AP Chemistry Thermodynamics Review Worksheet

1. Methane, CH_4 and chlorine, Cl_2, are reacted to form carbon tetrachloride, CCl_4 and hydrogen chloride, HCl at 25°C. The heat of reaction, ΔH°, is –429.8 kJ mol^{-1} of CH_4 reacted. The equation is:

$$CH_{4(g)} + 4\,Cl_{2(g)} \rightleftharpoons CCl_{4(l)} + 4HCl_{(g)}$$

Substance	Heat of formation, ΔH_f°, kJ mol^{-1}	Absolute entropy, S°, J mol^{-1}K^{-1}
$C_{graphite(s)}$	0	5.740
$CH_{4(g)}$	–74.86	186.2
$CCl_{4(l)}$	?	216.4
$Cl_{2(g)}$	0	223.0
$HCl_{(g)}$	–92.31	186.8

a) What is the standard heat of formation, ΔH_f°, for carbon tetrachloride at 25°C?

$$\Delta H^\circ = \sum \Delta H^\circ_{f(prod)} - \sum \Delta H^\circ_{f(react)}; -429.8 \text{ kJ/mol} = (\Delta H_f^\circ + 4(-92.31 \text{ kJ/mol})) - (-74.86 \text{ kJ/mol} + 4(0))$$

$$\Delta H^\circ_{f(CCl_4)} = -429.8 \text{ kJ/mol} + -74.86 \text{ kJ/mol} - (-369.24 \text{ kJ/mol}) = \boxed{-135.42 \text{ kJ/mol}}$$

b) Calculate the standard entropy change, ΔS°, for the reaction at 25°C.

$$\Delta S^\circ = \sum S^\circ_{(prod)} - \sum \Delta S^\circ_{(react)}; \Delta S^\circ = (216.4 \text{ J/mol}\cdot\text{K} + 4(186.8 \text{ J/mol}\cdot\text{K})) - (186.2 \text{ J/mol}\cdot\text{K} + 4(223.0 \text{ J/mol}\cdot\text{K}))$$

$$\Delta S^\circ = \boxed{-114.6 \text{ J/mol}\cdot\text{K}}$$

c) Theoretically, carbon tetrachloride can be formed by the reaction:

$$C_{graphite(s)} + 2Cl_{2(g)} \rightleftharpoons CCl_{4(l)}$$

Calculate the standard free energy of formation, ΔG_f°, for carbon tetrachloride at 25°C.

$$\Delta S_f^\circ = 216.4 \text{ J/mol}\cdot\text{K} - (5.740 \text{ J/mol}\cdot\text{K} + 2(223.0 \text{ J/mol}\cdot\text{K})) = -235.3 \text{ J/mol}\cdot\text{K}$$

$$\Delta G_f^\circ = \Delta H_f^\circ - T\Delta S_f^\circ = -135.42 \text{ kJ/mol} - (298 \text{ K})(-0.2353 \text{ kJ/mol}\cdot\text{K}) = \boxed{-65.3 \text{ kJ/mol}}$$

d) Calculate the value of the equilibrium constant, K, for the reaction in part (c).

$$\Delta G^\circ = -RT\ln K;\ K = e^{-\Delta G^\circ/RT} = e^{-(-65{,}300 \text{ J/mol})/(8.31 \text{ J/mol}\cdot\text{K}\times 298 \text{ K})} = \boxed{2.83\times 10^{11}}$$

2. For the reaction:

$$Fe_2O_{3(s)} + 3C_{(s)} \rightleftharpoons 2Fe_{(s)} + 3CO_{(g)}$$

ΔH°, ΔS°, and ΔG° are all positive when the substances are in their standard states at 25°C.

a) What is the physical significance of the signs of ΔH°, ΔS°, and ΔG° for this reaction?

- Positive ΔH° means the reaction is endothermic
- Positive ΔS° means the reaction increases in entropy ($\Delta n_{gas} > 0$)
- Positive ΔG° means the reaction is not spontaneous in the forward direction at this temperature (since ΔS° > 0, it will become spontaneous at higher T).

b) Which of the substances would exist in the highest amounts in an equilibrium mixture at 25°C? Explain how you determined your answer.

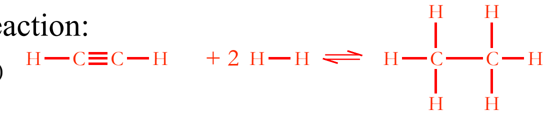
Since ΔG° > 0, K < 1, and reactants would be favored at this temperature.

c) This reaction is used as a step in the recovery of iron from its ore. Use thermodynamic concepts to explain how the yield of iron can be maximized.

