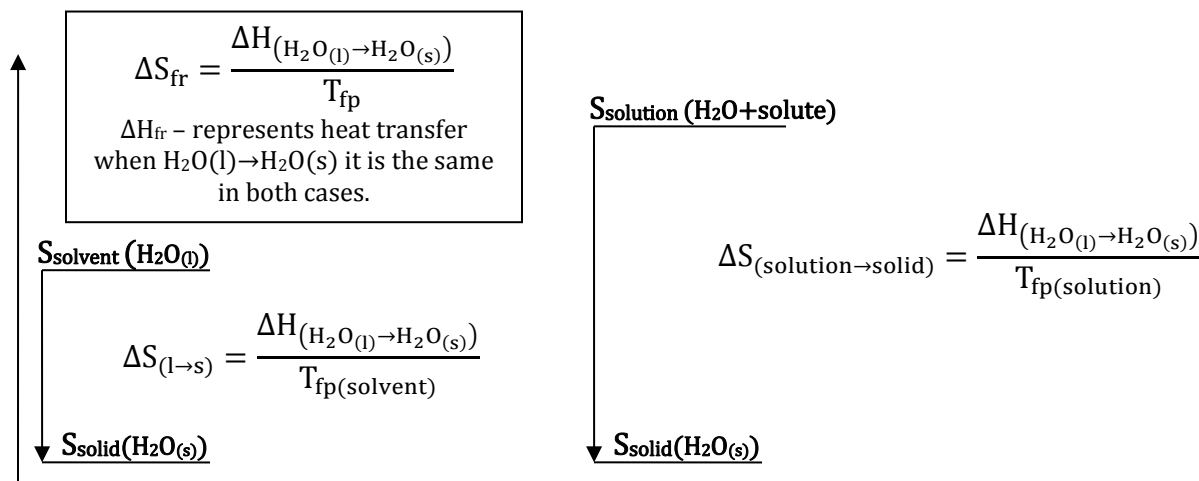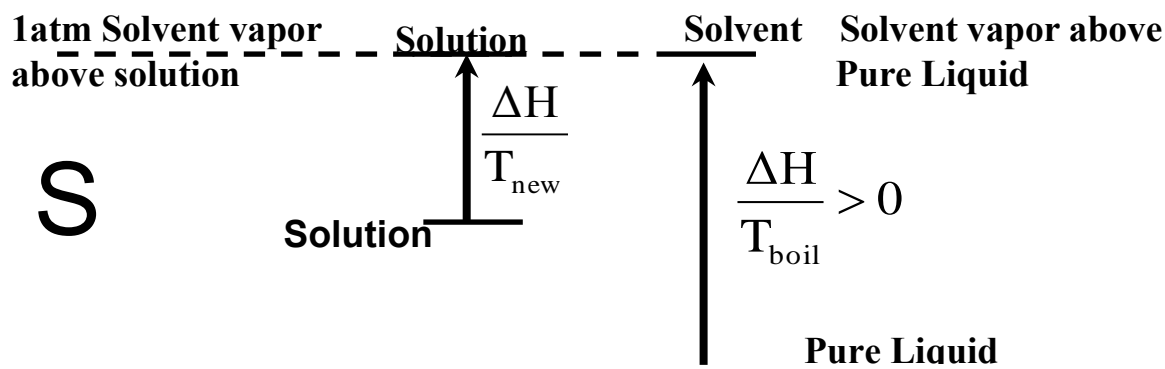Student name_____ TA name_____ Section_____

Things you should know when you leave Discussion today:

1. Second law of Thermodynamics: $\Delta S_{net} = \Delta S_{system} + \Delta S_{surrounding}$
   i. $\Delta S_{net} = \Delta S_{system} + \Delta S_{surrounding} > 0$ process is spontaneous
   ii. $\Delta S_{net} = \Delta S_{system} + \Delta S_{surrounding} < 0$ process is not spontaneous
   iii. $\Delta S_{net} = 0$ process is at Equilibrium $T = T_{equilibrium}$

2. $\Delta S_{surroundings} = \dfrac{\Delta H_{surr}}{T_{surr}} = -\dfrac{\Delta H_{system}}{T_{surr}}$
   i. ΔS_{sur} is thermal entropy due to distribution of quanta ($\mathbf{q}$) of energy among fixed particles ($\mathbf{m}$). Increase in number of quanta ($\mathbf{q}$) of energy will increase the number of distinguishable arrangements. More quanta ($\mathbf{q}$) of energy correspond to higher temperature.

