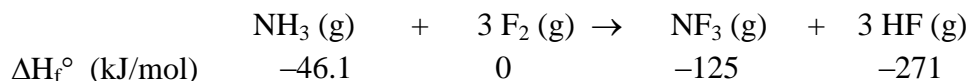


REVIEW QUESTIONS

## Chapter 18

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



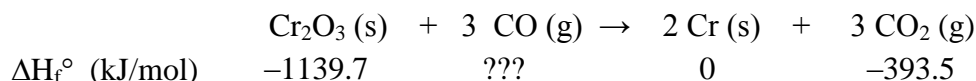
$$\Delta H^\circ = \sum \Delta H_f^\circ (\text{Products}) - \sum \Delta H_f^\circ (\text{Reactants})$$

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

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

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

2. Given  $\Delta H = +290.7$  kJ for the reaction shown below, calculate the  $\Delta H_f^\circ$  for CO (g).



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

$$+290.7 = [(3 \times -393.5)] - [(1 \times -1139.7) + 3 \Delta H_f^\circ (\text{CO})]$$

$$-3 \Delta H_f^\circ (\text{CO}) = +290.7 + 1180.5 - 1139.7 = +331.5 \text{ kJ}$$

$$\Delta H_f^\circ (\text{CO}) = \frac{-331.5 \text{ kJ}}{3} = -110.5 \text{ kJ}$$

3. The air within a piston equipped with a cylinder absorbs 565 J of heat and expands from an initial volume of 0.10 L to a final volume of 0.85 L against a pressure of 1.0 atm. What is the change in the internal energy of the air within the piston?

$$\Delta E = q + w$$

$$q = +565 \text{ J}$$

$$w = -P\Delta V = (1.0 \text{ atm})(0.75 \text{ L})\left(\frac{101.3 \text{ J}}{1 \text{ Latm}}\right) = -76 \text{ J} \quad (\text{work is done by the system})$$

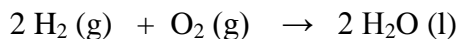
$$\Delta E = +565 \text{ J} - 76 \text{ J} = 489 \text{ J}$$

4. How much work (in J) is required to expand the volume of a pump by 2.5 L against an external pressure of 1.1 atm?

$$w = P\Delta V = (1.1 \text{ atm})(2.5 \text{ L})\left(\frac{101.3 \text{ J}}{1 \text{ Latm}}\right) = -280 \text{ J}$$

(negative sign indicates work is done by the system)

5. Calculate the work associated with the following reaction at 1.00 atm and 25°C. Is the work done by the system or on the system?



$$w = P\Delta V \quad \Delta V = \text{volume changed caused by change in moles of gas}$$

$$\Delta V = \frac{\Delta nRT}{P} = \frac{(3 \text{ mol})(0.0821)(298 \text{ K})}{1 \text{ atm}} = 73.4 \text{ L}$$

$$w = (1.00 \text{ atm})(73.4 \text{ L})\left(\frac{101.3 \text{ J}}{1 \text{ Latm}}\right) = 7440 \text{ J}$$

$w = + 7440 \text{ J}$  since work is done on the system due to compression

6. The enthalpy change for vaporization of methanol (CH<sub>3</sub>OH) at 25°C is 38.0 kJ/mol. If the entropy of methanol vapor at 25°C is 255 J/molK, what is the entropy of the liquid methanol at this temperature?



$$\Delta S_{\text{vap}} = \frac{-\Delta H_{\text{surr}}}{T} = \frac{-(-38.0 \times 10^3 \text{ J})}{298 \text{ K}} = 127.5 \text{ J/K}$$

$$\Delta S_{\text{vap}} = S_{\text{gas}} - S_{\text{liq}} = 127.5 \text{ J/K}$$

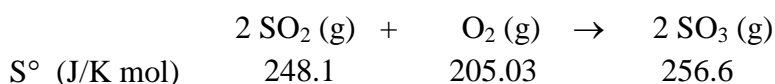
$$S_{\text{liq}} = S_{\text{gas}} - \Delta S_{\text{vap}} = 255 \text{ J/K} - (127.5 \text{ J/K}) = 127 \text{ J/K}$$

7. A reaction has  $\Delta H_{\text{rxn}} = -107 \text{ kJ}$  and  $\Delta S_{\text{rxn}} = 285 \text{ J/K}$ . At what temperature is the change in entropy for the reaction equal to the change in entropy for the surroundings?

$$\Delta S_{\text{surr}} = \frac{-\Delta H_{\text{sys}}}{T} \quad \Delta S_{\text{surr}} = \Delta S_{\text{sys}} = 285 \text{ J/K}$$

$$T = \frac{-\Delta H_{\text{sys}}}{\Delta S_{\text{sys}}} = \frac{-(-107 \times 10^3 \text{ J})}{285 \text{ J/K}} = 375 \text{ K}$$

