

6.E: Chemical Equilibrium (Exercises)

Q6.1

Imagine a catalytic reaction that changes a reagent between two states, i.e.:



The equilibrium constants K_c , K_χ , and K_p with respect to concentration, mole fraction, and pressure are given by

$$K_c = \frac{[Z]^z}{[Y]^y} \quad (6.E.2)$$

$$K_\chi = \frac{\chi_Z^z}{\chi_Y^y} \quad (6.E.3)$$

$$K_p = \frac{P_Z^z}{P_Y^y} \quad (6.E.4)$$

Given this information, express K_p in terms of K_c and K_χ .

Q6.2a



- The partial pressure of CO_2 is 0.1 atm, calculate K_p
- If the reaction occurred in a 1L flask, what is the amount of CaO formed when 0.12 moles $CaCO_3$ was set to react?
- What is the minimum amount of CaO needed to cause the formation of $CaCO_3$?

Q6.2b

The decomposition of sodium chlorate is:



Suppose 0.760 mole of sodium chlorate was to be decomposed in a 3.75 L container. At the temperature $336^\circ C$, the percent decomposition of $NaClO_3$ is 3.5%. Find the

- pressure of O_2 gas in the container in atm and
- equilibrium constant K_p of the reaction. Assume O_2 gas is an ideal gas.

Hint: Use partial pressure and look at [chemical equilibrium of gaseous systems](#)

S6.2b

a) number of moles of $NaClO_3$ decomposed is:

$$\frac{\#moles\ decomposed}{.760moles} = 0.035 \Rightarrow \#mole\ decomposed = 0.0266mole\ NaClO_3 \quad (6.E.7)$$

number of moles of O_2 formed is:

$$0.0266mol\ NaClO_3 \times \frac{3mol\ O_2}{2mol\ NaClO_3} = 0.0399mol\ O_2 \quad (6.E.8)$$

$$P_{O_2}V = nRT \Rightarrow P_{O_2} = \frac{nRT}{V} \quad (6.E.9)$$

$$P_{O_2} = \frac{(0.0399mol)(0.08206\frac{L \cdot K}{K \cdot mol})(336 + 273)K}{3.75L} = 0.532atm \quad (6.E.10)$$

b)

$$K_p = \frac{P_{O_2}}{P^\circ} = \frac{0.532 \text{ atm} \times \frac{1.013 \text{ bar}}{1 \text{ atm}}}{1 \text{ bar}} = 0.539 \quad (6.E.11)$$

Q6.2c

Using the decomposition reaction of hydrogen peroxide (H_2O_2), assume that at 1048°C and the pressure of the oxygen gas (O_2) is 1.5 bar.



- Determine the K_P for the reaction above.
- If 0.92 mole of H_2O_2 is placed in a 3.0-L beaker at 1048°C , determine the fraction of H_2O_2 that will decompose.
- Determine the same as (b) if 1.3 moles of H_2O_2 were placed inside the beaker instead.
- What is the minimum amount of H_2O_2 (in moles) necessary in order to reach equilibrium?

S6.2c

$$\text{a. } K_P = \frac{P_{O_2}}{P^\circ} = \frac{1.5 \text{ bar}}{1 \text{ bar}} = 1.5$$

b. In order to calculate the number of moles of H_2O_2 that are decomposed, you first need to determine the moles of O_2 formed by the reaction. Treat O_2 as an ideal gas.

$$\begin{aligned} \text{Number of moles of } O_2 \text{ formed} &= \frac{PV}{RT} = \frac{(1.5 \text{ bar}) \left(\frac{1 \text{ atm}}{1.013 \text{ bar}} \right) (3.0 \text{ L})}{(0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}) (1321 \text{ K})} \\ &= 41.0 \times 10^{-3} \text{ mol} \\ \text{Number of moles of } H_2O_2 \text{ decomposed} &= (41.0 \times 10^{-3} \text{ mol } O_2) \left(\frac{2 \text{ mol } H_2O_2}{1 \text{ mol } O_2} \right) \\ &= 0.0802 \text{ mol} \\ \text{Fraction of } H_2O_2 \text{ decomposed} &= \frac{0.0802 \text{ mol}}{0.92 \text{ mol}} = 0.09 \end{aligned}$$

c. If 1.3 moles of H_2O_2 were used instead of 0.92 mole, the pressure of the O_2 would not be affected and would remain at 1.5 bar. The number of moles of H_2O_2 decomposed would still be 0.0802 mole, therefore, the fraction of H_2O_2 decomposed would be as follows:

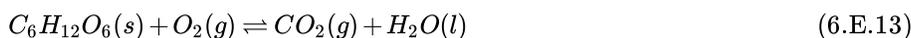
$$\text{Fraction of } H_2O_2 \text{ decomposed} = \frac{0.0802 \text{ mol}}{1.3 \text{ mol}} = 0.062$$

d. The pressure of O_2 must be greater than or equal to 1.5 bar in order for equilibrium to take place, therefore, the number of moles of H_2O_2 cannot be less than 0.0802 mol.

