

Chem 1215 Unit 5 - Thermo Practice Problems - Solutions

1. (a) non-spontaneous (methane is a gas at RT + pressure so no tendency to condense + form a liquid at 25°C + 1 atm)
- (b) spontaneous
- (c) non-spontaneous (If it was spontaneous, the graphite used in pencil "lead" would turn into diamond!)
- (d) spontaneous
- (e) non-spontaneous (Bromine exists as a diatomic molecule.)

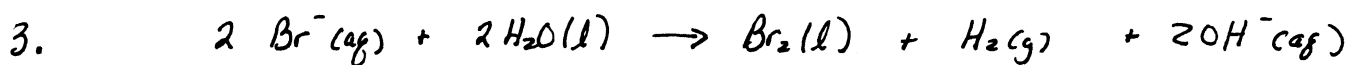
2. (a) $\Delta S = \text{positive}$

(b) $\Delta S = \text{positive}$ (2 mol gas \rightarrow 3 mol gas)

(c) $\Delta S = \text{negative}$ (2 "pieces" combine to form 1 larger "piece"; $af \rightarrow s$)

(d) $\Delta S = \text{positive}$ ($H_2O(s) \rightarrow H_2O(l)$)

(e) $\Delta S \approx \text{zero}$ (no change in # moles of gas)

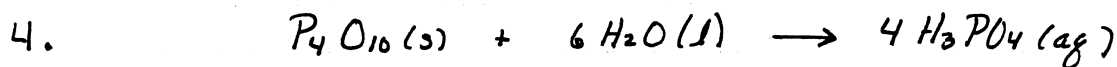


$$S^\circ: \quad \frac{80.71 \text{ J}}{\text{mol} \cdot \text{K}} \quad \frac{69.91 \text{ J}}{\text{mol} \cdot \text{K}} \quad \frac{152.3 \text{ J}}{\text{mol} \cdot \text{K}} \quad \frac{130.58 \text{ J}}{\text{mol} \cdot \text{K}} \quad \frac{-10.7 \text{ J}}{\text{mol} \cdot \text{K}}$$

$$\Delta S^\circ = \left[(1 \text{ mol } Br_2) \left(\frac{152.3 \text{ J}}{\text{mol} \cdot \text{K}} \right) + (1 \text{ mol } H_2) \left(\frac{130.58 \text{ J}}{\text{mol} \cdot \text{K}} \right) + (2 \text{ mol } OH^-) \left(\frac{-10.7 \text{ J}}{\text{mol} \cdot \text{K}} \right) \right] -$$

$$\left[(2 \text{ mol } Br^-) \left(\frac{80.71 \text{ J}}{\text{mol} \cdot \text{K}} \right) + (2 \text{ mol } H_2O) \left(\frac{69.91 \text{ J}}{\text{mol} \cdot \text{K}} \right) \right]$$

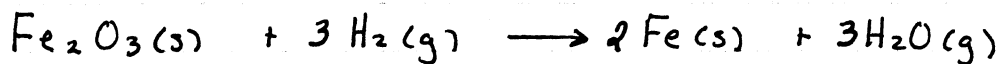
$$\Delta S = -39.76 \Rightarrow \boxed{-39.8 \text{ J/K}}$$



$$\Delta G_f^\circ: \quad -2675.2 \frac{\text{kJ}}{\text{mol}} \quad -237.13 \frac{\text{kJ}}{\text{mol}} \quad -1142.6 \frac{\text{kJ}}{\text{mol}}$$

$$\begin{aligned} \Delta G^\circ &= \left[(4 \text{ mol } H_3PO_4) \left(-1142.6 \frac{\text{kJ}}{\text{mol}} \right) \right] - \left[(1 \text{ mol } P_4O_{10}) \left(-2675.2 \frac{\text{kJ}}{\text{mol}} \right) + (6 \text{ mol } H_2O) \left(-237.13 \frac{\text{kJ}}{\text{mol}} \right) \right] \\ &= -472.42 \text{ kJ} \Rightarrow \boxed{-472.4 \text{ kJ}} \end{aligned}$$

5. Remember, if a reaction occurs, you must write a balanced equation:



(a) Since $T = 230.^\circ\text{C}$, you must use $\Delta G = \Delta H - T\Delta S$

$$\Delta H = \left[(3 \text{ mol } H_2O) \left(-241.82 \frac{\text{kJ}}{\text{mol}} \right) \right] - \left[(1 \text{ mol } Fe_2O_3) \left(-822.16 \frac{\text{kJ}}{\text{mol}} \right) \right]$$

$$\Delta H = 96.70 \text{ kJ}$$

$$\Delta S = \left[(2 \text{ mol } Fe) \left(27.15 \frac{\text{J}}{\text{mol}\cdot\text{K}} \right) + (3 \text{ mol } H_2O) \left(188.83 \frac{\text{J}}{\text{mol}\cdot\text{K}} \right) \right] -$$

