General Chemistry II
PLI August 3, 2021

1. One of the possible initial steps in the formation of acid rain is the oxidation of the pollutant SO_2 to SO_3 by the reaction:

$$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$$

Compound	ΔH_f° (kJ/mol)	ΔS°(J/mol*K)
SO2 (g)	-296.8	248.2
O2 (g)	0	205.2
SO3 (g)	-395.8	256.8

a. Calculate ΔG° and determine whether the reaction is product-favored at equilibrium at 25°C.

$$\Delta_r H^\circ = \left[2\ mol\ SO_3\text{*-}395.8\frac{kJ}{mol}\right]\text{-}\left[\left(2\ mol\ SO_2\text{*-}296.8\frac{kJ}{mol}\right) + \left(1\ mol\ O_2\text{*}0\frac{kJ}{mol}\right)\right]$$
$$= -198\frac{kJ}{mol}$$

$$\Delta_r S^\circ = \left[2\ mol\ SO_3 * 256.8\frac{J}{mol * K}\right]$$
$$-\left[\left(2\ mol\ SO_2 * 248.2\frac{J}{mol * K}\right) + \left(1\ mol\ O_2 * 205.2\frac{J}{mol * K}\right)\right]$$
$$= -188\frac{J}{mol * K} = -0.188\frac{kJ}{mol * K}$$

$$\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ = -198\frac{kJ}{mol} - (298.15\ K)\left(-0.188\frac{kJ}{mol * K}\right)$$
$$= -141.95\frac{kJ}{mol}$$

Now that we have calculated $\Delta_r G^\circ$, let's calculate K to find out whether it is reactant or product-favored.

$$\Delta_r G^\circ = -141.95\frac{kJ}{mol} = -RT\ln K$$

$$-141.95\frac{kJ}{mol} = -\left(8.314 * 10^{-3}\frac{kJ}{mol * K}\right)(298.15\ K)\ln K$$

$$K = 7.41 * 10^{24}$$

This K is massive and thus the reaction is product favored

b. Estimate the temperature at which the reaction switches between product-favored and reactant-favored at equilibrium.

The Gibbs free energy will be 0 when the reaction switches between product-favored and reactant-favored at equilibrium. Thus,

$$\Delta_r G° = 0 = \Delta_r H° - T\Delta_r S°$$

$$T = \frac{\Delta_r H°}{\Delta_r S}° = -\frac{198\frac{kJ}{mol}}{-0.188\frac{kJ}{mol * K}} = 1053\ K$$

2. For a certain chemical reaction, ΔH˚=-35.4 kJ and ΔS˚ = -85.5 J/K.
   a. Is the reaction exothermic or endothermic?

Change in enthalpy (ΔH) is negative, so reaction is exothermic.

   b. Does the reaction lead to an increase or decrease in the randomness/disorder of the system?

Change in entropy (ΔS) is negative, so there is a decrease in the randomness/disorder of system.

   c. Calculate the ΔG˚ for the reaction at 298 K.

$$\Delta_r G° = \Delta H - T\Delta S = -35.4\ kJ - 298\ K * \left(\frac{-0.0855\ kJ}{K}\right) = -9.9\ kJ$$

d. Is the reaction spontaneous at 298 K under standard conditions?

Yes, because Gibbs Free Energy is negative.

3. Classify each of the following reactions as one of the four possible types: (i) spontaneous at all temperatures, (ii) not spontaneous at any temperature; (iii) spontaneous at low T but not spontaneous at high T; (iv) spontaneous at high T but not spontaneous at low T.
   a. $N_2(g) + 3\,F_2(g) \rightarrow 2\,NF_3(g)$
      ΔH° = -249 kJ; ΔS°= -278 J/K

Type (iii). It is spontaneous at **VERY** low temperatures but not spontaneous at high temperatures.

   b. $N_2(g) + 3Cl_2(g) \rightarrow 2NFCl_3(g)$
      ΔH°= 460 kJ; ΔS°=-275 J/K

Type (ii). It is not spontaneous at any temperature, because we are always subtracting a negative number from a positive number.

   c. $N_2F_4(g) \rightarrow 2NF_2(g)$
      ΔH° = 85 kJ; ΔS° = 198 J/K

Type (iv).

True or False

(T / F) For a process that occurs at constant temperature, the change in Gibbs free energy depends on changes in the enthalpy and entropy of the system.
This is true as seen in the equation $\Delta G = \Delta H - T\Delta S$

(T / F) If ΔG is large and negative for a certain reaction, the rate at which the reaction occurs is fast.
Activation energy will still determine the kinetics, ΔG determines the spontaneity.