Q6.3

Find the value of K_p for cellular respiration if $P_{O_2} = 350 \text{ torr}$, with a 3:2 ratio to the pressure of CO_2

S6.3



$$P_{CO_2} = (350 \text{ torr}) \frac{2}{3} = 233.3 \text{ torr} \quad (6.E.14)$$

$$K_p = \frac{\frac{233.3 \text{ torr}}{750 \text{ torr}}}{\frac{350 \text{ torr}}{750 \text{ torr}}} = 0.666 \quad (6.E.15)$$

Q6.5

For the reaction of



with $K_p = 0.167$ at 300 K. If 1.0 g of N_2O_4 is placed into a 250.0 mL container:

- What would be its pressure if none dissociates?
- What is its partial pressure at equilibrium (with dissociation)?
- What is the total pressure in the container?

Q6.9a

Calculate $\Delta_{vap}H$ for the evaporation of methanol when the temperature is raised from 20 °C to 100 °C and if the K_2/K_1 ratio is 22.14?



Q6.9b

Using the decomposition reaction of copper (II) oxide below:



determine the standard enthalpy of the reaction. (Note: The equilibrium vapor pressures of O_2 are 15.4 mmHg at 600°C and 927 mmHg at 850°C).

S6.9b

In this case, we must use the [van't Hoff equation](#):

$$\ln \frac{K_2}{K_1} = \frac{\Delta_r H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (6.E.19)$$

in order to solve this particular problem. We can conclude that K_P is proportional to P_{CO_2} due to the defined relationship of:

$$K_P = \frac{P_{CO_2}}{P^\circ}$$

Therefore,

$$\begin{aligned} \ln \frac{P_{CO_2,2}}{P_{CO_2,1}} &= \frac{\Delta_r H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \\ \ln \frac{927 \text{ mmHg}}{15.4 \text{ mmHg}} &= \frac{\Delta_r H^\circ}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \left(\frac{1}{873.2 \text{ K}} - \frac{1}{1123.2 \text{ K}} \right) \\ \Delta_r H^\circ &= 1.34 \times 10^5 \text{ J mol}^{-1} \end{aligned}$$

Q6.10

A container of water at 20°C was placed in a freezer that was at a temperature of -5.0°C. The vapor pressure of water in the container went from 0.60 bar to 0.38 bar. Calculate the enthalpy of fusion for the reaction that took place.

S6.10

- $k_2 = 0.38 \text{ bar}$
- $k_1 = 0.60 \text{ bar}$
- $T_2 = 268 \text{ K}$
- $T_1 = 293 \text{ K}$

$$\ln \frac{k_2}{k_1} = \frac{\Delta_r H^\circ}{R} \frac{T_2 - T_1}{T_2 T_1} \quad (6.E.20)$$

$$\rightarrow \Delta_r H^\circ = \ln \frac{k_2}{k_1} (R) \frac{T_2 T_1}{T_2 - T_1} \quad (6.E.21)$$

$$\ln \frac{0.38 \text{ bar}}{0.60 \text{ bar}} 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} \frac{(293 \text{ K})(268 \text{ K})}{268 \text{ K} - 293 \text{ K}} \left(\frac{1 \text{ kJ}}{1000 \text{ J}} \right) = 11.9 \frac{\text{kJ}}{\text{mol}} \quad (6.E.22)$$

Q6.11

The chemical responsible for the brown air throughout the Los Angeles area is $\text{NO}_2(\text{g})$. To learn more about $\text{NO}_2(\text{g})$, you decide to study this pollutant spectroscopically (by light absorption). You fill a gas cell with N_2O_4 , equilibrate the temperature to 298.0 K and then open the stopcock on the cell to equilibrate the pressure to the barometric pressure (723.4 mm Hg) that day. You then reequilibrate the cell at 323.1 K, 348.0 K, and 372.9 K. The following data is obtained:

T/K	298.0	323.1	348.0	372.9
$[\text{NO}_2]/\text{M}$	0.01262	0.02140	0.02756	0.02920

Find K_p , $\Delta_{\text{rxn}} G$, $\Delta_{\text{rxn}} H$, and $\Delta_{\text{rxn}} S$ at each temperature for the reaction



Q6.14

What is the equilibrium constant and standard Gibbs energy change for:



Assume that when $\text{CO}(\text{g})$ dissociates into $\text{CO}(\text{g})$ and $\text{O}_2(\text{g})$ at 300 K and 1.5 atm, the overall dissociation is one two fifths complete.

Q6.15

The standard Gibbs energies of formation of propan-1-ol and propan-2-ol are $-171.3 \text{ kJ mol}^{-1}$ and $-180.3 \text{ kJ mol}^{-1}$, respectively. Find the ratio of equilibrium vapor pressures of each isomer at 300 K.

S6.15

The ratio of equilibrium pressure is : $171.3/180.3 = 0.95$

Q6.16

At what temperature does a particular reaction favor the formation of products at equilibrium if $\Delta_r H^\circ = 215.7 \text{ kJ mol}^{-1}$ and $\Delta_r S^\circ = 348.8 \text{ J mol}^{-1} \text{ K}^{-1}$?