3. $\Delta S_{system} = \Delta_r S° = \Sigma\,[n_i\,(S°)]_{product} - \Sigma\,[n_j\,(S°)]_{reactants} = S_{final} - S_{initial}$
   i. ΔS_{system} is positional entropy due to distribution of molecules. The more volume per molecule, the more distinguishable arrangements.
   ii. Where S° is Standard Entropy of Formation. Standard Entropy of Formation for elements in the standard state <u>does not equal zero</u>
   iii. $S_{gas} > S_{solution} > S_{solvent} > S_{solid}$
   iv. $\Delta S_{sys} = \dfrac{\Delta H_{sys}}{T_{equilibrium}}$

4. Entropy diagram for freezing point lowering of water

$$\Delta S_{fr} = \frac{\Delta H_{(H_2O_{(l)} \to H_2O_{(s)})}}{T_{fp}}$$

ΔH_{fr} – represents heat transfer when $H_2O(l) \to H_2O(s)$ it is the same in both cases.

$S_{solvent}\,(H_2O_{(l)})$

$$\Delta S_{(l \to s)} = \frac{\Delta H_{(H_2O_{(l)} \to H_2O_{(s)})}}{T_{fp(solvent)}}$$

$S_{solid}(H_2O_{(s)})$

$S_{solution}\,(H_2O + solute)$

$$\Delta S_{(solution \to solid)} = \frac{\Delta H_{(H_2O_{(l)} \to H_2O_{(s)})}}{T_{fp(solution)}}$$

$S_{solid}(H_2O_{(s)})$

1. Draw an entropy diagram that describes boiling point elevation. $T_{new} > T$

1atm Solvent vapor above solution   **Solution**   **Solvent**   **Solvent vapor above Pure Liquid**

S

$$\frac{\Delta H}{T_{new}}$$

Solution

$$\frac{\Delta H}{T_{boil}} > 0$$

Pure Liquid

a. Compare the entropy change when a pure solvent boiling and when a solution boiling:

$$\Delta S_{soln} > \Delta S_{pure} \qquad \Delta S_{soln} < \Delta S_{pure} \qquad \Delta S_{soln} = \Delta S_{pure}$$
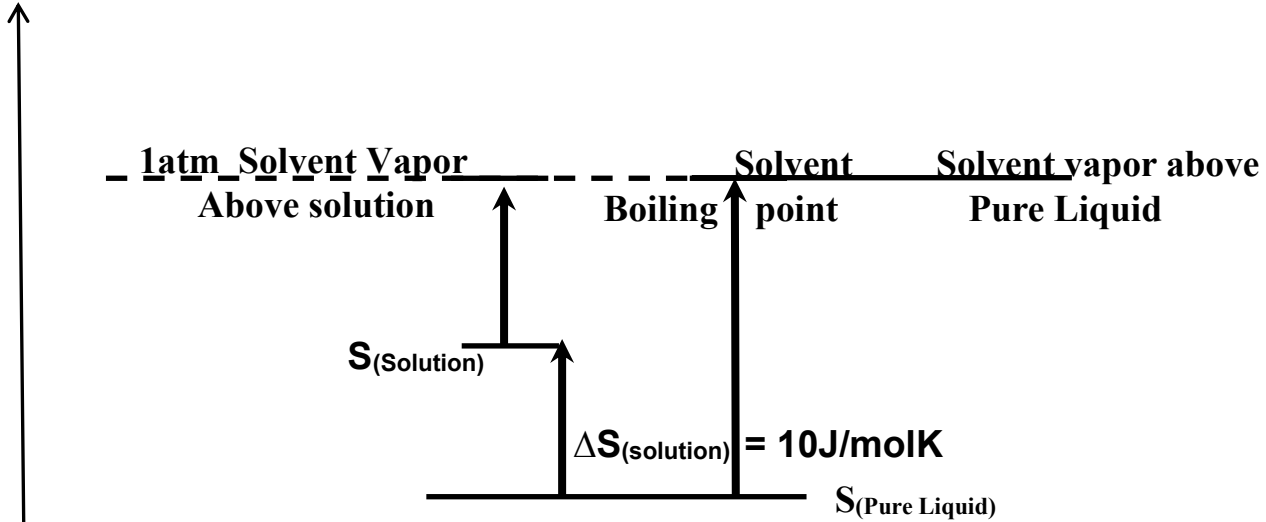
b. Compare the magnitudes of entropy change when a pure solvent boiling and when a solution boiling:

$$\left|\Delta S_{soln}\right| > \left|\Delta S_{pure}\right| \qquad \left|\Delta S_{soln}\right| < \left|\Delta S_{pure}\right| \qquad \Delta S_{soln} = \Delta S_{pure}$$

c. The magnitudes of enthalpy change ΔH_{vap} (water, $l\rightarrow$ water, g) compared to ΔH_{vap} (solution, $l\rightarrow$ water, g) is... Greater   smaller   the same

d. T_{bp} (solution) compared to T_{bp} (solvent) is ... Greater   Smaller   the same