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



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

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

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

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

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



$$\Delta H^\circ = +184 \text{ kJ}$$

$$\Delta S^\circ = +166 \text{ J/K}$$

$$\Delta G^\circ = +300 \text{ kJ}$$

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

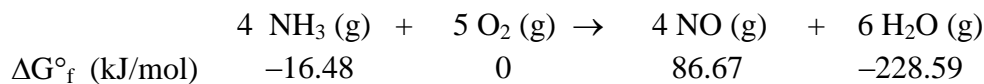
**Reaction reaches equilibrium when  $\Delta G^\circ = 0$       Therefore,**

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

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

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

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



$$\Delta G^\circ = \sum \Delta G^\circ_f \text{ (Products)} - \sum \Delta G^\circ_f \text{ (Reactants)}$$

$$\Delta G^\circ = [(4 \times 86.67) + 6 \times (-228.59)] - [4 \times (-16.48) + 5 \times (0)]$$

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

11. 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)
$\Delta H^\circ_f$ (kJ/mol)	-110.5	0	-238.6
$\Delta G^\circ_f$ (kJ/mol)	-137.3	0	-166.2
$S^\circ$ (J/mol K)	+197.9	???	+126.8

a) Calculate  $\Delta G^\circ$  and  $\Delta H^\circ$  for this reaction

$$\Delta G^\circ = \sum \Delta G^\circ_f \text{ (Products)} - \sum \Delta G^\circ_f \text{ (Reactants)}$$

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

$$\Delta H^\circ = \sum \Delta H^\circ_f \text{ (Products)} - \sum \Delta H^\circ_f \text{ (Reactants)}$$

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

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

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

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

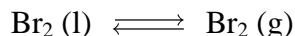
c) Calculate  $S^\circ$  for hydrogen.

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

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

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

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



a) What is  $\Delta G^\circ_{298}$  for this reaction?

$$\mathbf{K = K_p}$$

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

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

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

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

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

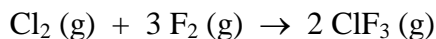
c) Calculate the normal boiling point of bromine. Assume  $\Delta H^\circ$  and  $\Delta S^\circ$  are not affected by temperature. (*Hint*: At the normal boiling point liquid and vapor are in equilibrium)

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

$$\mathbf{\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ = 0}$$

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

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



For  $\text{ClF}_3$ ,  $\Delta H^\circ_f = -163.2 \text{ kJ/mol}$  and  $\Delta G^\circ_f = -123.0 \text{ kJ/mol}$

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  $25^\circ\text{C}$ .

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

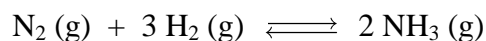
$$\Delta H^\circ = 2(-163.2 \text{ kJ}) - 0 = -326.4 \text{ kJ}$$

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

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.**

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



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

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

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

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

- 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  $\text{NH}_3$ .

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

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

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

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

15. What are the signs of  $\Delta H$ ,  $\Delta S$  and  $\Delta G$  for the sublimation of dry ice (solid  $\text{CO}_2$ ) at  $25^\circ\text{C}$ ?

Since sublimation of dry ice is endothermic,  $\Delta H = \text{positive (+)}$

Since gas has greater entropy than solid,  $\Delta S = \text{positive (+)}$

Since dry ice sublimates at  $25^\circ\text{C}$  spontaneously,  $\Delta G = \text{negative (-)}$

16. Using the following data, calculate the value of  $K_{sp}$  for  $Ba(NO_3)_2$ , one of the least soluble of the common nitrate salts.

Species	$\Delta G^\circ_f$
$Ba^{2+}$ (aq)	-561 kJ/mol
$NO_3^-$	-109 kJ/mol
$Ba(NO_3)_2$ (s)	-797 kJ/mol



$$\Delta G^\circ = \sum \Delta G^\circ_f (\text{Products}) - \sum \Delta G^\circ_f (\text{Reactants})$$

$$\Delta G^\circ = [(2 \times (-109)) + 1(-561)] - [1 \times (-797)] = -779 - (-797) = +18 \text{ kJ}$$

$$\Delta G^\circ = -RT \ln K \quad \ln K = \frac{\Delta G^\circ}{-RT} = \frac{18 \times 10^3 \text{ J}}{-(8.314 \text{ J/K})(298 \text{ K})} = -7.27$$

$$K = e^{-7.27} = 7.0 \times 10^{-4}$$

17. Show that hydrogen cyanide (HCN) is a gas at  $25^\circ\text{C}$  by estimating its normal boiling point from the following data:

	$\Delta H^\circ_f$ (kJ/mol)	$S^\circ$ (J/molK)
HCN (l)	108.9	113
HCN (g)	135.1	202

The normal boiling point of HCN is the temperature at which liquid and gaseous HCN are in equilibrium:



$$\Delta H^\circ = 135.1 - 108.9 = 26.2 \text{ kJ}$$

$$\Delta S^\circ = 202 - 113 = 89 \text{ J/K}$$

At equilibrium  $\Delta C^\circ = 0 = \Delta H^\circ - T\Delta S^\circ$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{26.2 \times 10^3 \text{ J/mol}}{89 \text{ J/mol K}} = 294 \text{ K} = 21^\circ\text{C}$$

Since  $21^\circ\text{C}$  is less than  $25^\circ\text{C}$ , HCN would exist as a gas at this temperature