Expt.#	[H <sub>2</sub> SeO <sub>3</sub> ] <sub>0</sub> , (mol/L)	$[H^+]_0,$ (mol/L)	$[\overline{I}]_0, M$ (mol/L)	Initial Rate (mol/L•s)
1	$1.0 \times 10^{-4}$	$2.0 \times 10^{-2}$ $2.0 \times 10^{-2}$ $4.0 \times 10^{-2}$ $4.0 \times 10^{-2}$ $1.0 \times 10^{-2}$	$2.0 \times 10^{-2}$	1.7 x 10 <sup>-7</sup>
2	2.0 x 10 <sup>-4</sup>		2.0 x 10 <sup>-2</sup>	3.5 x 10 <sup>-7</sup>
3	2.0 x 10 <sup>-4</sup>		2.0 x 10 <sup>-2</sup>	1.4 x 10 <sup>-6</sup>
4	2.0 x 10 <sup>-4</sup>		4.0 x 10 <sup>-2</sup>	2.7 x 10 <sup>-6</sup>
5	1.0 x 10 <sup>-4</sup>		1.0 x 10 <sup>-2</sup>	?

1. The following reaction was studied at a certain temperature and the data below were collected.

 $H_2 SeO_3(aq) + 6\bar{I}(aq) + 4H^+(aq) \rightarrow Se(s) + 2\bar{I}_3(aq) + 3H_2O(l)$ 

(a) Determine the rate order w.r.t. to each reactant and write rate law equation.

(b) Calculate the rate constant, *k*, with the correct unit.

(c) What is the initial rate for Experiment-#5?

- 2. The re-arrangement of methyl isonitrile to methyl cyanide: CH<sub>3</sub>NC  $\rightarrow$  CH<sub>3</sub>CN, follows *first order* rate law with rate constant,  $k = 3.3 \times 10^{-3} \text{ s}^{-1}$  at 250°C.
  - (a) What is the half-life for this reaction at  $250^{\circ}$ C?
  - (b) If  $[CH_3NC]_0 = 0.100 M$  and  $[CH_3CN]_0 = 0.000 M$ , what is  $[CH_3CN]$  after 10.0 minutes?
  - (c) How long does it take for 75.0% of the original amount of CH<sub>3</sub>NC to become CH<sub>3</sub>CN?

3. Consider the reaction for the decomposition of N<sub>2</sub>O<sub>5</sub>: 2N<sub>2</sub>O<sub>5</sub>(g)  $\rightarrow$  4NO<sub>2</sub>(g) + O<sub>2</sub>(g). The rate constant,  $k_1 = 2.70 \times 10^{-4} \text{ s}^{-1}$  at 40°C, and  $k_2 = 2.90 \times 10^{-3} \text{ s}^{-1}$ .

- (a) What is the half-life  $(t_{1/2})$  at each reaction temperature?
- (b) Calculate the activation energy,  $E_a$ , for the decomposition of N<sub>2</sub>O<sub>5</sub>. (R = 8.314 J/mol.K)
- (c) What is the rate constant (k) at  $25^{\circ}$ C? (Assume that  $E_{a}$  is independent of temperature.)

(d) Calculate the Arrhenius collisional frequency factor (A) at  $25^{\circ}$ C.

4. The reaction: 2NOBr(g)  $\rightarrow$  2NO(g) + Br<sub>2</sub>(g) has the rate law: Rate =  $-\frac{\Delta[\text{NOBr}]}{\Delta t} = k[\text{NOBr}]^2$ 

(a) At a certain temperature it takes 140 s for the concentration of NOBr to decrease from 0.20 *M* to 0.15 *M*. Calculate the rate constant *k* (with correct unit) for the decomposition of NOBr.
(b) How long will it take for the concentration of NOBr to decrease from 0.20 *M* to 0.10 *M*?
(c) If the initial concentration of NOBr was 0.20 *M*, what would be the concentration of Br<sub>2</sub> after 10.0 minutes of reaction?