2. A liquid boils at 400. K and its enthalpy of vaporization is $\Delta_{vap}H = 40.$ kJ/mol. When a nonvolatile solute is added to the liquid, the entropy of the solution at 400 K is 10. J/(mol/K) higher than that if the pure liquid at 400 K. Calculate the boiling point of the solution. *Hint: Draw the diagram.*
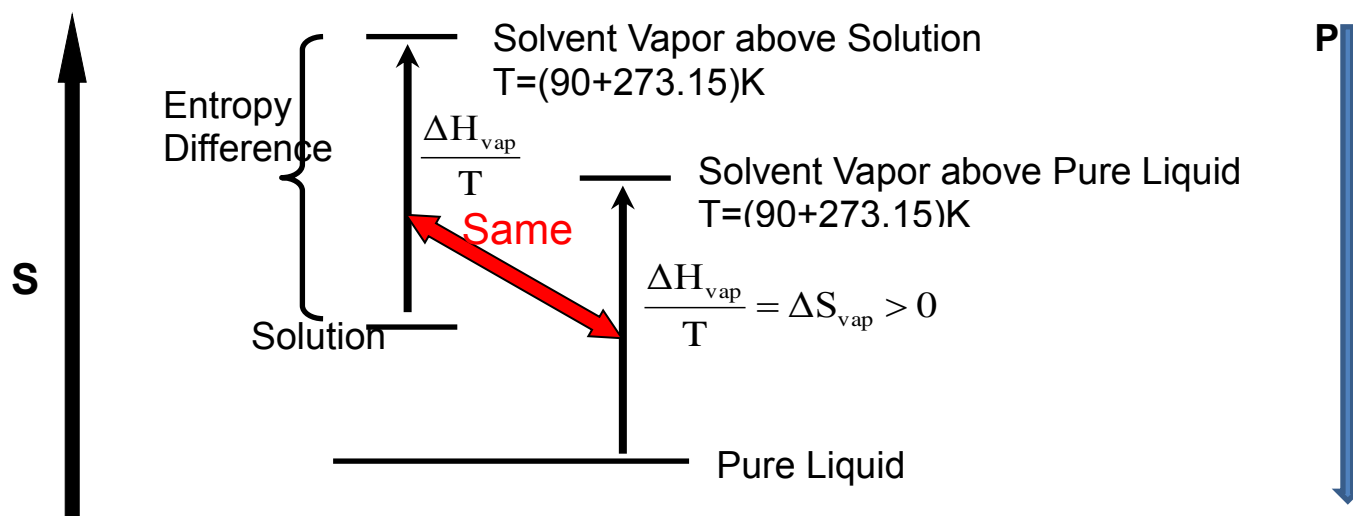
_ **1atm_Solvent Vapor** _ _ _ _ _ _ **Solvent** ___ **Solvent vapor above**
Above solution   **Boiling** ↑ **point**   **Pure Liquid**

$\mathbf{S}_{\textbf{(Solution)}}$

$\Delta\mathbf{S}_{\textbf{(solution)}}$ **= 10J/molK**

$\mathbf{S}_{\textbf{(Pure Liquid)}}$

$$\Delta S_{sys}\text{ (solvent-gas)}= \frac{\Delta H_{sys}}{T_{eq}} = \frac{\mathbf{\Delta H}_{\textbf{(H}_2\textbf{O(l)}\rightarrow\textbf{H}_2\textbf{O(s))}}}{\mathbf{T}_{\mathit{fp}}}$$

$$\Delta S_{sys}\text{ (solvent-gas)}= \frac{\Delta H_{sys}}{T_{eq}} = \frac{40000 J\,/\,mol}{400\,K} = 100\,\frac{J}{molK}$$

ΔS_{sys}(solution-gas) = ΔS_{sys} (solvent-gas)− 10J/molK= 90J/molK;

$$\mathbf{T_{eq}}= \frac{\Delta H_{sys}}{\Delta S_{sys}} = \frac{40000J\,/\,mol}{90\,\dfrac{J}{molK}} = 444K$$