Increasing T will make ΔG° become negative at high enough temperature (ΔG° = ΔH° – TΔS°), so K will increase. Decreasing pressure (increasing volume) will also cause the reaction to produce more product.

3. Ethane can be made from ethyne according to the following reaction:

$$C_2H_{2(g)} + 2H_{2(g)} \rightleftharpoons C_2H_{6(g)}$$



Substance	S° (J mol^{-1} K^{-1})	ΔH_f° (kJ mol^{-1})
$C_2H_{2(g)}$	200.9	226.7
$H_{2(g)}$	130.7	0
$C_2H_{6(g)}$	—	–84.7

Bond	Bond energy kJ mol^{-1}
C–C	347
C=C	611
C–H	414
H–H	436

a) If the value of the standard entropy change, ΔS°, for the reaction is –232.7 joules per mole·Kelvin, calculate the standard molar entropy, S° of C_2H_6 gas.

$\Delta S^\circ = \sum S^\circ_{(prod)} - \sum \Delta S^\circ_{(react)}; \Delta S^\circ = -232.7 \text{ J/mol}\cdot\text{K} = (S^\circ_{(C_2H_6)}) - (200.9 \text{ J/mol}\cdot\text{K} + 2(130.7 \text{ J/mol}\cdot\text{K})$

$S^\circ_{(C_2H_6)} = -232.7 \text{ J/mol}\cdot\text{K} + 200.9 \text{ J/mol}\cdot\text{K} + 261.4 \text{ J/mol}\cdot\text{K} = \boxed{229.6 \text{ J/mol}\cdot\text{K}}$

b) Calculate the value of the standard free-energy change, ΔG°, for the reaction at 25°C. What does the sign of the ΔG° indicate about the reaction?

$\Delta H^\circ = \sum \Delta H^\circ_{f(Prod)} - \sum \Delta H^\circ_{f(react)} = (-84.7 \text{ kJ/mol}) - (226.7 \text{ kJ/mol}) = -311.4 \text{ kJ/mol}$

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -311.4 \text{ kJ/mol} - (298 \text{ K})(-0.2327 \text{ kJ/mol}\cdot\text{K}) = \boxed{-242 \text{ kJ/mol}}$

Since ΔG° < 0, the reaction is spontaneous at this temperature.

c) Calculate the value of the equilibrium constant, K, for the reaction at 298 K.

$\Delta G^\circ = -RT\ln K; K = e^{-\Delta G^\circ/RT} = e^{-(-242{,}000 \text{ J/mol})/(8.31 \text{ J/mol}\cdot\text{K}\times 298 \text{ K})} = \boxed{2.76\times 10^{42}}$

d) Calculate the bond energy of the carbon–carbon triple bond in C_2H_2 in kilojoules per mole.

$\Delta H^\circ = \sum BE_{broken} - \sum BE_{formed};\ -311.4 \text{ kJ/mol} = (BE_{C\equiv C} + 2(436 \text{ kJ/mol})) - (347 \text{ kJ/mol} + 4(414 \text{ kJ/mol}))$

$BE_{C\equiv C} = -311.4 \text{ kJ/mol} - 872 \text{ kJ/mol} + 347 \text{ kJ/mol} + 1656 \text{ kJ/mol} = \boxed{820. \text{ kJ/mol}}$ (see above)

4. For the gaseous equilibrium represented below, it is observed that greater amounts of PCl_3 and Cl_2 are produced when the temperature is increased.

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$$

a) What is the sign of ΔS° for the reaction? Explain.

ΔS° is positive since $\Delta n_{gas} > 0$.

b) What change, if any, will occur in ΔG° for the reaction as the temperature is increased? Explain your answer in terms of thermodynamic principles.

Since ΔS° > 0, the term TΔS° in ΔG° = ΔH° – TΔS° will get larger as T increases, so ΔG° will become more negative and the reaction will become more spontaneous.

c) If He gas is added to the original reaction mixture at constant volume and temperature, what will happen to the partial pressure of Cl_2? Explain.

Addition of the inert gas will have no effect on the partial pressures of any of the products or reactants as long as the volume remains constant.

d) If the volume of the reaction mixture is decreased at constant temperature to half the original volume, what will happen to the number of moles of Cl_2 in the reaction vessel? Explain.

Reduction in volume will increase the pressure, which will cause the reaction equilibrium to shift to the side of fewer moles of gas to reduce the pressure. Thus the equilibrium will shift left, reducing moles of Cl_2.