

PROBLEM SET No. 8 THERMODYNAMICS

1. (a) Use enthalpies of formation to calculate the value of ΔH° for the reaction:



Enthalpies of formation:

$\text{NH}_3(\text{g})$	$= -46.19 \text{ kJ/mol}$
$\text{CH}_4(\text{g})$	$= -74.86 \text{ kJ/mol}$
$\text{HCN}(\text{g})$	$= +130.5 \text{ kJ/mol}$
$\text{H}_2\text{O}(\text{l})$	$= -285.9 \text{ kJ/mol}$

- (b) Use bond energies to calculate ΔH° for the above reaction.

N-H (389 kJ/mol)	C-H (414 kJ/mol)	O=O (494 kJ/mol)
C≡N (879 kJ/mol)	O-H (463 kJ/mol)	

2. Given the thermochemical equation: $2\text{NaN}_3(\text{s}) \rightarrow 2\text{Na}(\text{s}) + 3\text{N}_2(\text{g})$ $\Delta H^\circ = +42.7 \text{ kJ}$

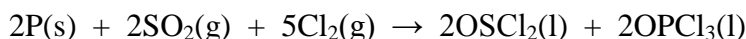
(a) Calculate $\Delta H^\circ_{\text{f}, 298}$ for $\text{NaN}_3(\text{s})$

(b) Calculate ΔE°_{298} for the above reaction

3. A 2.30 g sample of quinone, $\text{C}_6\text{H}_4\text{O}_2$, was burned in excess oxygen in a bomb calorimeter. The calorimeter contained 1000 g of water and the calorimeter itself had a heat capacity of $3.27 \text{ kJ/}^\circ\text{C}$. The temperature of the calorimeter and contents increased from 19.22°C to 27.07°C . What quantity of heat would be liberated by the combustion of one mole of quinone under these conditions?

4. Given:
- | | |
|--|--------------------------------------|
| $\text{OSCl}_2(\text{l}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{SO}_2(\text{g}) + 2\text{HCl}(\text{l})$ | $\Delta H^\circ = +10.3 \text{ kJ}$ |
| $\text{PCl}_3(\text{l}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{OPCl}_3(\text{l})$ | $\Delta H^\circ = -325.1 \text{ kJ}$ |
| $\text{P}(\text{s}) + \frac{3}{2} \text{Cl}_2(\text{g}) \rightarrow \text{PCl}_3(\text{l})$ | $\Delta H^\circ = -306.7 \text{ kJ}$ |
| $4\text{HCl}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{Cl}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$ | $\Delta H^\circ = -202.6 \text{ kJ}$ |

Calculate the value of ΔH° for the reaction:



5. The combustion of 1.000 g of cyclohexane, $\text{C}_6\text{H}_{12}(\text{l})$, in a bomb calorimeter evolves 46.86 kJ of heat. The products of combustion are carbon dioxide gas and liquid water. The molar mass of cyclohexane is 84.16 g/mol.
- (a) Calculate ΔE° for the combustion of one mole of cyclohexane.
- (b) Write the chemical equation for combustion reaction and calculate ΔH° for the reaction.
- (c) Calculate the enthalpy of formation of cyclohexane from your calculated value of ΔH° and the molar enthalpies of formation of $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$.
6. A balloonist is preparing to make a trip in a helium-filled balloon. The trip begins in the early morning when the temperature is 15°C . By midafternoon, the temperature has increased to 30°C . Assuming the pressure remains constant at 1.00 bar, for each mole of helium, calculate:

