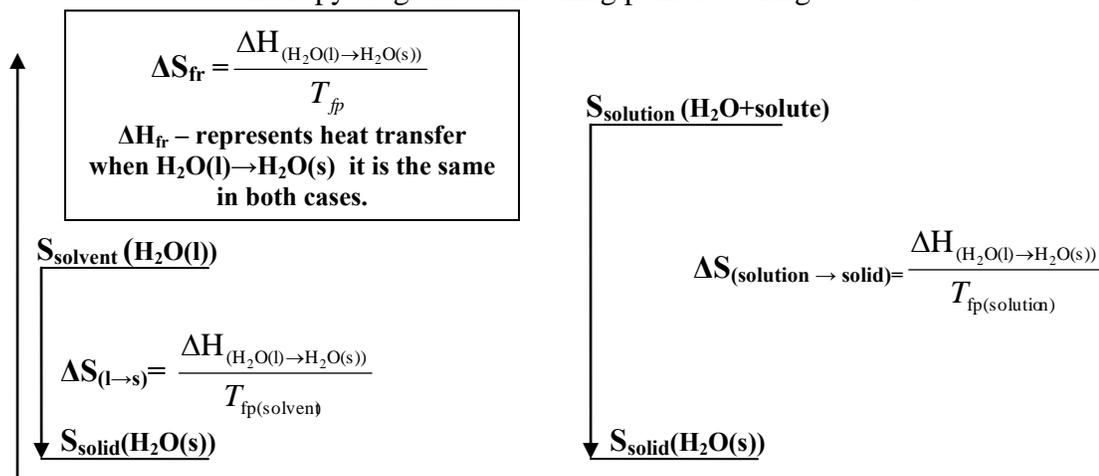


**Things you should know when you leave Discussion today:**

- Second law of Thermodynamics:  $\Delta S_{\text{net}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$ 
  - $\Delta S_{\text{net}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}} > 0$  process is *spontaneous*
  - $\Delta S_{\text{net}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}} < 0$  process is not *spontaneous*
  - $\Delta S_{\text{net}} = 0$  process is at *Equilibrium*  $T = T_{\text{equilibrium}}$
- $\Delta S_{\text{surroundings}} = \frac{\Delta H_{\text{sur}}}{T_{\text{sur}}} = -\frac{\Delta H_{\text{system}}}{T_{\text{sur}}}$ 
  - $\Delta S_{\text{sur}}$  is thermal entropy due to distribution of quanta (**q**) of energy among fixed particles (**m**). Increase in number of quanta (**q**) of energy will increase the number of distinguishable arrangements. More quanta (**q**) of energy correspond to higher temperature.
- $\Delta S_{\text{system}} = \Delta_r S^\circ = \sum [n_j(S^\circ)]_{\text{product}} - \sum [n_j(S^\circ)]_{\text{reactants}} = S_{\text{final}} - S_{\text{initial}}$ 
  - $\Delta S_{\text{system}}$  is positional entropy due to distribution of molecules. The more volume per molecule, the more distinguishable arrangements.
  - Where  $S^\circ$  is Standard Entropy of Formation. Standard Entropy of Formation for elements in the standard state does not equal zero
  - $S_{\text{gas}} > S_{\text{solution}} > S_{\text{solvent}} > S_{\text{solid}}$
  - $\Delta S_{\text{sys}} = \frac{\Delta H_{\text{system}}}{T_{\text{equilibrium}}}$
- $\Delta G^\circ = -T \Delta S_{\text{net}} = \Delta H_{\text{sys}}^\circ - T \Delta S_{\text{sys}}^\circ$ 
  - $\Delta G^\circ_{\text{rxn}}$  (at 25°C only) =  $\sum n_p (\Delta G_f^\circ) - \sum n_R (\Delta G_f^\circ)$
  - $\Delta G^\circ = -RT \ln K = -2.3 \cdot RT \cdot \log K$
  - $K = 10^{-\frac{\Delta G^\circ}{RT \cdot 2.3}}$
  - $\Delta G^\circ = -n_e \cdot F \cdot E^\circ = -q \cdot E^\circ$
- $\Delta G = RT \ln\left(\frac{Q}{K}\right) = 2.3 \cdot RT \cdot \log\left(\frac{Q}{K}\right) = \Delta G^\circ + RT \ln Q$ 
  - $Q = 10^{\frac{\Delta G - \Delta G^\circ}{RT \cdot 2.3}}$
  - $\Delta G = -T \Delta S_{\text{net}} = \Delta H_{\text{sys}} - T \Delta S_{\text{sys}}$
  - $\Delta G = -n_e \cdot FE = -q \cdot E$ 
    - $\Delta G < 0$  process is Spontaneous
    - $\Delta G > 0$  process is Not Spontaneous
    - $\Delta G = 0$  process is at Equilibrium
- Entropy diagram for freezing point lowering of water