5. The following mechanism has been proposed for the formation of nitrosyl bromide:

Step 1: NO + $Br_2 \rightleftharpoons NOBr_2$	(fast, equilibrium)
Step 2: $NOBr_2 + NO \rightarrow 2NOBr$	(slow, rate-determining)

- (a) Write the equation for the overall reaction.
- (b) Identify all reaction intermediates.
- (c) Derive the rate law for the overall reaction.

6. Indicate the temperature conditions (high or low) the following reactions are spontaneous or nonspontaneous when performed under standard conditions?

(a)	$CO(g) + 2 H_2(g) \rightarrow CH_3OH(g);$	$\Delta H^{\rm o} = -90.5 \text{ kJ}$
(b)	$CH_4(g) \ + \ H_2O(g) \ \rightarrow \ CO(g) + 3 \ H_2(g);$	$\Delta H^{\rm o} = +206 \text{ kJ}$
(c)	$N_2(g) + 2H_2(g) \rightarrow N_2H_4(l);$	$\Delta H^{\rm o} = +51 \text{ kJ}$
(d)	$CH_4(g) + 2 O_2(g) \rightarrow CO_2(g) + 2H_2O(g);$	$\Delta H^{\rm o} = -803 \text{ kJ}$

7. Given the following reactions:

$2NO_2(g) \rightarrow 2NO(g) + O_2(g);$	$\Delta G^{\rm o} = +71.2 \text{ kJ}$
$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g);$	$\Delta G^{\rm o} = -141.6 \text{ kJ}$

Calculate  $\Delta G^{\circ}$  and  $K_{\rm p}$  for the following reaction at 25°C? Indicate if the forward reaction is spontaneous or nonspontaneous at 25°C under standard condition.

 $SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g);$ 

8. Given the following Thermodynamic data:

	H <sub>2</sub> (g)	$H_2O(g)$	CH <sub>4</sub> (g)	CO(g)
$\Delta H^{\rm o}_{\rm f}$ (kJ/mol):	0.0	-241.8	-74.9	-110.5
$S^{o}$ (J/K.mol):	130.7	188.8	186.3	197.7

(a) Calculate  $\Delta H^{\circ}$ ,  $\Delta S^{\circ}$ ,  $\Delta G^{\circ}$  and  $K_{p}$  for the following reaction at 298 K. Indicate whether the reaction is spontaneous at this temperature.

 $CH_4(g) \ + \ H_2O(g) \ \rightarrow \ CO(g) \ + \ 3H_2(g)$ 

(b) Calculate  $\Delta G^{\circ}$  and  $K_{\rm p}$  at 1220 K, and predict whether the reaction is spontaneous at this temperature. (c) At what temperature this reaction will have  $\Delta G^{\circ} = 0.0$  kJ?

9. Given the following Thermodynamic data:

	$H_2(g)$	CO(g)	CH <sub>3</sub> OH(g)
$\Delta H^{\rm o}{}_{\rm f}$ (kJ/mol):	0.0	-110.5	-201.0
$S^{o}$ (J/K.mol):	130.7	197.7	239.9

(a) Calculate  $\Delta H^{\circ}$ ,  $\Delta S^{\circ}$ ,  $\Delta G^{\circ}$  and  $K_{p}$  for the following reaction at 298 K. Indicate whether the reaction is spontaneous at this temperature.

 $CO(g) + 2H_2(g) \rightarrow CH_3OH(g)$ 

(b) Calculate  $\Delta G^{\circ}$  and  $K_{\rm p}$  at 500. K, and predict whether the reaction is spontaneous at this temperature. (c) Calculate  $\Delta G$  at 473 K under the following partial pressures condition and determine if the reaction is spontaneous under this condition: P<sub>H2</sub> = 40. atm; P<sub>CO</sub> = 20. Atm, and P<sub>CH3OH</sub> = 5.0 atm.

