

PROBLEM SET No. 13: THERMODYNAMICS

1. (a) Use enthalpies of formation to calculate the value of ΔH° for the reaction below. (**-1250 kJ**)
$$2 \text{X}(g) + 2 \text{Y}(g) + 3 \text{O}_2(g) \rightarrow 2 \text{W}(g) + 6 \text{Z}(\ell)$$

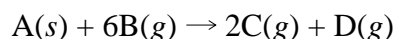
Enthalpies of formation:

X(g)	= -50 kJ/mol
Y(g)	= -75 kJ/mol
W(g)	= +150 kJ/mol
Z(ℓ)	= -300 kJ/mol

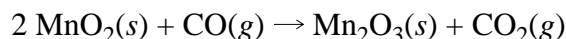
- (b) Calculate ΔE°_{298} for the above reaction. (**-1237.5 kJ**)

2. Given the thermochemical equation: $2 \text{NaN}_3(s) \rightarrow 2 \text{Na}(s) + 3 \text{N}_2(g)$ $\Delta H_{298}^\circ = +42.7 \text{ kJ}$
Calculate $\Delta H^\circ_{f,298}$ for $\text{NaN}_3(s)$. (**-21.35 kJ/mol**)

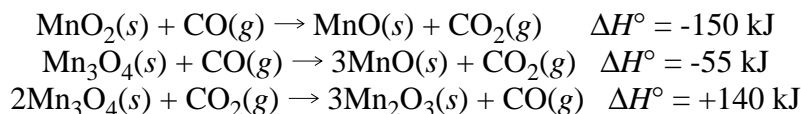
3. A 10.00 mmole sample of $\text{A}(s)$ was reacted with excess $\text{B}(g)$ in a bomb calorimeter. The total heat capacity of the calorimeter was 10.00 kJ/ $^\circ\text{C}$. The temperature of the calorimeter and its contents increased from 24.00 $^\circ\text{C}$ to 26.00 $^\circ\text{C}$. Calculate ΔH_{298}° for the reaction below. (**-2007.5 kJ**)



4. Determine the ΔH° for the reaction



from the following given data. (**about -217 kJ**)



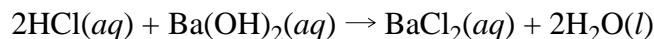
5. Given the $\Delta H_f^\circ(\text{CH}_4(g)) = -75 \text{ kJ/mol}$ and for the reaction,
$$2\text{H}_2(g) + \text{C}(g) \rightarrow \text{CH}_4(g) \quad \Delta H = -792 \text{ kJ}$$

Calculate $\Delta H_{\text{sublimation}}$ of $\text{C}(\text{graphite})$ in kJ/mol. (**+717 kJ/mol**)

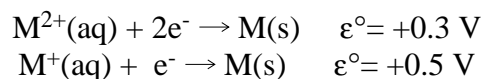
6. For oxygen difluoride, $\text{OF}_2(g)$, the Gibbs free energy of formation is +41 kJ/mol.
(a) Is the preparation of $\text{OF}_2(g)$ from its elements at 25 $^\circ\text{C}$ a spontaneous reaction? **EXPLAIN. (NO)**
(b) For ozone, $\text{O}_3(g)$, the Gibbs free energy of formation is +163 kJ/mol. Why isn't the Gibbs free energy of formation of ozone = 0? (**See your class notes**)
(c) Is it theoretically possible to prepare $\text{OF}_2(g)$ at 25 $^\circ\text{C}$ by the reaction below? (**YES**)
$$3 \text{F}_2(g) + \text{O}_3(g) \rightarrow 3 \text{OF}_2(g)$$

7. The standard enthalpy of formation of $\text{CS}_2(\ell)$ at 298 K is +90 kJ/mol. The absolute molar entropy (S°) of $\text{C}(\text{graphite})$ at 298 K is 6 J/mol-K, of $\text{S}(\text{rhombic})$ is 32 J/mol-K, and of $\text{CS}_2(\ell)$ is 151 J/mol-K. Calculate the standard Gibbs free energy of formation of $\text{CS}_2(\ell)$ at 298 K. ($\Delta G^\circ_{f,298} \cong +66 \text{ kJ/mol}$)

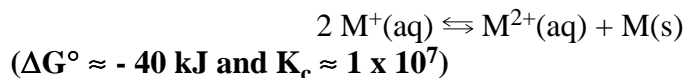
8. When 100 mL of 0.1250 M HCl at 24.00°C was mixed with 250 mL of 0.1000 M Ba(OH)₂ at 24.00°C (assume the calorimeter constant = 0 J/°C), the temperature rose to 24.50°C. Calculate ΔH for the reaction below. Assume the specific heat for the solution is 4.184 J/g·°C. In calculating heat flow assume no heat is lost to the surroundings and ignore the small amount of water formed in the reaction. **(-117 kJ)**



9. For the reaction, $\text{A}(s) \rightleftharpoons 2\text{B}(g) + \text{C}(g)$
 $\Delta G^\circ_{298} = +23.0 \text{ kJ}$ and $\Delta H^\circ_{298} = +150 \text{ kJ}$
- (a) Calculate the approximate value of K_p at 298 K. **(1 x 10⁻⁴)**
 (b) Calculate the P_B and P_C at equilibrium at 298 K. **($P_B \approx 6 \times 10^{-2} \text{ atm}$ and $P_C \approx 3 \times 10^{-2} \text{ atm}$)**
 (c) Calculate the approximate value of K_p at 500 K. **(1 x 10⁶)**
 (d) Calculate the absolute molar entropy of B at 298 given the following absolute molar entropies: $C(g) = 200 \text{ J/mol-K}$ and $A(s) = 150 \text{ J/mol-K}$. **(185 J/mol-K)**
10. Given the following standard electrode potentials and Gibbs free energies of formation at 298 K answer the questions given below.
(You may use the value for the Faraday as $1 \times 10^5 \text{ Coulombs}$ for these calculations.)



- (a) Calculate ϵ° for the reaction: $\text{M}^{2+}(aq) + e^- \rightarrow \text{M}^+(aq)$
($\epsilon^\circ = +0.1 \text{ V}$) (b) Calculate ΔG° and K_c at 298 K for the following reaction:



11. For the reaction, $\text{Ag}^+(aq) + \text{I}^-(aq) \rightarrow \text{AgI}(s)$

$$\epsilon^\circ_{298} = +0.95 \text{ Volt} \quad \text{and} \quad \Delta G^\circ_{328} = -90 \text{ kJ}$$

(You may use the value for the Faraday as $1 \times 10^5 \text{ Coulombs}$ for these calculations.)

- (a) Calculate ΔG° for the above reaction at 298 K. **(-95 kJ)**
 (b) Calculate ΔS° and ΔH° for this reaction at 298 K. Assume that ΔS° and ΔH° are independent of temperature. **($\Delta S^\circ \approx -170 \text{ J/K}$ and $\Delta H^\circ \approx -146 \text{ kJ}$)**
 (c) Given that the Gibbs free energy of formation of $\text{Ag}^+(aq)$ at 298 K is +77 kJ/mol, calculate the ΔG°_{298} and ϵ°_{298} for the half-reaction, **($\epsilon^\circ_{298} = +0.18$ and $\Delta G^\circ_{298} = -18 \text{ kJ}$)**

