REVIEW QUESTIONS
Chapter 18

1. Calculate the heat of reaction (ΔH^0) in kJ/mol for the reaction shown below, given the ΔH_f^0 values for each substance:

	NH_3 (g) +	$3\ F_2$ (g) →	NF_3 (g) +	3 HF (g)
ΔH_f^0 (kJ/mol)	–46.1	0	–125	–271

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

$\sum \Delta H_f^0$ (Products) = (1 x -125) + (3 x -271) = -938 kJ

$\sum \Delta H_f^0$ (Reactants) = (1 x -46.1) + (3 x 0) = -46.1 kJ

ΔH^0 = -938 - (-46.1) = - 892 kJ

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

	$2\ SO_2$ (g) +	O_2 (g) →	$2\ SO_3$ (g)
S^0 (J/K mol)	248.1	205.03	256.6

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

$\sum S^0$ (Products) = (2 x 256.6) = 513.2 J/K

$\sum S^0$ (Reactants) = (2 x 248.1) + (1 x 205.03) = 701.23 J/K

ΔS^0 = 513.2 - 701.23 = - 188.0 J/K

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

$$CaCO_3\ (s) \rightarrow CaO\ (s) + CO_2\ (g)$$

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

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

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

Therefore,

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

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

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

4. Calculate the free energy (ΔG^0) in kJ for the reaction shown below, given the ΔG_f^0 values for each substance:

	$4\ NH_3\ (g)$ +	$5\ O_2\ (g)$ $\rightarrow$	$4\ NO\ (g)$ +	$6\ H_2O\ (g)$
ΔG_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_2 (g) →	CH_3OH (l)
ΔH_f^0 (kJ/mol)	–110.5	0	–238.6
ΔG_f^0 (kJ/mol)	–137.3	0	–166.2
S^0 (J/mol K)	+197.9	???	+126.8

a) Calculate ΔG^0 and ΔH^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 ΔS^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.

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

$$\Delta S^0 = (1 \times 126.8) - [(1 \times 197.9) + (2 \times S^0_{H_2}) = -333 \text{ J/K}$$

$$S^0_{H_2} = \frac{333 + 126.8 - 197.9}{2} = 131 \text{ J/mol K}$$

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

$$Br_2\,(l) \Leftrightarrow Br_2\,(g)$$

a) What is ΔG^0_{298} for this reaction?

$K = K_p$

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

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

b) If requires 193 J to vaporize 1.00 g of liquid bromine at 25°C and 1.00 atm. Calculate ΔH^0 and ΔS^0 at 25°C for this reaction.

$$\Delta H^0 = \frac{193 \text{ J}}{1 \cancel{g}} \times \frac{159.8 \cancel{g}}{1 \text{ mol}} = 3.0\underline{8}4 \times 10^4 \text{ J/mol}$$

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T} = \frac{(30\underline{8}40 - 3140) \text{ J/mol}}{298 \text{ K}} = 92.9 \text{ J/mol K}$$

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

At normal boiling point $\Delta G^0 = 0$

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

$$T = \frac{\Delta H^0}{\Delta S^0} = \frac{30\underline{8}40 \cancel{\text{J/mol}}}{92.9 \cancel{\text{J/mol}} \text{ K}} = 332 \text{ K}$$

7. ClF_3 can be prepared by the reaction shown below:

$$Cl_2\,(g) + 3\,F_2\,(g) \rightarrow 2\,ClF_3\,(g)$$

For ClF_3, $\Delta H_f^0 = -163.2$ kJ/mol and $\Delta G_f^0 = -123.0$ kJ/mol

a) Calculate the value of the equilibrium constant for this reaction at 25°C.

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

$\Delta G^0 = -RT \ln K$

$$\ln K = \frac{\Delta G^0}{-RT} = \frac{-246\text{x}10^3\ \cancel{J}}{-(8.314\ \cancel{J}/\cancel{K})(298\ \cancel{K})} = 99.3$$

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

b) Calculate ΔS^0 for this reaction at 25°C.

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

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

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T} = \frac{(-326.4\text{x}10^3\text{J}) - (-246\text{x}10^3\text{ J})}{298\text{ K}} = -270\text{ J/K}$$

c) If ClF_3 produced were a liquid instead of a gas, how would the ΔS for the reaction be different (sign and magnitude) than calculated above? Explain.

If ClF_3 produced was a liquid, ΔS 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:

$$N_2\,(g) + 3\,H_2\,(g) \Leftrightarrow 2\,NH_3\,(g)$$

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

a) Calculate ΔG^0 for this reaction at 500°C. Assume ΔH^0 and ΔS^0 are not temperature dependent.

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

$$\Delta G^0_{500} = -92.38 \text{ kJ} - (773 \text{ \sout{K}})(198.3\text{x}10^{-3} \text{ kJ/\sout{K}}) = 60.9 \text{ kJ}$$

b) Calculate ΔG at 25°C for this reaction if the reaction mixture consists of 1.0 atm of N_2, 3.0 atm of H_2 and 1.0 atm of NH_3.

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

$$Q = \frac{P^2_{NH_3}}{P_{N_2} P^3_{H_2}} = \frac{(1.0)^2}{(1.0)(3.0)^3} = 3.7\text{x}10^{-2}$$

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

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