

## WEEK 10 KEY

### 1. What is the second law of thermodynamics?

The total entropy of an isolated system increases over time and the entropy of the universe is always increasing. In other words, the quantity of matter and energy in the universe are constant, but usable energy is inevitably converted into unusable energy over time through non-reversible processes.

$$\text{Generally: } \Delta S_{\text{univ}} > 0$$

### 2. For any process, what are the four possible combinations of $\Delta H$ and $\Delta S$ ? Which of these correspond to always spontaneous or always non-spontaneous reactions? Under what conditions would the last two combinations be spontaneous?

$\Delta H > 0$ (endothermic)	$\Delta S > 0$	Spontaneous at <b>HIGH</b> temperatures (as $T \rightarrow \infty$ , $\Delta G$ will become negative in $\Delta G = \Delta H - T\Delta S$ )
$\Delta H > 0$ (endothermic)	$\Delta S < 0$	<b>Non-spontaneous at all temps.</b>
$\Delta H < 0$ (exothermic)	$\Delta S > 0$	<b>Spontaneous at all temps.</b>
$\Delta H < 0$ (exothermic)	$\Delta S < 0$	Spontaneous at <b>LOW</b> temps.

### 3. What is the third law of thermodynamics?

**The entropy of a system at absolute zero is a well-defined constant.** For all intents and purposes, the entropy of a system at absolute zero is zero (but this is technically only true for perfect crystalline substances). This is what allows us to calculate standard molar entropies at defined temperatures.

### 4. For a gas phase reaction, how do you determine the sign of $\Delta S^\circ$ ? How about phase change?

For a gas phase reaction, entropy is **higher on the side with more moles of gas** (i.e. increased entropy and more available states/configurations). So a reaction of  $2A + 3B \rightarrow 6C$  has  $\Delta S > 0$  since moles increased. For a phase change, **less ordered structures are associated with higher entropy**, therefore sublimation (solid  $\rightarrow$  gas) would be  $\Delta S > 0$  but freezing (liquid  $\rightarrow$  solid) would be  $\Delta S < 0$ .

### 5. For a liquid, would you expect $\Delta S_{\text{fusion}}$ or $\Delta S_{\text{evaporation}}$ to be larger? Why?

**Evaporation (liquid  $\rightarrow$  gas) would be much larger** than evaporation (solid  $\rightarrow$  liquid) because a gas is much more entropically favorable and has more available states to increase the entropy.

### 6. True or False: High temperatures are favorable to a reaction both kinetically and thermodynamically? Explain.

**True – sort of.** High temperatures favor faster kinetics by increasing the number of molecular collisions. Higher temperatures tend to lead to a lower (more spontaneous)  $\Delta G$  because higher temperatures results in a larger entropic term in  $\Delta G = \Delta H - T\Delta S$ . **HOWEVER, this is only true if  $\Delta S > 0$ , if  $\Delta S < 0$ , the reaction will NOT be favored at higher temperatures.**

1. Calculate the standard entropy change for the following reaction at 25 °C:



$$\Delta S^\circ = \sum nS^\circ (\text{products}) - \sum nS^\circ (\text{reactants})$$

$$\Delta S^\circ = \left[ 3\text{mol} \left( 41.6 \frac{\text{J}}{\text{mol}\cdot\text{K}} \right) + 1\text{mol} \left( 50.99 \frac{\text{J}}{\text{mol}\cdot\text{K}} \right) \right] - \left[ 2\text{mol} \left( 28.3 \frac{\text{J}}{\text{mol}\cdot\text{K}} \right) + 3\text{mol} \left( 43.9 \frac{\text{J}}{\text{mol}\cdot\text{K}} \right) \right]$$

$$\Delta S^\circ = -12.5 \text{ J/K}$$

2. A certain reaction has  $\Delta H^\circ = -19.5 \text{ kJ}$  and  $\Delta S^\circ = 42.7 \text{ J K}^{-1}$ .

a. Calculate  $\Delta G^\circ$  for the reaction.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$= -19.5 \text{ kJ} - (298.15 \text{ K}) \left( 42.7 \text{ J K}^{-1} \right) \left( \frac{1 \text{ kJ}}{1000 \text{ J}} \right)$$

$$\Delta G^\circ = -32.2 \text{ kJ}$$

b. Is the reaction spontaneous under standard conditions?