S6.16

The reaction favors the formation of products at equilibrium when

$$\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ < 0 \quad (6.E.25)$$

$$\Delta_r H^\circ - T\Delta_r S^\circ = 215.7 * 10^3 \text{ J mol}^{-1} - T(348.8 \text{ J mol}^{-1} \text{ K}^{-1}) < 0 \quad (6.E.26)$$

$$T > \frac{215.7 * 10^3 \text{ J mol}^{-1}}{348.8 \text{ J mol}^{-1} \text{ K}^{-1}} \quad (6.E.27)$$

$$T > 616 \text{ K} \quad (6.E.28)$$

Q6.17

Using a table of thermodynamic data, find K_{sp} at 298.15K for:



(Hint, this problem can be solved using the van't Hoff equation in its integrated form)

Q6.18

Consider the the [Haber process](#):



How does the equilibrium shift under the following changes

- the volume of nitrogen gas is increased
- the temperature is decreased
- the pressure of the system is decreased

S6.18

- The reaction shifts to the right : more products formed.
- The reaction shifts to the right : favor exothermic reaction
- The reaction shifts to the left : more pressure applied.

Q6.19

Given the general reaction $A(g) \rightleftharpoons 2B(g)$, calculate the degree of dissociation of A at 25°C and 7.00 bar if $\Delta_r G^\circ = 6.76 \text{ kJ mol}^{-1}$. According to Le Chatelier's Principal, in what direction should this reaction proceed?

S6.19

$$\Delta_r G^\circ = -RT \ln K_P \quad (6.E.31)$$

$$K_P = e^{\frac{\Delta_r G^\circ}{-RT}} = e^{-\frac{6.76 * 10^3 \text{ J mol}^{-1}}{(8.314 \text{ J mol}^{-1} \text{ K}^{-1})298 \text{ K}}} \quad (6.E.32)$$

$$K_P = 0.0653 \quad (6.E.33)$$

$$K_P = \frac{4\alpha^2}{1-\alpha^2} P \quad (6.E.34)$$

$$\frac{4\alpha^2}{1-\alpha^2} = \frac{0.0653}{7} \quad (6.E.35)$$

$$\alpha = .048 \quad (6.E.36)$$

Degree of dissociation $\alpha = 0.048$, the reaction proceeds 4.8%. Le Chatelier's Principal says that reactions will move towards the side with fewer moles of gas at high pressures.

Q6.19

How does Le Chatelier's Principle relate to the following equation?

$$\ln \frac{K_2}{K_1} = \frac{\Delta_r H^\circ}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

S6.19

Le Chatelier's Principle basically states that a system will adjust itself in efforts to re-establish equilibrium when an outside stress is placed on it. Using the equation provided, we can conclude that raising the temperature causes the equilibrium to shift from left to right in an endothermic reaction. This suggests that it is favoring the formation of products. We can also conclude that the opposite is true. This conclusion reinforces Le Chatelier's Principle because the temperature acts as the external stress placed on the system in this case.

Q6.20

H_2 and H molecules are at equilibrium pressures of .35 bar and .30 bar, respectively. If the size of the container they are in is reduced by a factor of two, what will be the new partial pressures?

S6.20



$$K_p = \frac{P_H^2}{P_{H_2}} = \frac{.30^2}{.35} = .675 \quad (6.E.38)$$

At new volume:

$$P_H = .60 \quad (6.E.39)$$

$$P_{H_2} = .70 \quad (6.E.40)$$

Pressures will increase with decreased volume. Less molecules of gas will be favored.

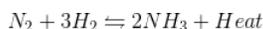
P_H	P_{H_2}
0.60 bar - 2x	0.70 bar + x

$$.675 = \frac{.60 - (2x^2)}{.70 + x} \rightarrow 4x^2 + .675x + .113 \rightarrow x = .272 \quad (6.E.41)$$

$$P_{H_2} = .70\text{bar} + .272\text{bar} = .972\text{bar} \quad (6.E.42)$$

$$P_H = .60\text{bar} - (2).272\text{bar} = .056\text{bar} \quad (6.E.43)$$

Q6.21



With Le Chatlier's principle in mind, does raising the temperature favor the forward reaction or the reverse?

S6.21

This reaction favors the reverse reaction.

Q6.23a

When a gas was heated at atmospheric pressure and 25°C, its color deepened. Heating above 150°C caused the color to fade, and at 550°C the color was barely detectable. At 550°C, however, the color was partially restored by increasing the pressure of the system. Which of the following scenarios best fits the above description? Justify your answer.

- A mixture of Gas A and Gas B
- Pure Gas B
- A mixture of Gas X and Gas Y

(Hint: Gas B is bluish, and Gas Y is yellow. The other gases are colorless. Gas A and B are in their natural state, Gas AB has a $\Delta_f H^\circ = -43.2 \text{ kJ/mol}$. The reaction of Gas X into Gas Y is endothermic.)