3. At 90 °C the vapor pressure of water is 0.9 atm and the vapor pressure of an aqueous glucose solution is 0.8 atm. Construct an entropy diagram for vapor pressure lowering and answer the questions below using your drawing. *Hint: have both entropy and pressure scales, and remember that $S \propto W \propto V \propto \frac{1}{P}$.*

S

Entropy Difference {

Solvent Vapor above Solution T=(90+273.15)K

$\frac{\Delta H_{vap}}{T}$

Same

Solution

$\frac{\Delta H_{vap}}{T} = \Delta S_{vap} > 0$

Solvent Vapor above Pure Liquid T=(90+273.15)K

Pure Liquid

P

a. ΔH_{vap} (water$_{(l)} \rightarrow$ water$_{(g)}$) compared to ΔH_{vap} (glucose solution$_{(l)} \rightarrow$ water$_{(g)}$) is...

      Greater   smaller   the same

b. S (water $_{(l)}$) compared to S (glucose solution$_{(l)}$) is...   Greater   smaller   the same

c. S (water$_{(g)}$) compared to S (glucose solution$_{(g)}$) is...   Greater   smaller   the same

d. ΔS_{vap} (water$_{(l)} \rightarrow$ water$_{(g)}$) compared to ΔS_{vap} (glucose solution$_{(l)} \rightarrow$ water$_{(g)}$) is...

      Greater   smaller   the same

4. An ionic solid $M_2X_{3(s)}$ is highly soluble in water at 300 K and when it dissolves in water to form M^{3+} (aq) and $X^{2-}_{(aq)}$, the entropy change of the system is −450 J/(K mol). Compared to its solubility at 300 K, the solubility of $M_2X_{3(s)}$ in boiling water will be ... Circle the correct answer and explain why:
        <u>lower</u>   the same   higher
$\Delta S_{system} < 0$ for the process to be spontaneous $\Delta S_{surrounding}$ has to be positive and

$|\Delta S_{sur}| > |\Delta S_{sys}|$ since $\Delta S_{sur} = -\frac{\Delta H_{sys}}{T} > 0$ this means that process is exothermic $\Delta H_{sys} \underline{\le 0}$

Increasing the T of an exothermic reaction makes it less spontaneous and solid less soluble.

5. To melt a certain liquid $\Delta H°_{fus} = 15.0$ kJ/mol. And the freezing point is at 45°C. Calculate ΔS_{sys} of the substance going from liquid to solid.
$\Delta H°_{sys} = -\Delta H°_{fus}$

$\Delta S_{sys} = \frac{\Delta H_{sys}}{T} = -15000/(273+45) = -47.2$ J/mol·K

3

6. A liquid freezes at 215. K and its $\Delta_{fuss}H = 25.$ kJ/mol. When a nonvolatile solute is added to the liquid, the entropy of the solution is 15. J/(mol/K) higher than that of the pure liquid at 215K. Calculate the freezing point of the solution. Hint: use the diagram on page 1 for help

7. Compare the entropy change when a pure solvent freezes and when a solution freezes:

$$\Delta S_{soln} > \Delta S_{pure} \qquad \Delta S_{soln} < \Delta S_{pure} \qquad \Delta S_{soln} = \Delta S_{pure}$$

8. Compare the magnitudes of entropy change when a pure solvent freezes and a solution freezes:

$$\left|\Delta S_{soln}\right| > \left|\Delta S_{pure}\right| \qquad \left|\Delta S_{soln}\right| < \left|\Delta S_{pure}\right| \qquad \Delta S_{soln} = \Delta S_{pure}$$

9. Compare the entropy change when vapor forms over pure water and over a solution, both at 25 C:

$$\Delta S_{soln} > \Delta S_{pure} \qquad \Delta S_{soln} < \Delta S_{pure} \qquad \Delta S_{soln} = \Delta S_{pure}$$

10. Calculate the temperature (in K) at which melting 36.0 grams of water (molar mass of water is 18.0 g/mol) changes the entropy of the universe by –16.0 J/K. For water, $\Delta_{fus}H = 6.00$ kJ/mol and $\Delta_{fus}S = 22.0$ J/(mol K).

$$\Delta S_{univ} = \Delta S_{system} + \Delta S_{surrounding} = \Delta S_{system} - \frac{\Delta H_{system}}{T_{sur}}$$

