

Kitchen Sink Equilibria: Everything but the...

 ΔG and K : Oh rats!

$$\Delta G^\circ = -RT \ln K$$

R = universal gas constant = $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

T = temperature in Kelvin

K = equilibrium constant

This equation can be rewritten to give: $K = e^{-\Delta G^\circ/RT}$

And of course, don't forget the connection between electrochemistry and equilibrium!

 ΔG and E° : I've had enough!

$$\Delta G^\circ = -nFE^\circ$$

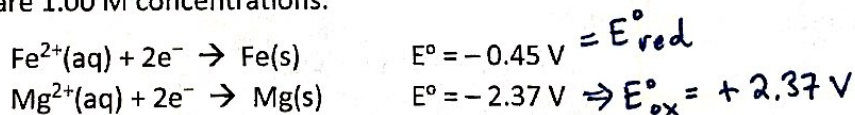
n = number of moles of electrons

F = Faraday's constant = 96,485 coulombs per mole of electrons

1. Calculate Gibb's free energy, in $\text{kJ/mol}_{\text{rxn}}$, for the reaction of glucose and ATP to give glucose-6-phosphate and ADP, given that the equilibrium constant, K , is 5000. at a temperature of 38°C .

$$\begin{aligned} \Delta G &= -RT \ln K = -(8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}})(311 \text{ K}) \ln(5000.) \\ &= -22,023 \frac{\text{J}}{\text{mol}_{\text{rxn}}} = \boxed{-22.0 \frac{\text{kJ}}{\text{mol}_{\text{rxn}}}} \end{aligned}$$

2. Assume that iron and magnesium half-cells are suitable connected at 298 K and standard conditions and that both aqueous solutions are 1.00 M concentrations.



Calculate the cell potential, the free energy change (in kJ/mol), and the equilibrium constant for this voltaic cell.

$$\begin{aligned} E_{\text{cell}} &= E^\circ_{\text{red}} + E^\circ_{\text{ox}} = -0.45 + 2.37 = \boxed{1.92 \text{ V}} \quad V = \frac{\text{J}}{\text{C}} \\ \Delta G^\circ &= -nFE^\circ_{\text{cell}} = -(2 \frac{\text{mole}^-}{\text{mol}_{\text{rxn}}})(96,485 \frac{\text{C}}{\text{mol} \cdot \text{e}^-})(1.92 \text{ V}) = -370,502.4 \frac{\text{J}}{\text{mol}} \\ \Delta G^\circ &= -RT \ln K \Rightarrow \ln K = \frac{\Delta G^\circ}{-RT} = \frac{-370,502.4 \frac{\text{J}}{\text{mol}}}{(-8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}})(298)} \\ &= 149.54 \\ K &= e^{149.54} = \boxed{8.82 \times 10^{64}} \end{aligned}$$

Upping the Pressure

$$PV = nRT$$

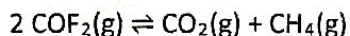
P = pressure (in atm, torr, or mmHg)

R = universal gas constant (0.08206 L atm mol⁻¹ K⁻¹ or 62.36 L torr mol⁻¹ K⁻¹)

T = temperature in Kelvin

The ideal gas law can be used to calculate the partial pressure of a gas at equilibrium if you know the equilibrium concentration of the gas.

3. If Consider the following reaction:



$$K_c = 2.00 \text{ at } 1000^\circ\text{C}$$

In an equilibrium mixture, the concentration of COF₂ is 0.255 M and the concentration of CH₄ is 0.118 M. What is the partial pressure of CO₂ at equilibrium? (in atm)

$$K = \frac{[\text{CO}_2][\text{CH}_4]}{[\text{COF}_2]^2} = \frac{[\text{CO}_2](0.118)}{(0.255)^2} = 2.00$$

$$[\text{CO}_2] = \frac{(2.00)(0.255)^2}{0.118} = 1.10 \text{ M}$$

$$PV = nRT \Rightarrow P = \frac{nRT}{V} = MRT = (1.10 \frac{\text{mol}}{\text{L}}) \left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) (1,273 \text{ K})$$

\uparrow b/c $\frac{n}{V} = M$

$$= \boxed{115 \text{ atm}}$$

1000°C + 273
↓

Equilibrium and Thermodynamic Favorability

4. For the gaseous equilibrium represented below, it is observed that greater amounts of PCl₃ and Cl₂ are produced as the temperature is increased.] ⇒ endo



- a. What is the sign of ΔS° for the reaction? Justify.

+ΔS°, b/c # of moles of gas increased from 1 on reactant side to 2 on product side

- b. What change, if any, will occur in ΔG° for the reaction as the temperature is increased? Explain your reasoning in terms of Le Chatelier's principle.

Since greater amounts of products (PCl₃ and Cl₂) are produced when temp. increases, the rxn must have shifted right to partially undo the stress of the temp. change. That means the value of K increased, and so, b/c ΔG = -RT ln K, ΔG will increase as well (aka the rxn is more thermodynamically favorable at higher temp.)