1. Draw an entropy diagram that describes boiling point elevation.

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

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

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

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

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

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

2. A liquid boils at 400. K and its enthalpy of vaporization is  $\Delta_{\text{vap}}H = 40.$  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 of the pure liquid at 400 K. Calculate the boiling point of the solution.(Draw the diagram)  
(Answer: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  $S \sim W \sim V \sim \frac{1}{P}$ )

- $\Delta H_{\text{vap}}$  (water,  $l \rightarrow$  water,  $g$ ) compared to  $\Delta H_{\text{vap}}$  (glucose solution,  $l \rightarrow$  water,  $g$ ) is...

**Greater                  smaller                  the same**

- $S$  (water,  $l$ ) compared to  $S$  (glucose solution,  $l$ ) is... **Greater                  smaller                  the same**

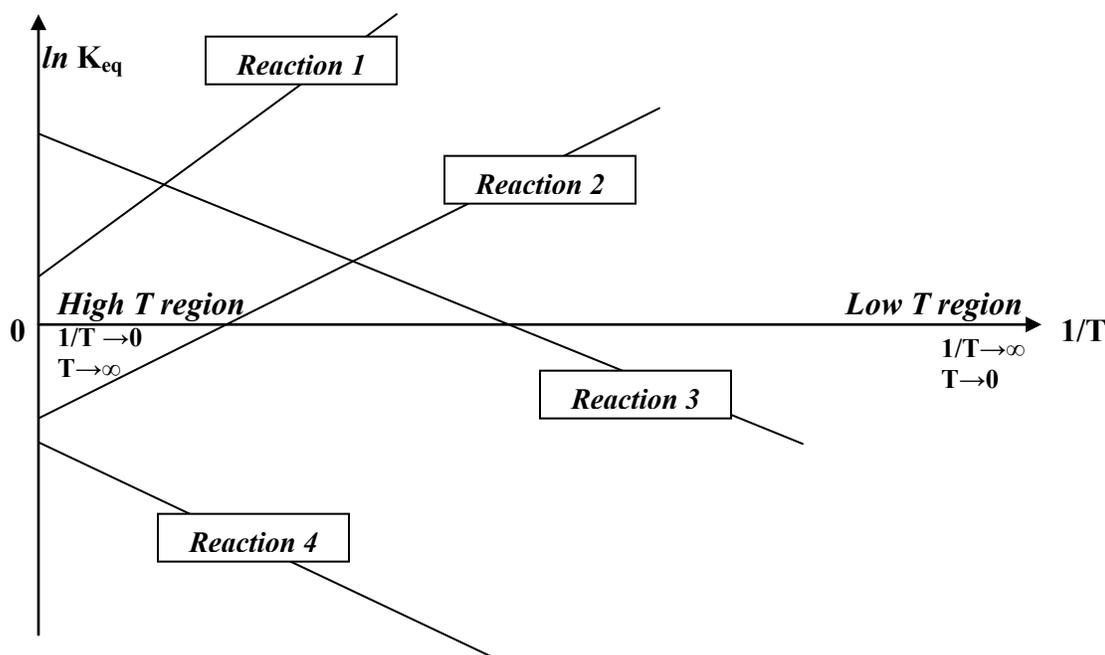
- $S$  (water,  $g$ ) compared to  $S$  (glucose solution,  $g$ ) is... **Greater                  smaller                  the same**

- $\Delta S_{\text{vap}}$  (water,  $l \rightarrow$  water,  $g$ ) compared to  $\Delta S_{\text{vap}}$  (glucose solution,  $l \rightarrow$  water,  $g$ ) is...

**Greater                  smaller                  the same**

4. Remember that  $\Delta G^\circ = -RT \ln K = \Delta H^\circ_{\text{sys}} - T\Delta S^\circ_{\text{sys}}$  and so we can derive

$$\ln K = -\frac{\Delta H^\circ_{\text{sys}}}{RT} + \frac{\Delta S^\circ_{\text{sys}}}{R}$$



- When  $\ln K$  is positive. What does it mean? Why?
- When  $\ln K$  is negative. What does it mean? Why?
- When  $\ln K$  is zero. What does it mean? Why?