Since we have 2 moles of water:

$$-16.0 \text{ J/K} = 22.0 \text{ J/(mol K)} * 2 \text{moles} - \frac{6.00\frac{kJ}{molK} \cdot 2moles \cdot 1000\frac{J}{kJ}}{T_{sur}}.$$

T=200. K

1. $\Delta G° = -T \cdot \Delta S_{net} = \Delta H°_{sys} - T \Delta S°_{sys}$

$$\Delta G°_{reaction} = \sum_{products} n_j (\Delta G_f°) - \sum_{reactants} n_j (\Delta G_f°) \qquad @25°C$$

   a. $\Delta G° = -R \cdot T \cdot \ln(K) = -2.3 \cdot R \cdot T \cdot \log(K)$

   b. $K = 10^{-\left(\frac{\Delta G°}{R \cdot T \cdot 2.3}\right)}$

   c. $\Delta G° = -n_e \cdot F \cdot E° = -q \cdot E°$

2. $\Delta G = R \cdot T \cdot \ln\left(\frac{Q}{K}\right) = 2.3 \cdot R \cdot T \cdot \log\left(\frac{Q}{K}\right) = \Delta G° + R \cdot T \cdot \ln(Q)$

   a. $Q = 10^{\left(\frac{\Delta G - \Delta G°}{R \cdot T \cdot 2.3}\right)}$

   b. $\Delta G = -T \Delta S_{net} = \Delta H_{sys} - T \Delta S_{sys}$

   c. $\Delta G = -n_e \cdot F E = -q \cdot E$

      i. $\Delta G < 0$ process is Spontaneous

      ii. $\Delta G > 0$ process is Not Spontaneous

      iii. $\Delta G = 0$ process is at Equilibrium

11. Remember that $\Delta G° = -RT \ln K = \Delta H°_{sys} - T \Delta S°_{sys}$ and so we can derive

$$\ln K = -\frac{\Delta H°_{sys}}{RT} + \frac{\Delta S°_{sys}}{R}$$
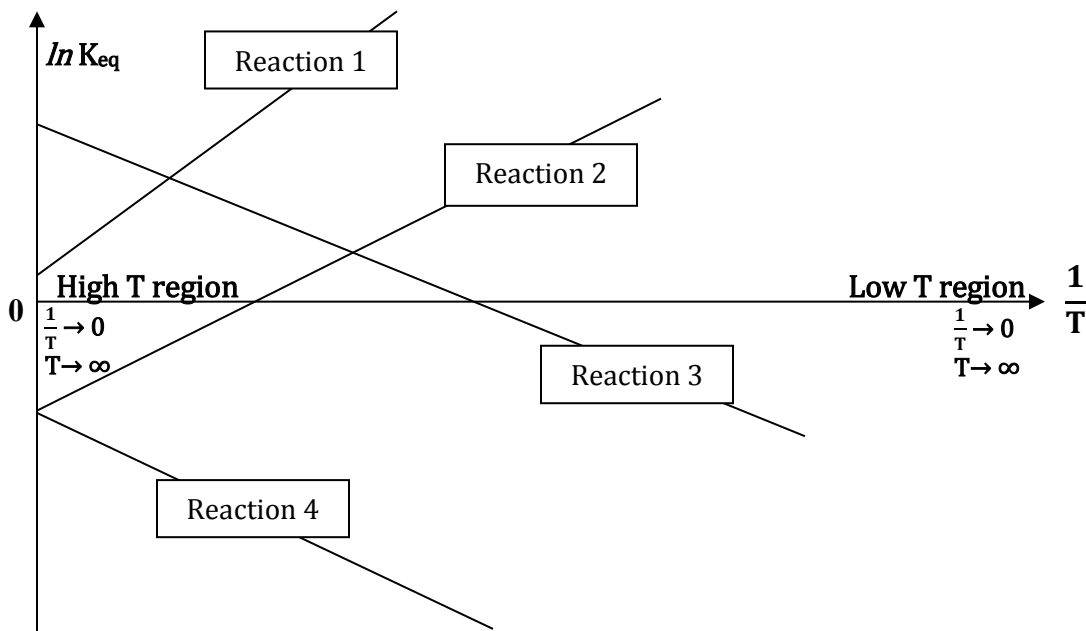
a. When $\ln K$ is positive. What does it mean? Why?

b. When $\ln K$ is negative. What does it mean? Why?

c. When $\ln K$ is zero. What does it mean? Why?

