 m, and 2.0 J are released as
  heat due to friction during the process. Find the q, w, and U for the gas piston.
  $w = - mg(\Delta h) = - (1.0 \text{ kg})(9.8 \text{ m/s}^2)(- 1.5 \text{ m}) = + 14.7 \text{ kg·m}^2/\text{s}^2 = + 14.7 \text{ J}$ (Gas absorbs E)
  $q = - 2.0 \text{ J}$ (Gas releases E) $\Delta U = q + w = (- 2.0) + (+ 14.7) = + 12.7 \text{ J}$

Enthalpy
− $H = U + PV$ and $\Delta H = H_{final} - H_{initial} = \Delta U + \Delta(PV)$
− If pressure is constant, then $\Delta P = 0$. This gives us $\Delta H = \Delta U + P(\Delta V)$.
− $\Delta U = q - P(\Delta V)$ can be substituted into the equation.
  The result is: $\Delta H = q - P(\Delta V) + P(\Delta V) = q_P$
  So, the change in enthalpy is equal to the heat of reaction at constant pressure.
− See Appendix G or here for standard enthalpies of formation ($\Delta H°_f$) for chemical substances.
− Standard enthalpy of reaction ($\Delta H°$) is at 1 atm and 298 K.
  It can be found by the difference between enthalpies of formation for products and reactants.
− $\Delta H° = \sum n\Delta H_f° \text{ (prod)} - \sum m\Delta H_f° \text{ (react)}$ where n and m are stoichiometric coefficients.

Example 18.01 Enthalpy for Decomposition of Urea into Ammonia and Carbon Dioxide
- $1(NH_2)_2CO_{(s)} + 1H_2O_{(L)} \rightleftharpoons 2NH_{3(g)} + 1CO_{2(g)}$ (Except for urea, refer to <u>Appendix G</u>)
- $\Delta H^o = [2 \times \Delta H^o_f(NH_{3(g)}) + 1 \times \Delta H^o_f(CO_{2(g)})] - [1 \times \Delta H^o_f((NH_2)_2CO_{(s)}) + 1 \times \Delta H^o_f(H_2O_{(L)})]$
- $\Delta H^o = [2 \times (-45.9) + (-393.51)] - [(-333.2) + (-285.83)] = +133.7$ kJ per mol of urea

Entropy
- Entropy (S) is a measure of the randomness or disorder in a system.
- It measures how dispersed the energy of a system is among the possible energy states. That is, it describes how randomly the energy is distributed.
- Randomized energy is disordered and is not usable to perform work (w).
- Entropy is equivalent to the amount of randomized (unusable) energy per unit temperature and is measured in units of energy divided by temperature (J/K).

Entropy of a Phase Change
- Heat flow is needed for a phase change, and it involves entropy because it disperses energy.
- Heat flow randomizes energy, and entropy associated with heat flow equals q/T.
- For a phase change, or for any process that occurs only near equilibrium (Q stays near K), no other entropy is created and $\Delta S = q/T$.
- **$\Delta S = \Delta H/T$ for a phase change** (melting, freezing, etc.)

2nd Law of Thermodynamics
- **The total combined entropy of a system and its surroundings always increases for a spontaneous process, that is (Entropy Created) > 0**
- A spontaneous process is one which randomizes (releases) energy and creates disorder.
- For a spontaneous process: $\Delta S = $ (entropy created) $+ q/T$. The result is that $\Delta S > q/T$ because (entropy created) > 0.
- If $\Delta S > \Delta H/T$, then **$\Delta H - T\Delta S < 0$ for a spontaneous process**.
- $\Delta H - T\Delta S > 0$ for a nonspontaneous process
- $\Delta H - T\Delta S = 0$ for an equilibrium process.

3rd Law of Thermodynamics
- **A perfectly crystalline solid at absolute zero (0 K) has S = 0. That is, it has no disorder.**
- Standard Entropy (S^o) for an atom, molecule, or ion is measured at 1 atm and 298 K.
- See <u>Appendix G</u> or <u>here</u> for standard entropy values (S^o) of chemical substances.
- There is no "Δ" or "$_f$" in S^o because it is not measured the same way as ΔH^o_f.
- S^o is actual total entropy. It is measured by integrating from absolute zero (0 K), where S = 0, up to the final T of 298 K.
- ΔH^o_f is based completely on chemical reactions at 298 K.
- Unlike ΔH^o_f, values of S^o are nonzero and positive for elements.
- For a chemical reaction: **$\Delta S^o = \sum nS^o(\text{prod}) - \sum mS^o(\text{react})$** where n and m are stoichiometric coefficients.