$$\left[(1 \text{ mol } Fe_2O_3) \left(89.96 \frac{\text{J}}{\text{mol}\cdot\text{K}} \right) + (3 \text{ mol } H_2) \left(130.58 \frac{\text{J}}{\text{mol}\cdot\text{K}} \right) \right]$$

$$\Delta S = 139.09 \frac{\text{J}}{\text{K}}$$

$$\Delta G = \Delta H - T\Delta S \quad (\text{Remember to convert } T \text{ to Kelvin})$$

$$\Delta G = 96.70 \text{ kJ} - \left[(503 \text{ K}) \left(139.09 \frac{\text{J}}{\text{K}} \right) \left(\frac{1 \text{ kJ}}{1000 \text{ J}} \right) \right]$$

$$= 96.70 \text{ kJ} - 69.96 \text{ kJ}$$

$$= 26.74 \Rightarrow \boxed{26.7 \text{ kJ}}$$

5. (b) No. $\Delta G > 0$ so it is nonspontaneous at this temperature.

(c) The reaction will be spontaneous at temperatures that are higher than the temperature required to reach equilibrium.

At equilibrium, $\Delta G = 0$ so

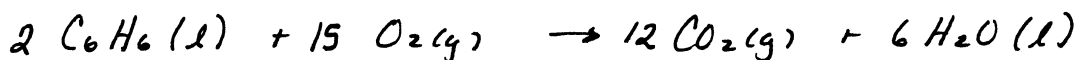
$$\Delta G = \Delta H - T\Delta S = 0 \Rightarrow \Delta H = T\Delta S$$

$$T = \frac{\Delta H}{\Delta S} = 96.70 \text{ kJ} \times \frac{\text{K}}{139.09 \text{ J}} \times \frac{1000 \text{ J}}{\text{kJ}} = 695.23 \text{ K}$$

$$T = 695.23 \text{ K} - 273.15 = 422.08^\circ\text{C} \Rightarrow 422.1^\circ\text{C}$$

The reaction will be spontaneous when $T > 422.1^\circ\text{C}$.

6. * Write a balanced equation:



* Calculated ΔG_{rxn} using ΔG_f° from Appendix C:

$$\Delta G_{\text{rxn}} = \left[(12 \text{ mol}) \left(\frac{-394.4 \text{ kJ}}{\text{mol}} \right) + (6 \text{ mol}) \left(\frac{-237.13 \text{ kJ}}{\text{mol}} \right) \right] - \left[(2 \text{ mol}) \left(\frac{124.5 \text{ kJ}}{\text{mol}} \right) \right]$$

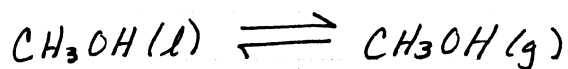
$$\Delta G_{\text{rxn}} = -6404.58 \text{ kJ}$$

* Calculated ΔG for 74.3 g C_6H_6 :

$$W_{\text{max}} = \frac{-6404.58 \text{ kJ}}{2 \text{ mol C}_6\text{H}_6} \times \frac{1 \text{ mol C}_6\text{H}_6}{78.11 \text{ g C}_6\text{H}_6} \times 74.3 \text{ g C}_6\text{H}_6$$

$$W_{\text{max}} = -3046.09 \text{ kJ} \Rightarrow \boxed{-3050 \text{ kJ}}$$

7. At the boiling point, $\text{CH}_3\text{OH}(l)$ + $\text{CH}_3\text{OH}(g)$ are in equilibrium:



$$\Delta H_f^\circ \quad -238.6 \text{ kJ/mol} \quad -201.2 \text{ kJ/mol} \quad \Delta H_{\text{rxn}} = 37.4 \text{ kJ}$$

$$S^\circ \quad 126.8 \text{ J/mol}\cdot\text{K} \quad 237.6 \text{ J/mol}\cdot\text{K} \quad \Delta S_{\text{rxn}} = 110.8 \text{ J/K}$$

At equilibrium, $\Delta G = 0$ so $\Delta G = \Delta H - T\Delta S = 0$

$$\therefore T = \frac{\Delta H}{\Delta S} = 37.4 \text{ kJ} \times \frac{\text{K}}{110.8 \text{ J}} \times \frac{1000 \text{ J}}{\text{kJ}} = 337.5 \text{ K}$$

$$\text{BP} = 337.5 \text{ K} - 273 = 64.5^\circ\text{C} \Rightarrow \boxed{65^\circ\text{C}}$$

8. (a) dissolution of $\text{Mg}(\text{OH})_2$ in water:



$$\Delta G_f^\circ \quad -833.7 \text{ kJ/mol} \quad -454.8 \text{ kJ/mol} \quad -157.3 \text{ kJ/mol}$$

$$\Delta G^\circ = \left[(1 \text{ mol}) \left(\frac{-454.8 \text{ kJ}}{\text{mol}} \right) + (2 \text{ mol}) \left(\frac{-157.3 \text{ kJ}}{\text{mol}} \right) \right] - \left[(1 \text{ mol}) \left(\frac{-833.7 \text{ kJ}}{\text{mol}} \right) \right]$$

