

REVIEW QUESTIONS

## Chapter 18

1. Calculate the heat of reaction ( $\Delta H^0$ ) in kJ/mol for the reaction shown below, given the  $\Delta H_f^0$  values for each substance:

	NH <sub>3</sub> (g)	+	3 F <sub>2</sub> (g)	→	NF <sub>3</sub> (g)	+	3 HF (g)
$\Delta H_f^0$ (kJ/mol)	-46.1		0		-125		-271

$$\Delta H^0 = \sum \Delta H_f^0 (\text{Products}) - \sum \Delta H_f^0 (\text{Reactants})$$

$$\sum \Delta H_f^0 (\text{Products}) = (1 \times -125) + (3 \times -271) = -938 \text{ kJ}$$

$$\sum \Delta H_f^0 (\text{Reactants}) = (1 \times -46.1) + (3 \times 0) = -46.1 \text{ kJ}$$

$$\Delta H^0 = -938 - (-46.1) = -892 \text{ kJ}$$

2. Determine the entropy change ( $\Delta S^0$ ) in J/K for the reaction shown below, given the standard entropies for each:

	2 SO <sub>2</sub> (g)	+	O <sub>2</sub> (g)	→	2 SO <sub>3</sub> (g)
$S^0$ (J/K mol)	248.1		205.03		256.6

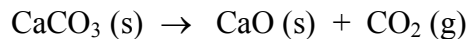
$$\Delta S^0 = \sum S^0 (\text{Products}) - \sum S^0 (\text{Reactants})$$

$$\sum S^0 (\text{Products}) = (2 \times 256.6) = 513.2 \text{ J/K}$$

$$\sum S^0 (\text{Reactants}) = (2 \times 248.1) + (1 \times 205.03) = 701.23 \text{ J/K}$$

$$\Delta S^0 = 513.2 - 701.23 = -188.0 \text{ J/K}$$

3. Given the following thermodynamic data, estimate the temperature (°C) at which the reaction shown below becomes spontaneous.



$$\Delta H^0 = +184 \text{ kJ} \quad \Delta S^0 = +166 \text{ J/K} \quad \Delta G^0 = +300 \text{ kJ}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

**Reaction reaches equilibrium when  $\Delta G^0 = 0$**

**Therefore,**

$$T\Delta S^0 = \Delta H^0 = +184 \text{ kJ}$$

$$T = \frac{+184 \text{ kJ}}{\Delta S^0} = \frac{+184 \text{ kJ}}{+0.166 \text{ kJ/K}} = 1108 \text{ K} = 835 \text{ }^\circ\text{C}$$

**Temperature must be greater than 835 °C for reaction to become spontaneous**

4. Calculate the free energy ( $\Delta G^0$ ) in kJ for the reaction shown below, given the  $\Delta G_f^0$  values for each substance:

	$4 \text{ NH}_3 (\text{g}) + 5 \text{ O}_2 (\text{g}) \rightarrow 4 \text{ NO} (\text{g}) + 6 \text{ H}_2\text{O} (\text{g})$			
$\Delta G_f^0$ (kJ/mol)	-16.48	0	86.67	-228.59

$$\Delta G^0 = \sum \Delta G_f^0 (\text{Products}) - \sum \Delta G_f^0 (\text{Reactants})$$

$$\sum \Delta G_f^0 (\text{Products}) = (4 \times 86.67) + (6 \times -228.59) = -1024.86 \text{ kJ}$$

$$\sum \Delta G_f^0 (\text{Reactants}) = (4 \times -16.48) + (5 \times 0) = -65.92 \text{ kJ}$$

$$\Delta G^0 = -1024.86 - (-65.92) = -958.9 \text{ kJ}$$

5. Methanol can be produced by the reaction shown below, with the following thermodynamic data given at 25°C.

	CO (g) +	2 H <sub>2</sub> (g) →	CH <sub>3</sub> OH (l)
$\Delta H_f^0$ (kJ/mol)	-110.5	0	-238.6
$\Delta G_f^0$ (kJ/mol)	-137.3	0	-166.2
$S^0$ (J/mol K)	+197.9	???	+126.8

- a) Calculate  $\Delta G^0$  and  $\Delta H^0$  for this reaction.

$$\Delta G^0 = \sum \Delta G_f^0 \text{ (Products)} - \sum \Delta G_f^0 \text{ (Reactants)}$$

$$\Delta G^0 = (1 \times -166.2) - [(1 \times -137.3) + 0] = -28.9 \text{ kJ}$$

$$\Delta H^0 = \sum \Delta H_f^0 \text{ (Products)} - \sum \Delta H_f^0 \text{ (Reactants)}$$

$$\Delta H^0 = (1 \times -238.6) - [(1 \times -110.5) + 0] = -128.1 \text{ kJ}$$

- b) Calculate  $\Delta S^0$  (in J/K) for this reaction.