Q6.23b

Hydrogen gas and iodine react at equilibrium in a glass canister to form Hydrogen Iodide, a strong acid:



Iodine gas is a deep purple color. Both Hydrogen Iodide and hydrogen gas are colorless. Assume that iodine sublimates readily at 37° C, and that the reaction is endothermic in the direction written. What color is the gas mixture in the canister in the following scenarios? Provide an explanation for each.

- The canister is heated to 40° C
- The canister is heated to 500° C
- Negative pressure is applied to the cannister at 500° C

Hint: At room temperature, the gas is colorless. Solid iodine must be in gas phase to react.

S6.23b

- The color of the gas will be a deep purple. The iodine will have sublimated, but the temperature is not high enough to drive the reaction forward.
- The gas will be colorless, or almost completely so. This is because an increase in the temperature in an endothermic reaction drives the equilibrium constant higher. This can be justified using [Le Chatelier's principle](#), which states that added stress to an

equilibrium will be offset by the system.



Thus, when heat is added, the system will compensate by driving the reactants of the reaction forward into products. Another way to assess this is by the altered form of the [van't Hoff equation](#):

$$\ln K = -\frac{\Delta_r H^\circ}{RT} + \frac{\Delta_r S^\circ}{R} \quad (6.E.46)$$

Assuming that neither change in entropy nor enthalpy changes due to change in temperature, and that in an endothermic reaction the enthalpy is positive, as the temperature increases, so does K.

c.) The gas will become slightly purple. This is because a decrease in pressure will alter K and drive the reaction in the direction which produces more moles of gas. By this, Le Chatelier's principle once again holds.

Q6.24



Write the two separate reactions happening here. Label which one is happening at the cathode end and which is happening at the anode end.

S6.24

Cathode:



Anode:



Q6.24

The reaction of $N_2(g)$ and $H_2(g)$ gas produces $NH_3(g)$. This reaction is exothermic explain what happens when you increase the temperature of the reaction. What happens when you increase the pressure?

S6.24

Since this reaction is exothermic heat is produced. Using Le Chatelier's principle we see that an increase in the temperature of the reaction will drive the reaction backward since heat is already in the product side. If we increase pressure we decrease the volume of the reaction therefore by Le Chatelier's principle an increase in the pressure should drive the reaction forward.

Q6.25

At places such as high mountain, the air pressure is lower than 1 atm, resulting lower partial pressure of Oxygen. What would you expect for the concentration of hemoglobin for the people living at such places?

Q6.26

Show the steps to get from

$$Y = \frac{[PL]}{[L] + [P]} \quad (6.E.50)$$

to

$$\frac{1}{Y} = 1 + \frac{K_d}{L} \quad (6.E.51)$$

Q6.27

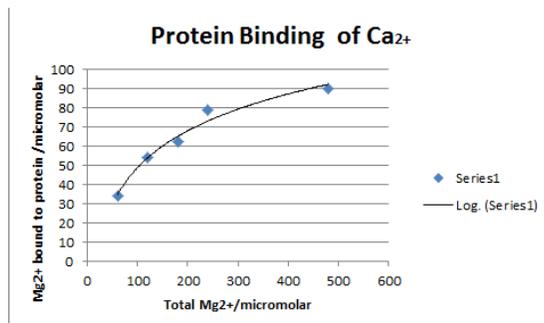
After an experiment of protein-binding you find the data respectively

$$\text{Total } \frac{Mg^{2+}}{\mu M}: 60 \ 120 \ 180 \ 240 \ 480$$

$$\frac{Mg^{2+} \text{ bound to protein}}{\mu M}: 33.8 \ 120 \ 180 \ 240 \ 480$$

Determine the dissociation constant of Ca^{2+} graphically. The protein concentration was kept at $96 \mu M$ for each run.

Solution:



$$54.2 \mu M \text{ pH} = pK_a \quad (6.E.52)$$

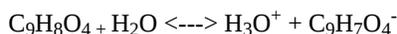
$$54.2 \mu M \left(\frac{1 \times 10^6 M}{1 \mu M} \right) = 5.42 \times 10^{-5} \quad (6.E.53)$$

$$K_a = 10^{-5.42E-5} \quad (6.E.54)$$

$$K_a = .9998 \quad (6.E.55)$$

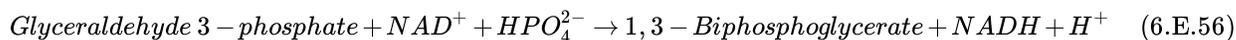
Q6.28

The dissociation constant for the following reaction is 3.2×10^{-4} . Dissolve $0.02 M$ of $C_9H_8O_4$ in water, calculate the molarity of reactants at equilibrium.