   Remember that $\ln K = -\frac{\Delta H°_{sys}}{R \cdot T} + \frac{\Delta S°_{sys}}{R}$ and that equations of the line is $y = mx + b$

d. What is the y-intercept of the expression for $\ln K$?

e. What is slope of the expression for $\ln K$?

f. The slope is positive. What does it mean? Why?

g. The slope is negative. What does it mean? Why?

For Reactions 1, 2, 3 and 4 in the plot above, answer the following questions.

h. Is the reaction endothermic or exothermic and at what temperatures?

   Reaction 1:   Reaction 2:   Reaction 3:   Reaction 4:

i. If the reaction above are redox reactions, which ones will have positive standard voltages and at what temperatures?

   Reaction 1:   Reaction 2:   Reaction 3:   Reaction 4:

j. At what temperatures each of reactions will increase or decrease entropy of the system?

   Reaction 1:   Reaction 2:   Reaction 3:   Reaction 4:

k. For each reaction choose at what temperatures the ratio of product to reactants will be greater than 1 or smaller than 1?

   Reaction 1:   Products/ Reactants >1:   High T   Low T   never   always

                 Products/ Reactants <1:   High T   Low T   never   always

   Reaction 2:   Products/ Reactants >1:   High T   Low T   never   always

                 Products/ Reactants <1:   High T   Low T   never   always

   Reaction 3:   Products/ Reactants >1:   High T   Low T   never   always

                 Products/ Reactants <1:   High T   Low T   never   always

   Reaction 4:   Products/ Reactants >1:   High T   Low T   never   always

                 Products/ Reactants <1:   High T   Low T   never   always

l. It is a well-known fact that mixing any group 1 metal and water leads to an explosion. The plot of which reaction corresponds to the reaction between Na and water:

$$2Na_{(s)} + 2H_2O_{(l)} \leftrightharpoons 2Na^+_{(aq)} + 2\,OH^-_{(aq)} + H_{2(g)}$$

   Reaction 1:   Reaction 2:   Reaction 3:   Reaction 4:

m. The plot of which reaction corresponds to freezing of water?

   Reaction 1:   Reaction 2:   Reaction 3:   Reaction 4:

12. For the following combustion reaction, calculate $\Delta G°$ at 25°C :

$$C_6H_{12}O_6\ (s) + 6O_2\ (g) \rightarrow 6\ CO_2\ (g) + 6\ H_2O\ (l)$$

	$\Delta G°_f$(kJ/mol) (only at 25°C)
$O_2(g)$	0.
$C_6H_{12}O_6\ (s)$	−900.
$CO_2\ (g)$	−400.
$H_2O(l)$	−240.

   a. Without doing a calculation, at what temperatures will this process cease to be spontaneous at standard states?

13. Circle the value of ΔG when both products and reactants are in their standard states. (Note: $Q=1$)

$$\Delta G = 1 \qquad \Delta G = 0 \qquad \Delta G = \Delta G° \qquad \text{None of these}$$

14. Circle the value of ΔG when $Q = K$.

$$\Delta G = 1 \qquad \Delta G = 0 \qquad \Delta G = \Delta G° \qquad \text{None of these}$$

15. Circle the value of $\Delta G°$ when $Q = K$.

$$\Delta G° = 1 \qquad \Delta G° = 0 \qquad \Delta G° = -RT\ln K \qquad \text{None of these}$$

16. Circle the value of $\Delta G°$ when $Q > K$.

$$\Delta G° = 1 \qquad \Delta G° = 0 \qquad \Delta G° = -RT\ln K \qquad \text{None of these}$$

17. When would $\Delta G° = 0$?

18. If $\Delta G = -5.0$ kJ/mol and $\Delta G° = 3.0$ kJ/mol circle everything that must be true:

$$Q = 1 \qquad Q > 1 \qquad Q < 1 \qquad Q < K \qquad Q = K \qquad Q > K$$

    a. Assuming temperature of 298 K, calculate the values of K and Q

19. Here are thermodynamic data for the gas phase dimerization. Calculate equilibrium constant at 37°C for the dimerization.