4. Balance each reaction in aqueous acidic solution.

a. $\boldsymbol{PbO_2(s) + I^-(aq) \rightarrow Pb^{2+}(aq) + I_2(s)}$

Balance each half reaction, first by mass and then by charge. Add H_3O^+ and H_2O where needed.

$$2I^-(aq) \rightarrow I_2(s) + 2e^-$$

$$2e^- + 4H_3O^+(aq) + PbO_2(s) \rightarrow Pb^{2+}(aq) + 6H_2O(l)$$

Since $2e^-$ are already on both sides, add the two half reactions together to get the overall balanced redox reaction:

$$2I^-(aq) + 4H_3O^+(aq) + PbO_2(s) \rightarrow I_2(s) + Pb^{2+}(aq) + 6H_2O(l)$$

b. $\boldsymbol{SO_3^{2-}(aq) + MnO_4^-(aq) \rightarrow SO_4^{2-}(aq) + Mn^{2+}(aq)}$

$$3H_2O(l) + SO_3^{2-}(aq) \rightarrow SO_4^{2-}(aq) + 2H_3O^+(aq) + 2e^-$$

$$5e^- + 8H_3O^+(aq) + MnO_4^-(aq) \rightarrow Mn^{2+}(aq) + 12H_2O(l)$$

Scale the half reactions to get the same number of electrons, then add them:

$$15H_2O(l) + 5SO_3^{2-}(aq) \rightarrow 5SO_4^{2-}(aq) + 10H_3O^+(aq) + 10e^-$$

$$10e^- + 16H_3O^+(aq) + 2MnO_4^-(aq) \rightarrow 2Mn^{2+}(aq) + 24H_2O(l)$$

Overall reaction:

$$6H_3O^+(aq) + 5SO_3^{2-}(aq) + 2MnO_4^-(aq) \rightarrow 5SO_4^{2-}(aq) + 2Mn^{2+}(aq) + 9H_2O(l)$$

c. $\boldsymbol{Cr_2O_7^{2-}(aq) + HNO_2(aq) \rightarrow Cr^{3+}(aq) + NO_3^-(aq)}$

$$6e^- + 14H_3O^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq) + 21H_2O(l)$$

$$4H_2O(l) + HNO_2(aq) \rightarrow NO_3^-(aq) + 3H_3O^+(aq) + 2e^-$$

Multiply the second half reaction by 3 to get:

$$12H_2O(l) + 3HNO_2(aq) \rightarrow 3NO_3^-(aq) + 9H_3O^+(aq) + 6e^-$$

Add it to the first half reaction to get:

$$5H_3O^+(aq) + 3HNO_2(aq) + Cr_2O_7^{2-}(aq) \rightarrow 3NO_3^-(aq) + 2Cr^{3+}(aq) + 9H_2O(l)$$

d. $Fe_2O_3 + CO \rightarrow Fe + CO_2$

$$6e^- + 6H_3O^+ + Fe_2O_3 \rightarrow 2Fe + 9H_2O$$

$$3H_2O + CO \rightarrow CO_2 + 2H_3O^+ + 2e^-$$

Multiply the second half reaction by 3:

$$9H_2O + 3CO \rightarrow 3CO_2 + 6H_3O^+ + 6e^-$$

Add the two half reactions to get:

$$3CO + Fe_2O_3 \rightarrow 3CO_2 + 2Fe$$

e. $HCO_2H + MnO_4^- \rightarrow CO_2 + Mn^{2+}$

$$2H_2O + HCO_2H \rightarrow CO_2 + 2H_3O^+ + 2e^-$$

$$5e^- + 8H_3O^+ + MnO_4^- \rightarrow Mn^{2+} + 12H_2O$$

Multiply the first by 5 and the second by 2 and then add:

$$10H_2O + 5HCO_2H \rightarrow 5CO_2 + 10H_3O^+ + 10e^-$$

$$10e^- + 16H_3O^+ + 2MnO_4^- \rightarrow 2Mn^{2+} + 24H_2O$$

$$6H_3O^+ + 5HCO_2H + 2MNO_4^- \rightarrow 5CO_2 + 2Mn^{2+} + 14H_2O$$

5. Balance each reaction in basic aqueous solution

a. $ClO^-(aq) + Cr(OH)_4^-(aq) \rightarrow CrO_4^{2-}(aq) + Cl^-(aq)$

Balance each half reaction, first by mass and then by charge. Add OH^- and H_2O where needed. Balancing in basic solution is a bit trickier when deciding whether to add OH^- or H_2O to a given side. One thing that might work is to balance as if you were in acidic solution (add H_3O^+ to balance hydrogen) and then add an appropriate number of OH^- on both sides. Water should be created on the one side with H_3O^+ and OH^- will be left on the other side

$$2e^- + H_2O(l) + ClO^-(aq) \rightarrow Cl^-(aq) + 2OH^-(aq)$$

$$4H_2O(l) + Cr(OH)_4^-(aq) \rightarrow CrO_4^{2-}(aq) + 4H_3O^+(aq)$$

Add 4 OH^- to both sides:

$$4OH^-(aq) + 4H_2O(l) + Cr(OH)_4^-(aq) \rightarrow CrO_4^{2-}(aq) + 4H_3O^+(aq) + 4OH^-(aq)$$

