

Thermo2key

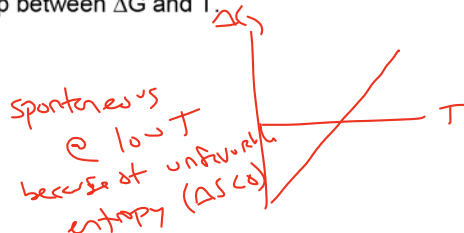
Thursday, November 10, 2016 3:01 PM

Thermodynamics.

1. For each reaction, select the correct answer for ΔH , ΔS , and ΔG .

$\Delta S \quad \ell \rightarrow s$ $H_2O_2(l) \rightleftharpoons H_2O_2(s)$ $\Delta H \rightarrow$ strengthening IMF	$\Delta S > 0$ $\Delta S < 0$	ΔS 5 molecules \rightarrow 1 $C(s) + 4 H(g) \rightleftharpoons CH_4(g)$ $\Delta H \rightarrow$ creating covalent bonds	$\Delta S > 0$ $\Delta S < 0$
	$\Delta H > 0$ $\Delta H < 0$		$\Delta H > 0$ $\Delta H < 0$
	$\Delta G > 0$ $\Delta G < 0$		$\Delta G > 0$ $\Delta G < 0$
	Temperature Dependent		Temperature Dependent

2. For each of the following reactions in problem 1, identify which graph most accurately reflects the relationship between ΔG and T.



3. For melting reaction, $\Delta G = 0$ at the melting temperature (T_m).

a. Write out an equilibrium showing the melting of Li (s). $Li(s) \rightleftharpoons Li(l)$

b. Why can't we write an equilibrium constant for this reaction? Solids + liquid are not included in K

c. Which of the graphs in problem 2 is most likely to represent the DG vs. T relationship for this melting reaction? Spontaneous @ high temps

d. At the melting temperature, is it more favorable to make solids or liquids? Why?

neither. $\Delta G = 0$ so @ equilibrium

e. With this in mind, rearrange $\Delta G = \Delta H - T\Delta S$ to show the relationship between ΔH and ΔS at the melting temperature (T_m).

$$0 = \Delta H - T\Delta S \quad \Delta H = T\Delta S \quad \Delta S = \frac{\Delta H}{T} \quad T = \frac{\Delta H}{\Delta S}$$

f. Use the equation that you developed in 3e to calculate the entropy of melting for lithium and sodium. The melting temperature and melting enthalpy are given below.

$$Li: \quad \Delta S = \frac{\Delta H}{T} = \frac{2990 \text{ J/mol}}{454 \text{ K}} \\ \Delta S = 6.59 \text{ J/mol}\cdot\text{K}$$

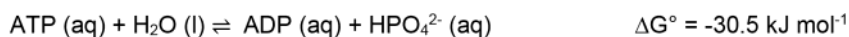
$$Na: \quad \frac{2600 \text{ J/mol}}{371 \text{ K}} = 7.01 \text{ J/mol}\cdot\text{K}$$

Metal	T_m (K)	ΔH_{fus} (kJ mol ⁻¹)
Li	454	2.99
Na	371	2.60

g. Do the signs of ΔH and ΔS make sense based on your understanding of the reaction?

Yes. endothermic (breaking IMF)
 $\Delta S > 0$ b/c $s \rightarrow \ell$

4. ATP hydrolysis is a very important reaction in biological systems. Consider the information given below:



- a. Does this reaction consume or produce energy? How do you know?

$$\Delta G^\circ < 0$$

- b. Calculate the equilibrium constant for this reaction.

$$\Delta G^\circ = -RT \ln K \quad -30,500 \frac{\text{J}}{\text{mol}} = \left(8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) (298.15 \text{ K}) \ln K$$

$$K = 2.21 \times 10^5$$

- c. Under the conditions below, will the reaction shift to make reactants or products? What do you predict the sign of ΔG to be?

$$[\text{ATP}] = 5.0 \text{ mM}, [\text{ADP}] = 0.50 \text{ mM}, \text{ and } [\text{HPO}_4^{2-}] = 5.0 \text{ mM}$$

$$Q = \frac{[\text{ADP}][\text{HPO}_4^{2-}]}{[\text{ATP}]} = \frac{(0.005)(0.5)}{0.005} = 0.5$$

$Q < K$ Products form

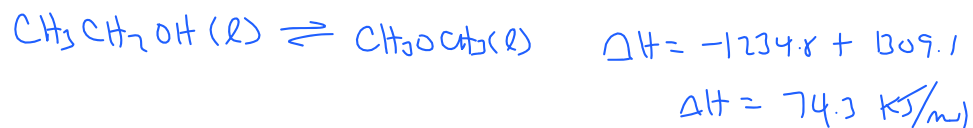
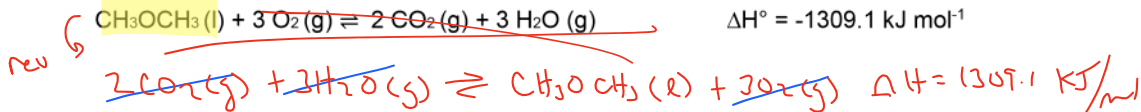
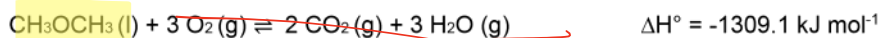
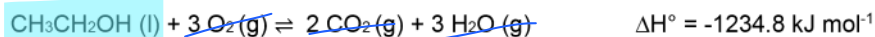
- d. For the conditions above, calculate ΔG at 37°C .