$$2\ HC(O)OH(g) \rightarrow (HC(O)OH)_2\ (g).$$

$\Delta_f H° (\ HC(O)OH(g)) = -350.0$ kJ/mol,
$\Delta_f H° (\ (HC(O)OH)_2\ (g)) = -800.0$ kJ/mol,
$S° (HC(O)OH(g)) = 250.0$ J/(K mol),
$S° (\ (HC(O)OH)_2\ (g)) = 350.0$ J/(K mol).
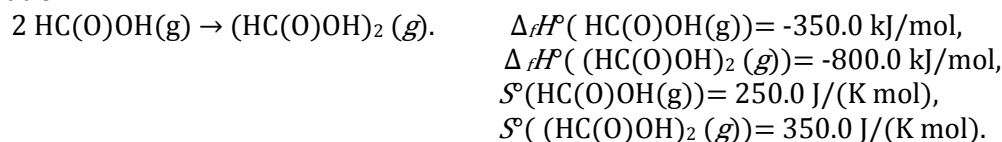
    a. Find $\Delta_{rxn} H° =$

    b. Find $\Delta_{rxn} S° =$

    c. Find $\Delta G°$ (Hint: $\Delta G° = \Delta H°_{sys} - T\Delta S°_{sys}$) :

    d. Calculate equilibrium constant: Hint: $\Delta G° = -RT \ln K$:

    e. Calculate the ΔG of dimerization reaction when the pressure of HC(O)OH is at 2.0 bars and the pressure of $(HC(O)OH)_2$ is at 3.5 bars at 37°C. Hint: $\Delta G = \Delta G° + RT \ln Q$

        i. Calculate Q:

        ii. $\Delta G =$

        iii. Calculate the total energy available for useful work from the dimerization of 1.00 kg of the reactant used at 37°C.

20. For autoionization of water at 330. K, $K_w = 1.0 \times 10^{-13}$ and at 300K, $K_w = 1.0 \times 10^{-14}$. Calculate the value of ΔH in kJ/mol and ΔS in $\dfrac{J}{molK}$. Do your calculations to 1 significant figure.

21. The standard free energy change for the process

$$A\ (aq) + B\ (aq) \leftrightharpoons 3C\ (aq) \text{ is } \Delta G° = +54 \text{ kJ/mol.}$$
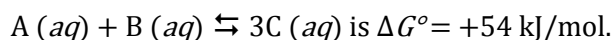
If the concentration of B is decreased from 1M to 0.50 M (but concentrations of A and C stay at standard states) circle the value of the free energy change, ΔG, relative to $\Delta G°$.
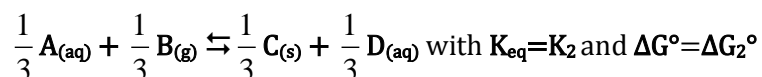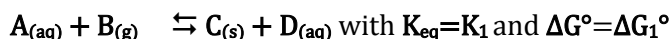
$$\Delta G < \Delta G° \qquad \Delta G = \Delta G° \qquad \Delta G > \Delta G°$$

22. If ΔG= 5.0 kJ/mol and $\Delta G°$= 4.0 kJ/mol circle everything that must be true:

$$Q=1 \quad Q>1 \quad Q<1 \qquad Q<K \quad Q=K \quad Q>K$$

a. Assuming temperature of 298 K calculate the values of K and Q. Useful Hint: at T=298K value of $2.3RT = 2.3 \cdot 8.314 (J.(mol \cdot K) \cdot 298K = 5698J/mol \approx 6kJ/mol$

23. Given the two reactions below, find the relationships between $\Delta G_1°$ and $\Delta G_2°$.

$$A_{(aq)} + B_{(g)} \leftrightarrows C_{(s)} + D_{(aq)} \text{ with } K_{eq}=K_1 \text{ and } \Delta G°=\Delta G_1°$$

$$\frac{1}{3} A_{(aq)} + \frac{1}{3} B_{(g)} \leftrightarrows \frac{1}{3} C_{(s)} + \frac{1}{3} D_{(aq)} \text{ with } K_{eq}=K_2 \text{ and } \Delta G°=\Delta G_2°$$

24. For the following reaction at 25°C using information below.

$$3H_2(g) + N_2(g) \leftrightarrows 2NH_3(g)$$
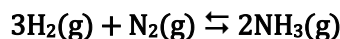
|	$\Delta G°$ kJ/mol	P (atm)
$H_2(g)$	0	0.010
$N_2(g)$	0	0.040
$NH_3(g)$	−16	0.20

a. Calculate value of $\Delta G°$.

b. Calculate value of K.

c. Calculate value of Q.

d. Calculate value of ΔG.

e. Based on your calculation, did the reaction pass an equilibrium point?

f. Based on your calculation, will the reverse reaction be spontaneous or not?