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T} = \frac{-128.1 \text{ kJ} - (-28.9 \text{ kJ})}{298 \text{ K}} = -0.333 \text{ kJ/K} = -333 \text{ J/K}$$

- c) Calculate  $S^0$  for hydrogen.

$$\Delta S^0 = \sum S^0 \text{ (Products)} - \sum S^0 \text{ (Reactants)}$$

$$\Delta S^0 = (1 \times 126.8) - [(1 \times 197.9) + (2 \times S_{\text{H}_2}^0)] = -333 \text{ J/K}$$

$$S_{\text{H}_2}^0 = \frac{333 + 126.8 - 197.9}{2} = 131 \text{ J/mol K}$$

6. At 25°C the equilibrium constant,  $K_p$ , for the reaction below is 0.281 atm.



a) What is  $\Delta G_{298}^0$  for this reaction?

$$K = K_p$$

$$\Delta G_{298}^0 = -RT \ln K_p = -(8.314 \text{ J/mol K})(298 \text{ K})(\ln 0.281)$$

$$\Delta G_{298}^0 = 3.14 \times 10^3 \text{ J/mol}$$

b) It requires 193 J to vaporize 1.00 g of liquid bromine at 25°C and 1.00 atm. Calculate  $\Delta H^0$  and  $\Delta S^0$  at 25°C for this reaction.

$$\Delta H^0 = \frac{193 \text{ J}}{1 \text{ g}} \times \frac{159.8 \text{ g}}{1 \text{ mol}} = 3.084 \times 10^4 \text{ J/mol}$$

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T} = \frac{(30840 - 3140) \text{ J/mol}}{298 \text{ K}} = 92.9 \text{ J/mol K}$$

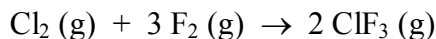
c) Calculate the normal boiling point of bromine. Assume  $\Delta H^0$  and  $\Delta S^0$  are not affected by temperature. (*Hint*: At the normal boiling point liquid and vapor are in equilibrium)

$$\text{At normal boiling point } \Delta G^0 = 0$$

$$\Delta G^0 = \Delta H^0 - T \Delta S^0 = 0$$

$$T = \frac{\Delta H^0}{\Delta S^0} = \frac{30840 \text{ J/mol}}{92.9 \text{ J/mol K}} = 332 \text{ K}$$

7.  $\text{ClF}_3$  can be prepared by the reaction shown below:



For  $\text{ClF}_3$ ,  $\Delta H_f^\circ = -163.2 \text{ kJ/mol}$  and  $\Delta G_f^\circ = -123.0 \text{ kJ/mol}$

a) Calculate the value of the equilibrium constant for this reaction at  $25^\circ\text{C}$ .

$$\Delta G^\circ = 2(-123 \text{ kJ}) - 0 = -246 \text{ kJ}$$

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

$$\ln K = \frac{\Delta G^\circ}{-RT} = \frac{-246 \times 10^3 \text{ J}}{-(8.314 \text{ J/K})(298 \text{ K})} = 99.3$$

$$K = e^{99.3} = 1.33 \times 10^{43}$$

b) Calculate  $\Delta S^\circ$  for this reaction at  $25^\circ\text{C}$ .

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

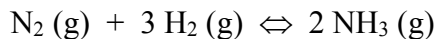
$$\Delta H = 2(-163.2 \text{ kJ}) - 0 = -326.4 \text{ kJ}$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} = \frac{(-326.4 \times 10^3 \text{ J}) - (-246 \times 10^3 \text{ J})}{298 \text{ K}} = -270 \text{ J/K}$$

c) If  $\text{ClF}_3$  produced were a liquid instead of a gas, how would the  $\Delta S$  for the reaction be different (sign and magnitude) than calculated above? Explain.

**If  $\text{ClF}_3$  produced was a liquid,  $\Delta S$  would be a larger negative number, since liquid is more ordered than gas and has less entropy.**

8. Production of ammonia from nitrogen and hydrogen gases is an important industrial reaction shown below:



$$\Delta H^0 = -92.38 \text{ kJ} \quad \Delta S^0 = -198.3 \text{ J/K}$$

- a) Calculate  $\Delta G^0$  for this reaction at  $500^\circ\text{C}$ . Assume  $\Delta H^0$  and  $\Delta S^0$  are not temperature dependent.

$$\Delta G^0 = \Delta H^0 - T \Delta S^0$$

$$\Delta G_{500}^0 = -92.38 \text{ kJ} - (773 \text{ K})(198.3 \times 10^{-3} \text{ kJ/K}) = 60.9 \text{ kJ}$$

- b) Calculate  $\Delta G$  at  $25^\circ\text{C}$  for this reaction if the reaction mixture consists of 1.0 atm of  $\text{N}_2$ , 3.0 atm of  $\text{H}_2$  and 1.0 atm of  $\text{NH}_3$ .

$$\Delta G = \Delta G^0 + RT \ln Q$$

$$Q = \frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} P_{\text{H}_2}^3} = \frac{(1.0)^2}{(1.0)(3.0)^3} = 3.7 \times 10^{-2}$$

$$\Delta G_{298}^0 = \Delta H^0 - T \Delta S^0 = -92.38 \text{ kJ} - (298 \text{ K})(-198.3 \times 10^{-3} \text{ kJ/K}) = -33.3 \text{ kJ}$$

$$\Delta G = -33.3 \text{ kJ} + \frac{(8.314 \text{ J/K})(298 \text{ K})(\ln 3.7 \times 10^{-2})}{10^3 \text{ J/kJ}} = -41.5 \text{ kJ}$$