Yes, since  $\Delta G$  is negative

3a. Using the data given below, calculate  $\Delta G^\circ$  for the reaction:  $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g})$

3b. Is this reaction spontaneous as written under standard conditions?

$$\Delta G^\circ = \sum n\Delta G^\circ (\text{products}) - \sum n\Delta G^\circ (\text{reactants})$$

$$= \left[ 2\text{mol} \left( -370.4 \frac{\text{kJ}}{\text{mol}} \right) \right] - \left[ 0 + 2\text{mol} \left( -300.4 \frac{\text{kJ}}{\text{mol}} \right) \right]$$

$$\Delta G^\circ = -140.0 \text{ kJ} \therefore \text{Yes, rxn is spontaneous}$$

3c. What is the equilibrium constant  $K$  for this reaction? @ 25 °C

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

$$-140.0 \text{ kJ} = -8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}} \left( \frac{1 \text{ kJ}}{1000 \text{ J}} \right) (298.15 \text{ K}) \ln(K)$$

$$\ln(K) = 56.479$$

$$K = 3.37 \times 10^{24}$$

4. Calculate  $\Delta G^\circ$  for the process:  $C(\text{diamond}) \leftrightarrow C(\text{graphite})$

Is the formation of graphite from diamond favored at  $25^\circ\text{C}$ ? If so, why is it that diamonds do not become graphite on standing?

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta H^\circ = 0 - (1\text{ mol})(1.90\text{ kJ/mol}) = -1.9\text{ kJ}$$

$$\Delta S^\circ = 1\text{ mol}(5.69\text{ J mol}^{-1}\text{K}^{-1}) - 1\text{ mol}(2.4\text{ J mol}^{-1}\text{K}^{-1}) = 3.29\text{ J}$$

$$\Delta G^\circ = -1.9\text{ kJ} - (298.15\text{ K})(3.29\text{ J})\left(\frac{1\text{ kJ}}{1000\text{ J}}\right)$$

$$\Delta G^\circ = -2.88\text{ kJ}$$

It is spontaneous, but the rate is too slow to observe.

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5. Consider the formation of a dimeric protein:  $2P \rightarrow P_2$ . At  $25^\circ\text{C}$ , we have  $\Delta H^\circ = 17\text{ kJ/mol}$  and  $\Delta S^\circ = 65\text{ J/mol}\cdot\text{K}$ . Is the dimerization favored at this temperature? What would be the effect of lowering the temperature?

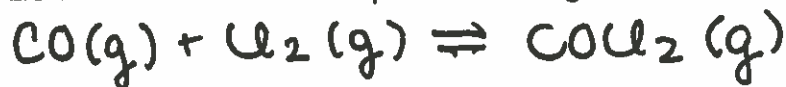
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$= (17\text{ kJ mol}^{-1}) - (298.15\text{ K})(0.065\text{ J mol}^{-1}\text{K}^{-1})$$

$$\Delta G^\circ = -2.38\text{ kJ mol}^{-1}$$

Yes, it is spontaneous at  $25^\circ\text{C}$ , but would be less favored as the temp is lowered.

6. The equilibrium constant  $K_P$  for the reaction below is  $5.62 \times 10^{35}$  at  $25^\circ\text{C}$ . What is  $\Delta G^\circ$  for  $\text{COCl}_2$  at  $25^\circ\text{C}$ ? Would you predict the  $\Delta S$  for this reaction to be positive or negative?



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

$$= -(8.314\text{ J/mol K})(298.15\text{ K}) \ln(5.62 \times 10^{35})$$

$$\Delta G^\circ = -204.0\text{ kJ mol}^{-1}$$

$\Delta S < 0$  because 2 mol gas  $\rightarrow$  1 mol gas

7. What is  $\Delta G^\circ$  for the reaction below at  $25^\circ\text{C}$ ?



$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta H^\circ = \left[ 3\text{mol}(-92.23 \frac{\text{kJ}}{\text{mol}}) + 1\text{mol}(-95.52 \frac{\text{kJ}}{\text{mol}}) + 1\text{mol}(-83.68 \frac{\text{kJ}}{\text{mol}}) \right] - \left[ 2\text{mol}(-74.85 \frac{\text{kJ}}{\text{mol}}) + 3\text{mol}(0) \right]$$