Knowing that  $\ln K = -\frac{\Delta H^\circ_{\text{sys}}}{RT} + \frac{\Delta S^\circ_{\text{sys}}}{R}$  and that equations of the line is  $y = mx + b$

- What is the  $y$ -intercept of the expression for  $\ln K$ ?
- What is slope of the expression for  $\ln K$ ?
- The slope is positive. What does it mean? Why?
- The slope is negative. What does it mean? Why?



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

6. Circle the value of  $\Delta G$  when both products and reactants are in their standard states. (Note:  $Q=1$ )

$\Delta G = 1$        $\Delta G = 0$        $\Delta G = \Delta G^\circ$       None of these

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

$\Delta G = 1$        $\Delta G = 0$        $\Delta G = \Delta G^\circ$       None of these

8. Circle the value of  $\Delta G^\circ$  when  $Q = K$ .

$\Delta G^\circ = 1$        $\Delta G^\circ = 0$        $\Delta G^\circ = -RT \ln K$       None of these

9. Circle the value of  $\Delta G^\circ$  when  $Q > K$ .

$\Delta G^\circ = 1$        $\Delta G^\circ = 0$        $\Delta G^\circ = -RT \ln K$       None of these

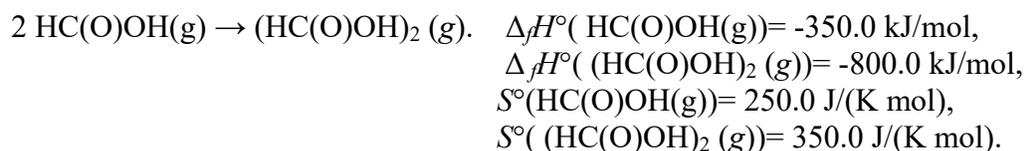
10. When would  $\Delta G^\circ = 0$ ?

11. If  $\Delta G = -5.0 \text{ kJ/mol}$  and  $\Delta G^\circ = 3.0 \text{ kJ/mol}$  circle everything that must be true:

$Q = 1$      $Q > 1$      $Q < 1$      $Q < K$      $Q = K$      $Q > K$

- a. **At home:** Assuming temperature of 298 K, calculate the values of K and Q. (Answers: 0.30, 0.040)

12. Here are thermodynamic data for the gas phase dimerization. Calculate equilibrium constant at 37°C for the dimerization. (Answers:  $(1.0121 \rightarrow 1.0399 \cdot 10^9)$ , -100.0, -150.0, -53.48, -53.84, -585.2)



- Find  $\Delta_{rxn} H^\circ =$
- Find  $\Delta_{rxn} S^\circ =$
- Find  $\Delta G^\circ$  (Hint:  $\Delta G^\circ = \Delta H^\circ_{\text{sys}} - T \Delta S^\circ_{\text{sys}}$ ) :
- Calculate equilibrium constant (Hint:  $\Delta G^\circ = -RT \ln K$ ) :

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

- Calculate Q:
- $\Delta G =$

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

13. 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  $\Delta H$  in kJ/mol and  $\Delta S$  in  $\frac{J}{molK}$ . Do your calculations to 1 significant figure.

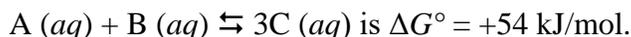
(Answers: 63, -57)

14. Your body needs glutamine (an amino acid used to make proteins) for your survival. While glutamate is useless to you as-is, you need to make glutamine out of glutamate and ammonium ions through the following reaction:

Glutamate +  $NH_4^+$   $\rightarrow$  glutamine ( $\Delta G^\circ_{rxn}=+14.2\text{kJ/mol}$ ) What problem(s) do you see with this process?

A wise man once said, "Don't panic!" You also make glutamine synthetase, an enzyme that helps this process along. If the process of :  $ATP \rightarrow ADP + PO_4^{-3}$  ( $\Delta G^\circ_{rxn}= -30\text{kJ/mol}$ ): were somehow 'linked' to the glutamine synthesis above, what would the new reaction be? (Don't worry about balancing.) What would the  $\Delta G^\circ_{rxn}$  for this new reaction be? (Answers:-15.8)

15. The standard free energy change for the process



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,  $\Delta G$ , relative to  $\Delta G^\circ$ .