$$\Delta G = -30,500 \frac{\text{J}}{\text{mol}} + 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} (37+273.15) \ln 0.5$$

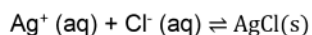
$$\Delta G = -32,287 \text{ J/mol}$$

$\Delta G < 0$

5. Calculate ΔH° for $\text{CH}_3\text{CH}_2\text{OH (l)} \rightleftharpoons \text{CH}_3\text{OCH}_3 \text{ (l)}$ noting that:



6. From the data below, calculate ΔG° and K for the following reaction at 25°C .



	$\text{Ag}^+(\text{aq})$	$\text{Cl}^-(\text{aq})$	$\text{AgCl}(\text{s})$
ΔG_f° (kJ mol ⁻¹)	77.1	-131.2	-109.8
S° (J mol ⁻¹ K ⁻¹)	72.7	56.5	96.3

$$\Delta G^\circ = -109.8 \frac{\text{kJ}}{\text{mol}} - \left[77.1 \frac{\text{kJ}}{\text{mol}} + (-131.2 \frac{\text{kJ}}{\text{mol}}) \right]$$

$$\Delta G^\circ = -55.7 \frac{\text{kJ}}{\text{mol}} = K = 5.7 \times 10^9$$

$$-55700 \frac{\text{J}}{\text{mol}} = -RT \ln K = -8.314 (298.15) \ln K$$

7. What do you think the sign of ΔH and ΔS will be for the reaction in problem 6? Explain your choice.

$\Delta S < 0$ - creating a solid

$\Delta H < 0$ - creating an ionic bond

8. For the reaction in problem 6, determine ΔS° and ΔH° .

$$\Delta S^\circ = 96.3 - [72.7 + 56.5] = -32.9 \frac{\text{J}}{\text{mol} \cdot \text{K}}$$

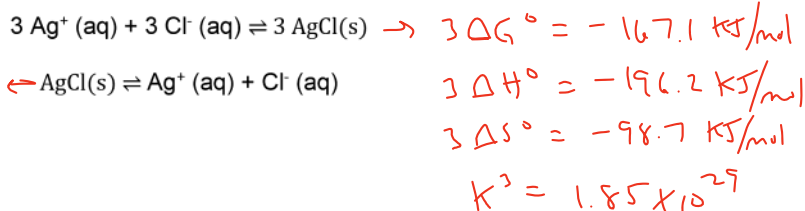
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta H^\circ = \Delta G^\circ + T\Delta S^\circ = -55700 \frac{\text{J}}{\text{mol}} + 298.15 \text{K} (-32.9 \frac{\text{J}}{\text{mol} \cdot \text{K}})$$

$$\Delta H^\circ = -65.4 \frac{\text{kJ}}{\text{mol}}$$

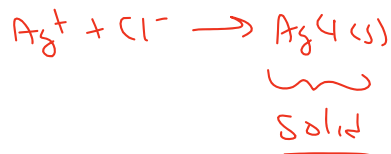
9. Using the information you determined in problems 6 and 7, determine K , ΔG° , ΔH° , and ΔS° for the following reactions:

$$\begin{aligned} -\Delta G^\circ &= 55.7 \frac{\text{kJ}}{\text{mol}} \\ -\Delta H^\circ &= 65.4 \frac{\text{kJ}}{\text{mol}} \\ -\Delta S^\circ &= 32.9 \frac{\text{J}}{\text{mol} \cdot \text{K}} \\ K^{-1} &= 1.74 \times 10^{-10} \end{aligned}$$



10. From what you learned in problem 6, explain why our solubility rules predict that AgCl is not soluble.

K is big meaning the products are strongly favored



11. Using the values from problems 6 and 8, determine the temperature that would be needed to make dissolving AgCl (s) favorable. Hint: you'll need to calculate K at 25°C and use ΔH from problem 8. Also, you should figure out what K value is needed when the reaction changes to being nonspontaneous.

↓
so K when $\Delta G = 0$

$$K = 1$$

$$\ln \frac{K_2}{K_1} = \frac{\Delta H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\ln \frac{1}{5.7 \times 10^9} = \frac{-65400}{8.314} \left(\frac{1}{298.15} - \frac{1}{T_2} \right)$$

$$-22.46 = -7866.2 \left(3.35 \times 10^{-3} - \frac{1}{T_2} \right)$$

$$2.855 \times 10^{-3} = 3.35 \times 10^{-3} - \frac{1}{T_2}$$

$$-4.95 \times 10^{-4} = -\frac{1}{T_2}$$

$$T_2 = 2021 \text{ K}$$

so AgCl will dissolve at 1750°C !

already done -5.7×10^9

done
 $\Delta H = -65,400 \frac{\text{J}}{\text{mol}}$