- (a) the initial and final volumes
 - (b) the change in internal energy, ΔE [Hint: Helium behaves like an ideal gas, so $E = 3/2nRT$]
 - (c) the work (w) done by the helium (in J)
 - (d) the heat (q) transferred (in J)
 - (e) ΔH for the process (in J)
 - (f) Explain the relationship between the answers to (d) and (e)
7. Benzene, C_6H_6 , and acetylene, C_2H_2 , have the same empirical formula, CH. Which releases more energy per mole of CH? (ΔH°_f for gaseous C_6H_6 is 82.9 kJ/mol)
 8. Olmsted 3.85
 9. Olmsted 3.101
 10. For oxygen difluoride, $OF_2(g)$, the Gibbs free energy of formation is +40.6 kJ/mol.
 - (a) Is the preparation of $OF_2(g)$ from its elements at 25°C a spontaneous process?
 - (b) For ozone, $O_3(g)$, the Gibbs free energy of formation is +163.43 kJ/mol. Is it theoretically possible to prepare $OF_2(g)$ at 25°C by the reaction:

$$3F_2(g) + O_3(g) \rightarrow 3OF_2(g)$$
 11. The standard enthalpy of formation of $CS_2(l)$ is +87.9 kJ/mol. The absolute molar entropy of C(graphite) is 5.69 J/mol-K, of S(rhombic) is 31.9 J/mol-K, and of $CS_2(l)$ is 151.0 J/mol-K. Calculate the standard Gibbs free energy of formation of $CS_2(l)$.
 12. Look up the necessary data in the appendices of your textbook to determine the K_p value for the following reaction at 298 K

$$SO_2(g) + NO_2(g) \leftrightarrow SO_3(g) + NO(g)$$
 13. Olmsted Chapter 12 problems: 14, 20, 41, 66, 84, 86, 95
 14. For the reaction: $NH_4CO_2NH_2(s) \leftrightarrow 2NH_3(g) + CO_2(g)$

$$\Delta G^\circ_{298} = +31.00 \text{ kJ and } \Delta H^\circ_{298} = +159.95 \text{ kJ}$$
 - (a) Calculate the value of K_p at 298 K
 - (b) Calculate the pressure of NH_3 and CO_2 at equilibrium at 298 K
 - (c) Calculate the value of K_p at 500 K
 - (d) Calculate the absolute molar entropy of NH_3 at 298 K given the following absolute molar entropies: $CO_2(g) = 213.60 \text{ J/mol-K}$ and $NH_4CO_2NH_2(s) = 166.10 \text{ J/mol-K}$.
 15. Given the following standard electrode potentials and Gibbs free energies of formation at 298 K answer the questions below.

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \quad \epsilon^\circ = +0.337 \text{ V}$$

$$Cu^+(aq) + e^- \rightarrow Cu(s) \quad \epsilon^\circ = +0.521 \text{ V}$$

$$\Delta G^\circ_{f,298}(Cu(OH)_2(s)) = -356 \text{ kJ/mol}$$
 - (a) Calculate ϵ° for the reaction: $Cu^{2+}(aq) + e^- \rightarrow Cu^+(aq)$
 - (b) Calculate ΔG° and K_c at 298 K for the reaction: $2Cu^+(aq) \leftrightarrow Cu^{2+}(aq) + Cu(s)$

- (c) Given the K_{sp} of $\text{Cu}(\text{OH})_2 = 1.6 \times 10^{-19}$ calculate $\Delta G^\circ_{f,298}$ for $\text{OH}^-(\text{aq})$.
 (d) Using the Gibbs free energies of formation at 298 K for the OH^- and H^+ ions along with the $\Delta G^\circ_{f,298}$ for $\text{H}_2\text{O}(\text{l}) = -237 \text{ kJ/mol}$, calculate the K_w for water at 25°C .

16. For the reaction: $\text{Ag}^+(\text{aq}) + \text{I}^-(\text{aq}) \rightarrow \text{AgI}(\text{s})$ $\varepsilon^\circ = +0.951 \text{ V}$, $K_{328} = 1.88 \times 10^{14}$
 (a) Calculate ΔG° for the above reaction at 298 K
 (b) Calculate ΔH° and ΔS° for this reaction at 298 K. Assume that ΔH° and ΔS° are independent of temperature.
 (c) Given that the Gibbs free energy of formation of $\text{Ag}^+(\text{aq})$ at 298 K is $+77.11 \text{ kJ/mol}$, calculate the ε°_{298} for the half reaction: $\text{Ag}(\text{s}) + \text{I}^-(\text{aq}) \rightarrow \text{AgI}(\text{s}) + \text{e}^-$