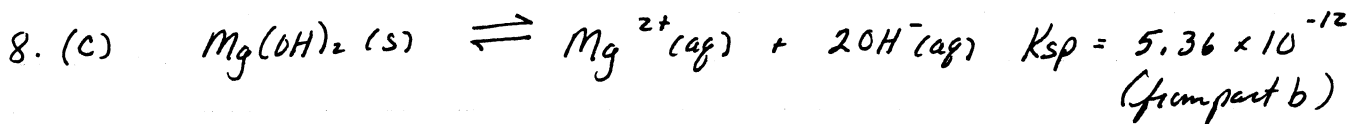
$$\boxed{\Delta G^\circ = 64.3 \text{ kJ}}$$

$$(b) \quad \Delta G^\circ = -RT \ln K_{\text{sp}}$$

$$K_{\text{sp}} = e^{-\Delta G^\circ/RT} = e^{-\frac{(64,300 \text{ J/mol})}{[(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K})]}}$$

$$K_{\text{sp}} = e^{-25.95282801} =$$

$$K_{\text{sp}} = 5.3559 \times 10^{-12} \Rightarrow \boxed{5.36 \times 10^{-12}}$$



I	0	0
Δ	$+x$	$+2x$
E	x	$2x$

$$K_{\text{sp}} = [\text{Mg}^{2+}] [\text{OH}^-]^2 = 5.36 \times 10^{-12}$$

$$(x)(2x)^2 = 5.36 \times 10^{-12}$$

$$4x^3 = 5.36 \times 10^{-12}$$

$$x^3 = 1.34 \times 10^{-12}$$

$$x = 1.102 \times 10^{-4}$$

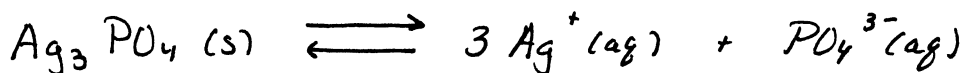
(Remember, the coefficient in front of the x must match the exponent)

$$[\text{OH}^-] = 2x = 2(1.102 \times 10^{-4} \text{ M}) = \boxed{2.20 \times 10^{-4} \text{ M}}$$

Double check by plugging $[\text{Mg}^{2+}] + [\text{OH}^-]$ into the expression for K_{sp} :

$$(1.10 \times 10^{-4})(2.20 \times 10^{-4})^2 = 5.32 \times 10^{-12} \text{ which is very close to } 5.36 \times 10^{-12}$$

9. Dissolution of silver phosphate:



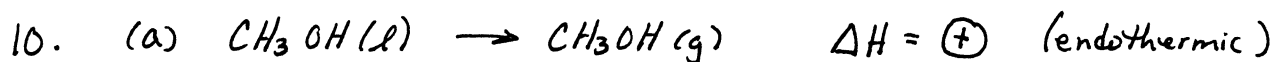
$$[\text{Ag}^+]_{\text{equil}} = \frac{4.14 \text{ mg Ag}^+}{300.0 \text{ mL}} \times \frac{1 \text{ g}}{1000 \text{ mg}} \times \frac{1 \text{ mol Ag}^+}{107.9 \text{ g Ag}^+} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 1.279 \times 10^{-4} \text{ M}$$

$$[\text{PO}_4^{3-}]_{\text{equil}} = 1.279 \times 10^{-4} \frac{\text{mol Ag}^+}{\text{L}} \times \frac{1 \text{ mol PO}_4^{3-}}{3 \text{ mol Ag}^+} = 4.263 \times 10^{-5} \text{ M}$$

$$K_{\text{sp}} = [\text{Ag}^+]^3 [\text{PO}_4^{3-}] = (1.279 \times 10^{-4})^3 (4.263 \times 10^{-5}) = 8.919 \times 10^{-17}$$

$$\Delta G^\circ = -RT \ln K = -\left(\frac{8.314 \text{ J}}{\text{mol} \cdot \text{K}}\right) (298 \text{ K}) \ln (8.919 \times 10^{-17})$$

$$\Delta G^\circ = 91,560.56 \frac{\text{J}}{\text{mol}} \approx \boxed{91,600 \frac{\text{J}}{\text{mol}} \text{ or } 91.6 \text{ kJ/mol}}$$

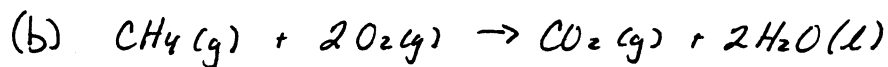


$$\Delta S = \oplus$$

$$\Delta G = \Delta H + -T\Delta S$$

$$\begin{array}{c} \oplus + \ominus \oplus \oplus \\ \oplus + \ominus \end{array}$$

ΔG will be negative at high T



combustion rxn $\Rightarrow \Delta H = \ominus$ (exothermic)

3 mol gas \rightarrow 1 mol gas $\Rightarrow \Delta S = \ominus$

$$\Delta G = \Delta H + -T\Delta S$$

$$\begin{array}{c} \ominus + \ominus \oplus \ominus \\ \ominus + \oplus \end{array}$$

This will be negative only at low T