ΔS^o (Entropy of Reaction)
- Entropy generally increases ($\Delta S^o > 0$) if any of the following occur:
  - o A molecule is broken into two or more smaller molecules. (decomposition or elimination)
  - o There is an increase in moles of gas.
  - o The phase changes from solid to liquid or gas, or from liquid to gas. (phase becomes less condensed)
- If the reverse of these conditions occur, then $\Delta S^o < 0$.

Example 18.02 Is ΔS^o positive or negative?
a. One mol of fructose (s) ferments into two mol of ethanol (liq) and two mol of CO_2 (g).
    This a decomposition reaction. Total moles and moles of gas both increase. $\Delta S^o > 0$
b. $2NH_{3(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(L)} + (NH_2)_2CO_{(aq)}$
    The total number of moles and the number of gas moles both decrease. $\Delta S^o < 0$
c. $CH_{4(g)} + 2O_{2(g)} \rightleftharpoons 2H_2O_{(g)} + CO_{2(g)}$
    The sign cannot be determined easily because both the total moles and the gas moles do not change. However, the absolute value would be a relatively small number (< 50 J/K).

Example 18.03 Calculating ΔS^o for a Reaction (Except for urea, refer to Appendix G)
- $1(NH_2)_2CO_{(s)} + 1H_2O_{(L)} \rightleftharpoons 2NH_{3(g)} + 1CO_{2(g)}$
- $\Delta S^o = [2\times S^o(NH_{3(g)}) + 1\times S^o(CO_{2(g)})] - [1\times S^o(\,(NH_2)_2CO_{(s)}) + 1\times S^o(H_2O_{(L)})]$
- $\Delta S^o = [2\times(192.8) + (213.8)] - [(104.6) + (70.0)] = (424.8 \text{ J/K})\left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right) = + 0.4288$ kJ/K

Gibb's Free Energy (G), named after J. Willard Gibbs, is found by $G = H - TS$
- For a chemical reaction, the change in free energy is $\mathbf{\Delta G^o = \Delta H^o - T\Delta S^o}$.
- ΔG^o is the maximum energy available to do useful work ($\mathbf{\Delta G^o = w_{max}}$) because it is the difference between the total energy change and the randomized (unusable) energy change.
- The degree sign symbol (^{o}) is for standard state, where $T = 298$ K and each solute's concentration is 1 mol/L. For a reaction involving only liquids and/or solids, the standard total pressure is 1 atm. If gases are involved, each gas has a partial pressure equal to 1 atm.
- If a reaction is **spontaneous**, then $\mathbf{\Delta G < 0}$ **(negative).**
  $\Delta H - T\Delta S < 0$ for all spontaneous processes according to the 2nd law of thermodynamics.
- ΔG^o_f is the free energy of formation from elements in their reference forms at standard state.
- Note: $\Delta G^o_f \neq \Delta H^o_f - TS^o$ does not work for individual substances because S^o is not ΔS^o_f.
- For a reaction $\mathbf{\Delta G^o = \sum n\Delta G^o_f (prod) - \sum m\Delta G^o_f (react)}$ where n and m are stoich coeffs.
- ΔG^o can be found from either the summation equation or the enthalpy/entropy equation.
- See Appendix G or here for standard Gibb's free energy values (ΔG^o_f) of substances.
- Convert S to kJ/K when using $G = H - TS$ equations, where G and H are already in kJ.

Example 18.04 Calculating ΔG^o from ΔH^o and ΔS^o for a reaction
- Use $\Delta H^o{}_f$ and S^o values from Appendix G.
- $1N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$
- $\Delta H^o = [2\times(-45.9)] - [1\times(0.0) + 3\times(0.0)] = -91.8$ kJ (exothermic)
- $\Delta S^o = [2\times(192.8)] - [(191.6) + 3\times(130.7)] = (-198.1$ J/K$)\left(\frac{1\ kJ}{1000\ J}\right) = -0.1981$ kJ/K
- $\Delta G^o = \Delta H^o - T\Delta S^o = (-91.8$ kJ$) - (298$ K$)(-0.1981$ kJ/K$) = -32.8$ kJ
- The reaction is spontaneous at standard state because ΔG^o is negative.