Q6.29

The reaction



$$\Delta_r G^\circ = 6.3 \text{ kJ mol}^{-1} \quad (6.E.57)$$

is catalyzed by GAPDH (Glyceraldehyde 3-phosphate Dehydrogenase). At 298 K , predict whether or not the reaction will be spontaneous with the following information:

$$[G3P] = 1.5 \times 10^{-5} \text{ M}; [BPG] = 3.0 \times 10^{-3} \text{ M}$$

$$[NAD^+] = 1.2 \times 10^{-5} \text{ M}; [NADH] = 1.0 \times 10^{-4} \text{ M}$$

$$[HPO_4^{2-}] = 1.2 \times 10^{-5} \text{ M}; \text{pH} = 7.5$$

S6.29

Use the following equation.

$$\Delta_r G = \Delta_r G^\circ + RT \ln \frac{([BPG]/1 \text{ M}) ([H^+]/(1 \cdot 10^{-7}))^x ([NADH]/1 \text{ M})}{([G3P]/1 \text{ M}) ([NAD^+]/1 \text{ M}) ([HPO_4^{2-}]/1 \text{ M})}$$

Calculate $[H^+]$

$$[H^+] = 10^{-7.5} = 3.162 \times 10^{-8} M \quad (6.E.58)$$

since $pH = -\log([H^+])$

Plug values into equation and solve. Note: Since there is no coefficient in front of H^+ in the reaction, $x=1$.

$$\Delta_r G = 6.3 \text{ kJ mol}^{-1} + \left(\frac{8.3145}{1000} \text{ kJ/mol}^{-1} \text{ K}^{-1}\right)(298 \text{ K}) \ln \quad (6.E.59)$$

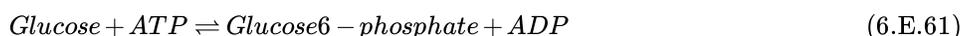
$$\frac{(3 \cdot 10^{-3} M)(3.162 \cdot 10^{-8} M / (1 \cdot 10^{-7}))^1 (1.0 \cdot 10^{-4} M)}{(1.5 \cdot 10^{-5} M) (1.2 \cdot 10^{-5} M) (1.2 \cdot 10^{-5} M)}$$

$$\underline{\Delta_r G = 49.90 \text{ kJ mol}^{-1}} \quad (6.E.60)$$

Click [here](#) for some more information on bioenergetics and free energy.

Q6.29

The reaction:



At 298K, the equilibrium constant for the reaction is 3.7×10^{-3} . Will the reaction occur spontaneously if the reaction is at the following concentrations:

$$[\text{Glucose}] = 3.2 \times 10^{-4} M, [\text{ATP}] = 2.5 \times 10^{-3} M, [\text{G-6-P}] = 1.2 \times 10^{-5} M, [\text{ADP}] = 1.0 \times 10^{-5} M.$$

S6.29

$$\Delta G^\circ = -RT \ln(K_{eq}) = -(8.314 \text{ J/K} \cdot \text{mol})(298 \text{ K}) \ln(3.7 \times 10^{-3})$$

$$= 13872.97 \text{ J/mol} = 13.87297 \text{ kJ/mol}$$

$$\Delta G = \Delta G^\circ + RT \ln\left(\frac{[\text{Product}]}{[\text{Reactant}]}\right)$$

$$= 13.87297 \text{ kJ/mol} + (8.314 \times 10^{-3} \text{ kJ/K} \cdot \text{mol})(298 \text{ K}) \ln\left(\frac{[1.2 \times 10^{-5}][1.0 \times 10^{-5}]}{[3.2 \times 10^{-4}][2.5 \times 10^{-3}]}\right)$$

$$= -7.942 \text{ kJ/mol}$$

ΔG is negative, so the reaction is spontaneous at the given concentrations.

Q6.30

The established standard Gibbs energy for hydrolysis of ATP to ADP at 310K is $-30.5 \text{ kJ mol}^{-1}$. At -4.6°C , determine the $\Delta_r G^{\circ'}$ in the process of the muscle of a hippo. (Hint: $\Delta_r H^{\circ'} = -20.1 \text{ kJ mol}^{-1}$)

S6.30

Step 1:

$$\Delta_r G^{\circ'} = \Delta_r H^{\circ'} - T \Delta_r S^{\circ'} \quad (6.E.62)$$

Step 2:

$$\Delta_r S^{\circ'} = \frac{\Delta_r H^{\circ'} - \Delta_r G^{\circ'}}{T} = \frac{(-20.1 \text{ kJ mol}^{-1}) - (-30.5 \text{ kJ mol}^{-1})}{310 \text{ K}} = 3.355 \times 10^{-2} \text{ kJ K}^{-1} \text{ mol}^{-1} \quad (6.E.63)$$

Step 3:

$$\Delta_r G^{\circ'} = \Delta_r H^{\circ'} - T \Delta_r S^{\circ'} \quad (6.E.64)$$

$$= (-20.1 \text{ kJ mol}^{-1}) - (298.15 \text{ K})(3.355 \times 10^{-2} \text{ kJ K}^{-1} \text{ mol}^{-1}) \quad (6.E.65)$$

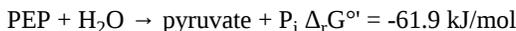
$$= -29.1 \text{ kJ mol}^{-1}$$

Q6.31a

Which step of glycolysis would not occur spontaneously at standard-state conditions and why?