25. For the following reaction: $Br_{2(l)} \leftrightarrows Br_{2(g)}$
For the reaction above at 343 K use the information given, to calculate ΔH_{sys}, ΔS_{sys}, ΔS_{sur}, ΔS_{univ}, $\Delta G°$ and the temperature at which process will cease to be spontaneous. Do your calculations to 2 significant figures. Assume that $\Delta H°_{rxn}$ and $\Delta S°_{rxn}$ are independent of temperature.

	$\Delta H°_f$ (kJ/mol)	S° (J/mol·K)	$\Delta G°_f$(kJ/mol) (only at 25°C)
$Br_{2(g)}$	30.	250.	3.0
$Br_{2(l)}$	0	150.	0

26. You have a buffer with a pH = 5 at two different temperatures: $T_1 = 300$ K and $T_2 = 330$ K

$$HA_{(aq)} + H_2O_{(l)} \leftrightarrows A^-_{(aq)} + H_3O^+_{(aq)}$$
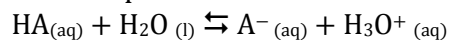
You need to have the following ratios of weak acid and conjugate base to make this happen:

at $T_1 \rightarrow [A^-]/[HA] = 1/2$

at T2→ $[A^-]/[HA] = 1/4$

To answer the following questions you need to draw the plot of lnK verses 1/T.

a. Will this reaction be exothermic, endothermic or neither.

b. The system entropy change will be: Circle one: $\Delta S > 0$ $\Delta S = 0$ $S < 0$

Answers:

1.
   a. $\Delta S_{soln} < \Delta S_{pure}$
   b. $|\Delta S_{soln}| < |\Delta S_{pure}|$
   c. the same
   d. greater
2. 444K
3.
   a. The same
   b. Smaller
   c. smaller
   d. The same
4. lower
5. -47.2 J/mol·K
6. 200.K
7. 190.K
8. $\Delta S_{soln} < \Delta S_{pure}$
9. $|\Delta S_{soln}| > |\Delta S_{pure}|$
10. $\Delta S_{soln} = \Delta S_{pure}$

Not part of exam 3
11.

   a. spontaneous; $\Delta G° < 0$
   b. non-spontaneous; $\Delta G° > 0$
   c. equilibrium; no more "potential" for the rxn to proceed
   d. $\Delta S°_{sys}/R$
   e. $\Delta H°_{sys}/R$
   f. exothermic; $\Delta H < 0$ for $-\Delta H°_{sys}/R$ to be (+)
   g. endothermic; $\Delta H > 0$ for $-\Delta H°_{sys}/R$ to be (-)
   h. Reaction 1: exo, all T
      Reaction 2: exo, all T

      Reaction 3: endo, all T
      Reaction 4: endo, all T
   j. Reaction 1: E° always (+)
      Reaction 2: E° only (+) at low T
      Reaction 3: E° only (+) at high T
      Reaction 4: E° never (+)
   k. Reaction 1: increase all T
      Reaction 2: decrease all T
      Reaction 3: increase all T
      Reaction 4: decrease all T
   l. Reaction 1: R/P > 1 always; R/P < 1 never
      Reaction 2: R/P > 1 low T; R/P < 1 high T
      Reaction 3: R/P > 1 high T; R/P < 1 low T
      Reaction 4: R/P > 1 never; R/P < 1 always
   m. Reaction 1
   n. Reaction 2

12. -2940kJ/mol
       a. $\Delta H°_{sys} < 0$ (exothermic) $\Delta S°_{sys} > 0$
13. $\Delta G = \Delta G°$
14. $\Delta G = 0$
15. $\Delta G° = $ -RT lnK
16. $\Delta G° = $ -RT lnK
17. K=1
18. $Q < 1$ $Q < K$
       a. 0.3. 0.040
19.
       a. -100.0 kJ/mol

9

    b. −150.0 J/(K mol)

    c. −53.48 kJ/mol

    d. $1.0399 \cdot 10^9$

    e.

          i. Q=0.875

         ii. *-53.84* kJ/mol

        iii. −585.2kJ

20. 60 kJ/mol; -60 J/mol·K

21. $\Delta G > \Delta G°$

22.

    a. Q>1; Q>K

    b. 0.2, 1.5

23. $K_2 = \sqrt[3]{K_1}$ $\Delta G_2° = \frac{1}{3}\Delta G_1°$

24.

    a. -32 kJ/mol

    b. $4.04 \cdot 10^5$

    c. $1 \cdot 10^6$

    d. 2.2kJ/mol

    e. Yes

    f. Spontaneous

25.

26.

    a. $\Delta H < 0$

    b. $S < 0$