Example 18.05 Calculating ΔG^o for a reaction by using $\Delta G^o{}_f$ for each substance
- Use $\Delta G^o{}_f$ values from Appendix G.
- $1C_2H_5OH_{(L)} + 3O_{2(g)} \rightleftharpoons 2CO_{2(g)} + 3H_2O_{(g)}$
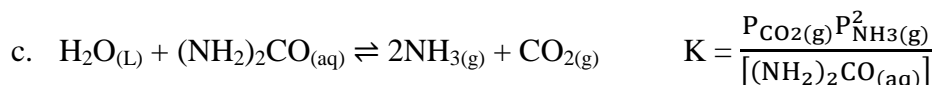- $\Delta G^o = [2\times(-394.36) + 3\times(-228.59)] - [1\times(-174.8) + 3\times(0.0)] = -1299.7$ kJ (Spontaneous)

Criterion for Spontaneity (This is similar to interpreting Kc)
- If ΔG^o is a **negative** number with a large magnitude, the reaction is **spontaneous** as written,
  and the reactants transform almost completely to form products.
- If ΔG^o is a large **positive** number, the reaction is **not spontaneous** as written,
  and the reactants do not form significant amounts of products.
  The reaction is generally spontaneous in reverse.
- If ΔG^o has a **small** magnitude (pos. or neg.), the reaction gives an equilibrium mixture
  containing significant amounts of **both reactants and products**.

Thermodynamic Equilibrium Constant (K)
- Includes **gas** concentrations expressed as the **partial pressure** (P, in atm),
  and dissolved (aqueous) **solute** concentrations expressed as **molarity** (M).
- The expression for K can include both gas pressures and solute molarities together.
- Solids and pure liquids are still omitted from the expression.
- If a reaction includes only gases, then $K = K_p$.
- If a reaction includes only aqueous solutes, then $K = K_c, K_a, K_b, K_{sp}, K_f$ or K_d.

Example 18.07 Writing Expressions for Thermodynamic K

a. $AgI_{(s)} \rightleftharpoons Ag^{+1}{}_{(aq)} + I^{-1}{}_{(aq)}$ $K = K_{sp} = [Ag^{+1}{}_{(aq)}][I^{-1}{}_{(aq)}]$

b. $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ $K = K_p = \dfrac{P^2_{NH3(g)}}{P_{N2(g)}P^3_{H2(g)}}$

c. $H_2O_{(L)} + (NH_2)_2CO_{(aq)} \rightleftharpoons 2NH_{3(g)} + CO_{2(g)}$ $K = \dfrac{P_{CO2(g)}P^2_{NH3(g)}}{[(NH_2)_2CO_{(aq)}]}$

Thermodynamic Reaction Quotient (Q)
- Q has the same form as K, but uses interim concentrations: $[A]_i$.
- ΔG at nonstandard concentrations and pressures is found by $\mathbf{\Delta G = \Delta G^o + (RT)ln[Q]}$
  $R = 8.314$ J/(K·mol) is the universal gas constant. The result for ΔG is in Joules.

Relating ΔG to Thermodynamic K
- What if Q = K?
  Then, no changes in concentration are spontaneous, which means ΔG = 0.
  Implies: $0 = \Delta G^o + (RT)ln[K]$ or $\mathbf{\Delta G^o = - (RT)ln[K]}$
- Also: $\mathbf{K = exp\left[-\dfrac{\Delta G^o}{RT}\right] = e^{[- \Delta G^o/RT]}}$
- $\mathbf{\Delta G = - (RT)ln[K] + (RT)ln[Q] = - (RT)ln\left[\dfrac{K}{Q}\right]}$