Q6.31b

Consider a hydrolysis of PEP, a phosphate compound.



At the temperature of 288K, the following reaction took place and has a reaction Gibbs free energy of -49.5 kJ/mole. Find the concentration of PEP for the reaction if the other concentrations are: $[\text{P}_i] = 3.54 \times 10^{-1} \text{ M}$, $[\text{Pyruvate}] = 1.85 \times 10^{-2} \text{ M}$.

Hint: Use equation $\Delta_r G^\circ = -RT \ln K_p$

S6.31b

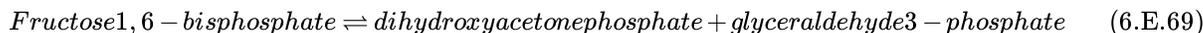
$$\Delta_r G = \Delta_r G^\circ + RT \ln \frac{[\text{pyruvate}][\text{P}_i]}{[\text{PEP}]} \quad (6.E.66)$$

$$-49500 \frac{\text{J}}{\text{mol}} = -61900 \frac{\text{J}}{\text{mol}} + (8.314 \frac{\text{J}}{\text{K} \cdot \text{mol}})(288\text{K}) \ln \frac{(1.85 \times 10^{-2} \text{ M})(3.54 \times 10^{-1} \text{ M})}{[\text{PEP}]} \quad (6.E.67)$$

$$[\text{PEP}] = 3.69 \times 10^{-5} \text{ M} \quad (6.E.68)$$

Q6.32

For the following reaction:



The $\Delta G^{\circ'} = 5.7 \text{ kcal/mol}$. Calculate the equilibrium constant and determine if the reaction is spontaneous or not at 310K.

S6.32

$$\Delta G^{\circ'} = 5.7 \text{ kcal/mol} = 23.8488 \text{ kJ/mol}$$

$$\Delta G^{\circ'} = -RT \ln(k'_{eq})$$

$$k'_{eq} = e^{-\frac{\Delta G^{\circ'}}{RT}} = e^{-\frac{23848.8 \text{ J/mol}}{(-8.314 \text{ J/K} \cdot \text{mol})(310\text{K})}} = 9.58 \times 10^{-5}$$

Small k'_{eq} suggest that this reaction is not a spontaneous process under the given conditions.

Q6.32a

Consider the following reaction:



Find:

- the value of the standard free energy at 300 K.
- the ratio between $\Delta_r G^{\circ'}$ at 300 K and $\Delta_r G^{\circ'}$ at 333 K.

S6.32a

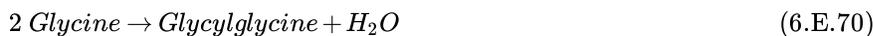
a) The standard free energy = $(-1544.3) - (-908.9 + -875.9) = 240.2 \text{ kJ/mol}$

b) ΔG° at 300 K = $\Delta G_1 + RT \ln Q = -34.6 \text{ kJ/mol}$

ΔG° at 333 K = $\Delta G_2 + RT \ln Q = -26.8 \text{ kJ/mol}$

Q6.32b

Consider the formation of the dipeptide glycylglycine. Using the following information, calculate the $\Delta_r G^\circ$.



$$\Delta_r G^\circ = 29.5 \text{ kJ mol}^{-1} \quad (6.E.71)$$

$$[\text{Glycine}] = 1.4 \text{ M} \quad (6.E.72)$$

$$[\text{Glycylglycine}] = 0.7 \text{ M} \quad (6.E.73)$$

$$[\text{H}_2\text{O}] = 1.0 \text{ M} \quad (6.E.74)$$

S6.32b

Use the following equation and plug in values.

$$\Delta_r G^\circ = \Delta_r G^\circ + RT \ln(K) \quad (6.E.75)$$

$$\Delta_r G^\circ = \Delta_r G^\circ + RT \ln \frac{[\text{Glycylglycine}] \cdot [\text{H}_2\text{O}]}{[\text{Glycine}]^2} \quad (6.E.76)$$

$$\Delta_r G^\circ = 29.5 \text{ kJ mol}^{-1} + \left(\frac{8.3145}{1000} \text{ kJ mol}^{-1} \text{ K}^{-1} \right) (298 \text{ K}) \ln \frac{0.7 \text{ M} \cdot 1.0 \text{ M}}{1.4^2 \text{ M}} \quad (6.E.77)$$

$$\Delta_r G^\circ = 26.7 \text{ kJ mol}^{-1} \quad (6.E.78)$$

Click [here](#) for some more information on bioenergetics and free energy.

Q6.32c

Consider the following reaction:



$$\Delta_f \bar{G}^\circ (\text{NH}_3(\text{g})) = -16.6 \frac{\text{kJ}}{\text{mol}} \quad (6.E.80)$$

$$\Delta_f \bar{G}^\circ (\text{H}_2\text{O}(\text{l})) = -237.2 \frac{\text{kJ}}{\text{mol}} \quad (6.E.81)$$

$$\Delta_f \bar{G}^\circ (\text{NH}_4^+(\text{aq})) = -79.3 \frac{\text{kJ}}{\text{mol}} \quad (6.E.82)$$

What is the equilibrium constant of this process? Is this process typically spontaneous process under standard conditions?