Simplify the equation and add electrons to balance charge:

$$4OH^-(aq) + Cr(OH)_4^-(aq) \rightarrow CrO_4^{2-}(aq) + 4H_2O(l) + 3e^-$$

Multiply the first half reaction by 3 and the second by 2:

$$6e^- + 3H_2O(l) + 3ClO^-(aq) \rightarrow 3Cl^-(aq) + 6OH^-(aq)$$

$$8OH^-(aq) + 2Cr(OH)_4^-(aq) \rightarrow 2CrO_4^{2-}(aq) + 8H_2O(l) + 6e^-$$

Add the two together to get the overall balanced redox equation:

$$2OH^-(aq) + 2Cr(OH)_4^-(aq) + 3ClO^-(aq) \rightarrow 3Cl^-(aq) + 2CrO_4^{2-}(aq) + 5H_2O(l)$$

b. $\boldsymbol{Ag(s) + Zn^{2+}(aq) \rightarrow Ag_2O(aq) + Zn(s)}$

$$2OH^-(aq) + 2Ag(s) \rightarrow Ag_2O(aq) + H_2O(l) + 2e^-$$

$$2e^- + Zn^{2+}(aq) \rightarrow Zn(s)$$

Add the two half reactions together:

$$2OH^-(aq) + 2Ag(s) + Zn^{2+}(aq) \rightarrow Ag_2O(aq) + Zn(s) + H_2O(l)$$

c. $\boldsymbol{CO + I_2O_5 \rightarrow CO_2 + I_2}$

$$3H_2O + CO \rightarrow CO_2 + 2H_3O^+$$

Add 2 OH^- to both sides

$$2OH^- + 3H_2O + CO \rightarrow CO_2 + 2H_3O^+ + OH^-$$

$$2OH^- + CO \rightarrow CO_2 + H_2O + 2e^-$$

Now, the second half reaction:

$$10H_3O^+ + I_2O_5 \rightarrow I_2 + 15H_2O$$

Add 10 OH^- to both sides:

$$10OH^- + 10H_3O^+ + I_2O_5 \rightarrow I_2 + 15H_2O + 10OH^-$$

$$10e^- + 5H_2O + I_2O_5 \rightarrow I_2 + 10OH^-$$

Multiply the first half reaction by 5 and add it to the second:

$$10OH^- + 5CO \rightarrow 5CO_2 + 5H_2O + 10e^-$$

$$5CO + I_2O_5 \rightarrow 5CO_2 + I_2$$

d. $O_2 + Sb \rightarrow H_2O_2 + SbO_2^-$

$$2H_3O^+ + O_2 \rightarrow H_2O_2 + 2H_2O$$

Add 2 OH⁻ to both sides:

$$2OH^- + 2H_3O^+ + O_2 \rightarrow H_2O_2 + 2H_2O + 2OH^-$$

$$2e^- + 2H_2O + O_2 \rightarrow H_2O_2 + 2OH^-$$

The second half reaction:

$$6H_2O + Sb \rightarrow SbO_2^- + 4H_3O^+$$

Add 4 OH⁻ to both sides:

$$4OH^- + 6H_2O + Sb \rightarrow SbO_2^- + 4H_3O^+ + 4OH^-$$

$$4OH^- + Sb \rightarrow SbO_2^- + 2H_2O + 3e^-$$

Multiply the first half reaction by 3 and the second by 2:

$$6e^- + 6H_2O + 3O_2 \rightarrow 3H_2O_2 + 6OH^-$$

$$8OH^- + 2Sb \rightarrow 2SbO_2^- + 4H_2O + 6e^-$$

Add the two together to get the overall balanced redox reaction:

$$2OH^- + 2Sb + 3O_2 + 2H_2O \rightarrow 3H_2O_2 + 2SbO_2^-$$

6. Consider a voltaic cell involving chromium (II) and gold (I)
   a. Balance the following reaction: $Au^+(aq) + Cr(s) \rightarrow Au(s) + Cr^{2+}(aq)$

$$e^- + Au^+(aq) \rightarrow Au(s)$$

$$Cr(s) \rightarrow Cr^{2+}(aq) + 2e^-$$

Multiply the first half reaction by 2:

$$2e^- + 2Au^+(aq) \rightarrow 2Au(s)$$

Add the two half reactions together:

$$2Au^+(aq) + Cr(s) \rightarrow Cr^{2+}(aq) + 2Au(s)$$

b. Sketch this cell, identifying the cathode and anode, the flow of electrons and the flow of cations and anions from the salt bridge (composed of $NaNO_3$).