Example 18.08 Find Thermodynamic K at 298 K from ΔG^o
- $(NH_2)_2CO_{(s)} + H_2O_{(L)} \rightleftharpoons 2NH_{3(g)} + CO_{2(g)}$
- ΔH^o and ΔS^o were calculated in Examples 18.01 and 18.03.
- $\Delta G^o = \Delta H^o - T\Delta S^o = (+ 133.7$ kJ$) - (298$ K$)(+ 0.4288$ kJ/K$) = + 5.9$ kJ
- $\Delta G^o = (+ 5.9$ kJ$)\left(\dfrac{1000\ J}{1\ kJ}\right) = + 5,900$ J
- $K = exp(-\Delta G^o/RT) = exp\left[\dfrac{- (+5,900\ J)}{\left(8.314\frac{J}{K}\right)(298\ K)}\right] = exp[- 2.38] = 9.26 \times 10^{-2}$

Example 18.09 Calculate K_{sp} from ΔG^o for $1AgCl_{(s)} \rightleftharpoons 1Ag^{+1}_{(aq)} + 1Cl^{-1}_{(aq)}$
- $\Delta G^o = [1\times(77.1) + 1\times(-131.2)] - [1\times(-109.8)] = (+ 55.7$ kJ$)\left(\dfrac{1000\ J}{1\ kJ}\right) = + 55,700$ J
- $K = exp(-\Delta G^o/RT) = exp\left[\dfrac{- (+ 55,700\ J)}{\left(8.314\frac{J}{K}\right)(298\ K)}\right] = exp[- 22.48] = 1.7 \times 10^{-10}$
- This value approximately matches the K_{sp} value in <u>Appendix J</u>.

Standard State Concentrations and Partial Pressures at Temperatures other than 298 K (ΔG_T^o)
- If ΔH and ΔS are approximately constant as T changes, then the equation
  at other temperatures simplifies to $\mathbf{\Delta G_T^o = \Delta H^o - T\Delta S^o}$.
- The spontaneity of a reaction at other temperatures can then be determined
  from the sign on ΔG, which is a <u>function</u> of the signs on ΔH and ΔS.

ΔH	ΔS	ΔG	Spontaneity
−	+	Always $\Delta G < 0$	Reaction is spontaneous at all T's.
+	−	Always $\Delta G > 0$	Reaction is not spontaneous at any T.
+	+	$\Delta G < 0$ if $T > \dfrac{\Delta H}{\Delta S}$	Reaction is spontaneous only at T's above that value.
−	−	$\Delta G < 0$ if $T < \dfrac{\Delta H}{\Delta S}$	Reaction is spontaneous only at T's below that value.

Example 18.10 Find ΔG_T^o and K at 1227 °C for $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$
- $\Delta H^o = +191.6$ kJ $\Delta S^o = (+141.9 \text{ J/K})\left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right) = +0.1419$ kJ/K
- $\Delta G^o_{1500 \text{ K}} = \Delta H^o - T\Delta S^o = +191.6$ kJ $- (1500 \text{ K})(0.1419 \text{ kJ/K}) = -21.3$ kJ
  $\Delta G^o_{1500 \text{ K}} = (-21.3 \text{ kJ})\left(\frac{1000 \text{ J}}{1 \text{ kJ}}\right) = -21,300$ J
  $\Delta G^o_{1500 \text{ K}} < 0$ So, the reaction is spontaneous at 1500 K.
- $K_{1500 \text{ K}} = \exp\left[\dfrac{-\Delta G^o_{1273K}}{RT}\right] = \exp\left[\dfrac{-(-21,300 \text{ J})}{\left(8.314 \frac{\text{J}}{\text{K}} \times 1500 \text{ K}\right)}\right] = \exp[+1.708] = 5.5$
  $K_{1500 \text{ K}} > 1$ This also indicates that the reaction is spontaneous at 1500 K.
- The equilibrium constant expression includes only the CO_2 gas and not the solids.
  $K_{1500 \text{ K}} = P_{CO2} = 5.5$ atm
- Also, since $\Delta H^o > 0$ and $\Delta S^o > 0$, ΔG_T^o is negative only at high temperatures.
  $\Delta G_T^o < 0$ at $T > \dfrac{\Delta H}{\Delta S}$ because $\Delta G_T^o = \Delta H^o - T\Delta S^o$
  $\dfrac{\Delta H}{\Delta S} = \dfrac{(+191.6 \text{ kJ})}{\left(0.1419 \frac{\text{kJ}}{\text{K}}\right)} = 1350$ K
  Reaction is spontaneous ($\Delta G_T^o < 0$) only at $T > 1350$ K.