S6.32c

To calculate change in Gibbs free energy for the equation, we use the standard molar Gibbs energies of formation for the reactants and products:

$$\Delta_r G = 2 \Delta_f \bar{G}^\circ (\text{NH}_4^+(\text{aq})) - \Delta_f \bar{G}^\circ (\text{H}_2\text{O}(\text{l})) - 2 \Delta_f \bar{G}^\circ (\text{NH}_3(\text{g})) \quad (6.E.83)$$

$$= 2 \left(-79.3 \frac{\text{kJ}}{\text{mol}} \right) - \left(-237.2 \frac{\text{kJ}}{\text{mol}} \right) - 2 \left(-16.6 \frac{\text{kJ}}{\text{mol}} \right) \quad (6.E.84)$$

$$= 141.8 \frac{\text{kJ}}{\text{mol}} \quad (6.E.85)$$

To calculate the equilibrium constant:

$$\ln K = -\frac{\Delta_r G}{RT} = -\frac{141800 \frac{\text{J}}{\text{mol}}}{\left(8.3145 \frac{\text{J}}{\text{K} \cdot \text{mol}} \right) (298 \text{ K})} = -57.23 \quad (6.E.86)$$

$$K = e^{-57.23} = 1.40 \times 10^{-25} \quad (6.E.87)$$

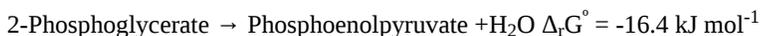
Because the K value is so low for this process, the reaction does not occur spontaneously at 25° C

Q6.33a

Calculate the $\Delta_r G^\circ$ and equilibrium constant for the following reaction at 298K:



Given that:



S6.33a

$$\Delta_r G^\circ = 4.2 \text{ kJ mol}^{-1} - 16.4 \text{ kJ mol}^{-1} = 12.2 \text{ kJ mol}^{-1}$$

$$\Delta_r G^\circ = -RT \ln K \quad (6.E.88)$$

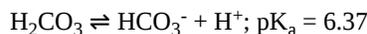
$$\ln K = \frac{12.2 * 10^3 \text{ J mol}^{-1}}{-(8.314 \text{ J mol}^{-1} \text{ K}^{-1}) 298 \text{ K}} \quad (6.E.89)$$

$$K = e^{.00492} \quad (6.E.90)$$

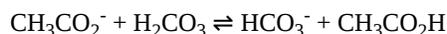
$$K = 1.00 \quad (6.E.91)$$

Q6.33b

Two acid dissociation reactions for carbonic and acetic acid and their corresponding pK_a values are displayed below.



Assuming the reactions take place at 298K, what is the equilibrium constant and change in gibbs' free energy associated with the following reaction?



Q6.34

Suppose the isomerization of DHAP to GAP in glycolysis has an enthalpy of -1.20 kJ/mol. At 25°C the Gibbs free energy of the reaction is 1.98 kJ/mol. Determine the equilibrium constant K of the isomerization at 25°C and at 35°C

Hint: Use [van't Hoff](#) equation

S6.34

For K at 25°C

$$\Delta_r G^\circ = -RT \ln K_{25^\circ} \quad (6.E.92)$$

$$1980 \frac{\text{J}}{\text{mol}} = -(8.314 \frac{\text{J}}{\text{K}})(25 + 273)K(\ln K_{25^\circ}) \Rightarrow K_{25^\circ} = 0.450 \quad (6.E.93)$$

For K at 35°C

$$\ln \frac{K_2}{K_1} = \frac{\Delta_r H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (6.E.94)$$

$$\ln \frac{K_{35^\circ}}{0.45} = \frac{-1200 \text{ J/mol}}{8.314 \frac{\text{J}}{\text{K} \cdot \text{mol}}} \left(\frac{1}{(25 + 273) \text{ K}} - \frac{1}{(35 + 273) \text{ K}} \right) \quad (6.E.95)$$

$$K_{35^\circ} = 0.152 \quad (6.E.96)$$

Q6.35a

Steady state and equilibrium state have an important role in understanding enzyme kinetics. What are some significant differences between the two?

S6.35a

In a steady state, there is no net change over time in concentrations of reactants and products of a reaction since they are being produced and consumed at constant rates. In this sense a steady state is a dynamic equilibrium. A steady state can be going in either the forward reaction or the backward reaction.

A chemical equilibrium on the other hand is when a reaction goes in the forward and backward reaction at the same rate so there is no net change in the system.

This is important because cells maintain steady states so that they are able to use particular reactions continuously. If a cell were at chemical equilibrium it would be dead because it would be at the point where all reactions are not going anymore, among other reasons.

Also, it is important to note that in a steady state, reactions are reversible compared to chemical equilibrium where the reaction rate is zero.

Click [here](#) to see more information about steady states.