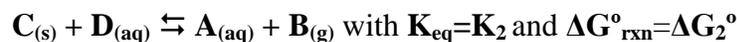
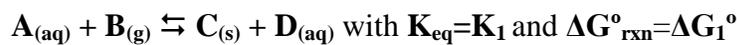
$$\Delta G < \Delta G^\circ \quad \Delta G = \Delta G^\circ \quad \Delta G > \Delta G^\circ$$

16. If  $\Delta G= 5.0 \text{ kJ/mol}$  and  $\Delta G^\circ= 4.0 \text{ kJ/mol}$  circle everything that must be true:

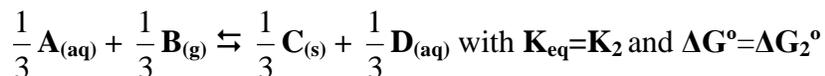
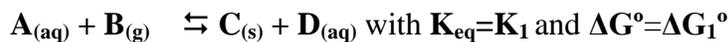
$$Q=1 \quad Q>1 \quad Q<1 \quad Q<K \quad Q=K \quad Q>K$$

- a. ( at home ) Assuming temperature of 298 K calculate the values of K and Q.(Useful Hint: at  $T=298\text{K}$  value of  $2.3RT = 2.3 \cdot 8.314(\text{J} \cdot \text{mol} \cdot \text{K}) \cdot 298\text{K} = 5698\text{J/mol} \approx 6\text{kJ/mol}$ )  
(Answers: 0.2, 1.5)

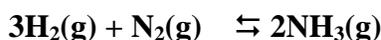
17. Given the two reactions below, find the relationships between  $\Delta G_1^\circ$  and  $\Delta G_2^\circ$ .



18. Given the two reactions below, find the relationships between  $\Delta G_1^\circ$  and  $\Delta G_2^\circ$ .



19. For the following reaction at 25°C using information below. (Answers: -32,  $4.04 \cdot 10^5$ ,  $1 \cdot 10^6$ , 2.2)



	$\Delta G^\circ$ kJ/mol	P (atm)
<b>H<sub>2</sub>(g)</b>	0	0.010
<b>N<sub>2</sub>(g)</b>	0	0.040
<b>NH<sub>3</sub>(g)</b>	-16	0.20

- Calculate value of  $\Delta G^\circ$
- Calculate value of K
- Calculate value of Q
- Calculate value of  $\Delta G$
- Based on your calculation, did the reaction pass an equilibrium point?
- Based on your calculation, will the reverse reaction be spontaneous or not?

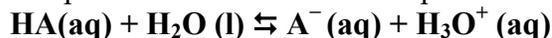
20. For the following reaction: **Br<sub>2</sub>(l)  $\rightleftharpoons$  Br<sub>2</sub>(g)**

For the reaction above at 300K, 315K, 340 K use the information given, to calculate  $\Delta H_{sys}$ ,  $\Delta S_{sys}$ ,  $\Delta S_{sur}$ ,  $\Delta S_{univ}$ ,  $\Delta G^\circ$  and the temperature at which process will cease to be spontaneous. ( Do your calculations to 2 significant figures. Assume that  $\Delta H^\circ_{rxn}$  and  $\Delta S^\circ_{rxn}$  are independent of temperature.)

	$\Delta H^\circ_f$ (kJ/mol)	$S^\circ$ (J/°Kmol)	$\Delta G^\circ_f$ (kJ/mol) (only at 25°C)
Br <sub>2</sub> (g)	30.	250.	3.0
Br <sub>2</sub> (l)	0	150.	0

21. 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  $-16.0 \text{ J/K}$ . For water,  $\Delta_{\text{fus}}H = 6.00 \text{ kJ/mol}$  and  $\Delta_{\text{fus}}S = 22.0 \text{ J/(mol K)}$ .

22. You have a buffer with a  $\text{pH} = 5$  at two different temperatures:  $T_1 = 300 \text{ K}$  and  $T_2 = 330 \text{ K}$



You need to have the following ratios of weak acid and conjugate base to make this happen:

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

$$\text{at } T_2 \rightarrow [\text{A}^{\text{-}}]/[\text{HA}] = 1/4$$

To answer the following questions you need to draw the plot of  $\ln K$  versus  $1/T$ .

(Hint:  $\ln K = 2.303 \log K$ )

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

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

23. A liquid freezes at  $215. \text{ K}$  and its  $\Delta_{\text{fuss}}H = 25. \text{ kJ/mol}$ . When a nonvolatile solute is added to the liquid, the entropy of the solution is  $15. \text{ J/(mol/K)}$  higher than that of the pure liquid at  $215\text{K}$ . Calculate the freezing point of the solution. (Hint: use the diagram on page 1 for help)  
(Answer:  $190.\text{K}$ )

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

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

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

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

26. Compare the entropy change when vapor forms over pure water and over a solution, both at  $25 \text{ C}$ :

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