$$\Delta H^\circ = -306.19 \text{ kJ}$$

$$\Delta S^\circ = \left[ 3\text{mol}(187 \frac{\text{J}}{\text{mol}\cdot\text{K}}) + 1\text{mol}(270.28 \frac{\text{J}}{\text{mol}\cdot\text{K}}) + 1\text{mol}(234.36 \frac{\text{J}}{\text{mol}\cdot\text{K}}) \right] - \left[ 2\text{mol}(186.2 \frac{\text{J}}{\text{mol}\cdot\text{K}}) + 3\text{mol}(223 \frac{\text{J}}{\text{mol}\cdot\text{K}}) \right]$$

$$\Delta S^\circ = 24.24 \text{ J/K} = 0.02424 \text{ kJ/K}$$

$$\Delta G^\circ = -306.19 \text{ kJ} - 298.15 \text{ K}(0.02424 \text{ kJ/K})$$

$$\Delta G^\circ = -313.4 \text{ kJ}$$

8. Consider the following reaction:



$$\Delta G^\circ_{\text{rxn}} = 35.4 \text{ kJ/mol}$$

Calculate  $\Delta G$  at  $25^\circ\text{C}$  for the reaction if the partial pressures of the initial mixture are

$P_{\text{PCl}_5} = 0.0029 \text{ atm}$ ,  $P_{\text{PCl}_3} = 0.27 \text{ atm}$ , and  $P_{\text{Cl}_2} = 0.40 \text{ atm}$ .

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

$$Q = \frac{P_{\text{Cl}_2} P_{\text{PCl}_3}}{P_{\text{PCl}_5}} = \frac{(0.4 \text{ atm})(0.27 \text{ atm})}{(0.0029 \text{ atm})} = 37.24$$

$$\Delta G = 35.4 \frac{\text{kJ}}{\text{mol}} + 8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}} \left( \frac{1 \text{ kJ}}{1000 \text{ J}} \right) (298.15 \text{ K}) \ln(37.24)$$

$$\Delta G = 44.37 \text{ kJ mol}^{-1}$$

9. Which of the following reactions would be spontaneous at 25°C? If either is non-spontaneous, at what temperature would it become spontaneous?

a.  $\Delta H = 10.5 \text{ kJ/mol}$ ,  $\Delta S = 30 \text{ J/molK}$

@ 25°C:  $\Delta G^\circ = 10.5 \text{ kJ mol}^{-1} - (298.15 \text{ K})(.03 \text{ kJ mol}^{-1} \text{ K}^{-1})$

$\Delta G^\circ = 1.55 \text{ kJ} \therefore \text{non-spontaneous}$

- set  $\Delta G^\circ$  to 0 & solve for T

$0 = 10.5 \text{ kJ mol}^{-1} - T(.03 \text{ kJ mol}^{-1} \text{ K}^{-1})$

$T = 350 \text{ K} \therefore \text{spontaneous when } T > 350 \text{ K}$

b.  $\Delta H = 1.8 \text{ kJ/mol}$ ,  $\Delta S = -113 \text{ J/molK}$

@ 25°C:  $\Delta G^\circ = 1.8 \frac{\text{kJ}}{\text{mol}} - 298.15 \text{ K}(-.113 \frac{\text{kJ}}{\text{mol K}})$

$\Delta G^\circ = 35.5$  \* non-spontaneous  
@ all temperatures

10. The equilibrium constant ( $K_P$ ) for the following reaction is 4.40 at 2000K.



a. Calculate  $\Delta G^\circ$  for the reaction at 2000K

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

$$\Delta G^\circ = -(.008314 \frac{\text{kJ}}{\text{mol K}})(2000 \text{ K}) \ln(4.4)$$

$\Delta G^\circ = -24.64$

b. Calculate  $\Delta G$  for the reaction when  $P_{\text{H}_2} = 0.78 \text{ atm}$ ,  $P_{\text{H}_2\text{O}} = 0.66 \text{ atm}$ , and  $P_{\text{CO}} = 1.20 \text{ atm}$ .

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

$$= -24.64 + .008314 \frac{\text{kJ}}{\text{mol K}}(2000 \text{ K}) \ln \left( \frac{1.2 \text{ atm}}{0.78 \cdot 0.66} \right)$$

$\Delta G = -10.6 \frac{\text{kJ}}{\text{mol}}$