Q6.35b

Is the following an example of a [steady state](#), [equilibrium state](#), or neither:

- Glycolysis, ingestion, and respiration
- $\text{NaCl}_{(s)} \rightleftharpoons \text{Na}^+_{(aq)} + \text{Cl}^-_{(aq)}$
- Sodium potassium ATPase
- Citric Acid Cycle
- oxidation of gold

S6.35b

- steady state
- equilibrium state
- steady state
- steady state
- neither

Q6.36

Diatomic hydrogen gas and diatomic iodine gas are in equilibrium with hydrogen Iodide gas in a closed environment of unknown volume at an unknown temperature.

Find the pressure equilibrium constant if the partial pressures of the gases are as follows: $P_{\text{H}_2} = 812 \text{ mmHg}$ $P_{\text{I}_2} = 587 \text{ mmHg}$ $P_{\text{HI}} = 980 \text{ mmHg}$

Find the activity equilibrium constant if the activity constants of the gases are as follows $\gamma_{\text{H}_2} = 1.45$ $\gamma_{\text{I}_2} = 0.844$ $\gamma_{\text{HI}} = 1.23$

Use your results to find the thermodynamic equilibrium constant.

S6.36

The reaction in question is $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$

The pressure equilibrium constant is given by $P_{\text{HI}}^2 / (P_{\text{H}_2} P_{\text{I}_2})$, the activity equilibrium constant is given by $\gamma_{\text{HI}}^2 / (\gamma_{\text{H}_2} \gamma_{\text{I}_2})$, and the thermodynamic equilibrium constant is given by the product of those two.

$$K_p = (980 \text{ mmHg})^2 / (812 \text{ mmHg} * 587 \text{ mmHg}) = 2.01$$

$$K_\gamma = 1.23^2 / (1.45 * 0.844) = 1.24$$

$$K_{\text{thermo}} = 1.24 * 2.01 = 2.49$$

Q6.38



This reaction happens at 273K. You are given a K_p of 0.683. The pressure for SO_2 is 0.58 bar for Cl_2 is 0.93 bar, and SO_2Cl_2 is 0.776 bar. From this information, determine $(\Delta_r)G$.

$$\Delta_r G^\circ = -RT \ln K_p$$

$$= (-8.314 \text{ J mol}^{-1} \text{ K}^{-1})(273 \text{ K}) \ln(0.683)$$

$$= -865.4 \text{ J mol}^{-1}$$

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

$$= 865.4 \frac{\text{J}}{\text{mol}} + (8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}})(273 \text{ K}) \ln \frac{0.776}{0.58 \cdot 0.93}$$

$$= 1.69 \text{ kJ mol}^{-1}$$

Q6.40

Assuming oxygen binding to hemoglobin can be represented by the following reaction:



If the value of $\Delta_r G^\circ$ for the reaction is $-11.2 \text{ kJ mol}^{-1}$ at 37°C , calculate the value of $\Delta_r G^\circ$ for the reaction.

Q6.42

At $T=300\text{K}$, given the mole ratio between 2 isomers Cis-2-butene and Trans-2-butene in an equilibrium mixture is 1:4. Evaluate $\Delta_r G$ of the reversible reaction:



Q6.44

When discussing the reaction in biological cells, why would you use concentrations instead of activities?

S6.44

Concentrations are generally smaller and it's easier to compare the concentrations between two parts of a cell or between different molecules in a reaction whereas activity describes behavior.

Q6.46

The following data shows the oxygen binding concentration in snails. The protein concentration is 15mM. Find n and K_d by using the *Scatchard plot*

$[\text{O}_2]_{total}$	10 mM	14 mM	18 mM	22 mM	26 mM	30 mM	34 mM	38 mM	42 mM	46 mM
$[\text{O}_2]_{bound}$	9 mM	12 mM	16 mM	19 mM	22 mM	25 mM	28 mM	32 mM	35 mM	39 mM

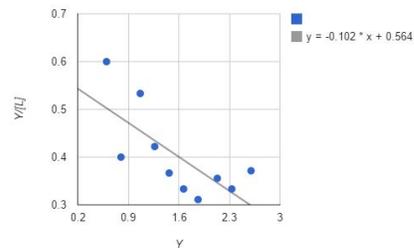
S6.46

$$y = mx + b$$

$$\frac{Y}{[L]} = \left(-\frac{1}{K_d}\right)Y + \frac{n}{K_d}$$

$$Y = \frac{[\text{O}_2]_{bound}}{[P]}$$

$$\cdot [L] = [\text{O}_2]_{free}$$



[O2]tot	10	14	18	22	26	30	34	38	42	46
[O2]bound	9	12	16	19	22	25	28	32	35	39
[O2]free	1	2	2	3	4	5	6	6	7	7
Y	0.6	0.8	1.067	1.267	1.467	1.667	1.867	2.133	2.333	2.6
Y/[L]	0.6	0.4	0.833	0.422	0.367	0.333	0.311	0.356	0.333	0.371

$$-\frac{1}{K_d} = -0.102$$

$$K_d = 9.804$$

$$\frac{n}{K_d} = 0.564$$

$$n = K_d * 0.564 = 5.529$$

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