10. Using the free energy ( $\Delta G^{\circ}$ ) for the following reactions:

$$C(s) + O_2(g) \rightarrow CO_2(g); \qquad \Delta G^\circ = -394 \text{ kJ}$$

$$C(g) + \frac{1}{2} O_2(g) \rightarrow CO(g); \qquad \Delta G^\circ = -137 \text{ kJ}$$

$$2Fe(s) + \frac{3}{2} O_2(g) \rightarrow Fe_2O_3(s); \qquad \Delta G^\circ = -740 \text{kJ}$$

Determine  $\Delta G^{\circ}$  for the reaction below and predict whether or not each reaction is spontaneous:

(a) 
$$2Fe_2O_3(s) + 3C(s) \rightarrow 4Fe(s) + 3CO_2(g);$$

- (b)  $Fe_2O_3(s) + 3CO(s) \rightarrow 2Fe(s) + 3CO_2(g);$
- 11. Given the following Reduction Potentials:

$$\begin{split} \text{NO}_{3}^{-}(aq) &+ 4\text{H}^{+} + 3\text{e}^{-} \rightarrow \text{NO} + 2\text{H}_{2}\text{O} & \boldsymbol{\mathcal{E}}^{0} &= 0.96 \text{ V} \\ & \text{Ag}^{+}(aq) + \text{e}^{-} \rightarrow \text{Ag(s)}, & \boldsymbol{\mathcal{E}}^{0} &= 0.80 \text{ V} \\ & \text{I}_{2}(aq) + 2\text{e}^{-} \rightarrow 2 \text{ I}^{-}(aq), & \boldsymbol{\mathcal{E}}^{0} &= 0.54 \text{ V} \\ & \text{Cu}^{2+}(aq) + 2\text{e}^{-} \rightarrow \text{Cu}_{(s)}, & \boldsymbol{\mathcal{E}}^{0} &= 0.34 \text{ V} \\ & 2\text{H}^{+}(aq) + 2\text{e}^{-} \rightarrow \text{H}_{2(g)}, & \boldsymbol{\mathcal{E}}^{0} &= 0.00 \text{ V} \\ & \text{Zn}^{2+}(aq) + 2\text{e}^{-} \rightarrow \text{Zn}_{(s)}, & \boldsymbol{\mathcal{E}}^{0} &= -0.76 \text{ V} \end{split}$$

Calculate the  $\mathcal{E}_{cell}^{o}$  for each of the following redox reaction and predict whether the reaction is spontaneous.

- (a)  $3Ag(s) + NO_{3}(aq) + 4H_{3}O^{+}(aq) \rightarrow 3Ag^{+}(aq) + NO(g) + 6H_{2}O(l);$
- (b) Cu(s) +  $2H^+(aq) \rightarrow Cu^{2+}(aq) + H_2(g);$
- (c)  $H_2(g) + 2Ag^+(aq) \rightarrow 2H^+(aq) + 2Ag(s);$
- (d)  $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s);$
- (e)  $Cu(s) + I_2(aq) \rightarrow CuI_2(aq);$

12. Balance the following net ionic equations for redox reactions in acidic solution:

(a) 
$$MnO_4^-(aq) + H_2C_2O_4(aq) \rightarrow Mn^{2+}(aq) + CO_2(g)$$

(b) 
$$Cr_2O_7^{2-}(aq) + H_2O_2(aq) \rightarrow Cr^{3+}(aq) + O_2(g)$$

13. Balance the following net ionic equations for redox reactions in basic solution:
(a) Al(s) + H<sub>2</sub>O(l) → Al(OH)<sub>4</sub><sup>-</sup>(aq) + H<sub>2</sub>(g)
(b) Zn(s) + NO<sub>3</sub><sup>-</sup>(aq) → Zn(OH)<sub>4</sub><sup>2-</sup>(aq) + NH<sub>3</sub>(aq)

14. Consider the following standard reduction (half-cell) potentials:

(a) Sketch a diagram of a voltaic cell using the Al(s) | Al(NO<sub>3</sub>)<sub>3</sub>(*aq*) and Cu(s) | Cu(NO<sub>3</sub>)<sub>2</sub>(*aq*) half-cells and KNO<sub>3</sub> as a salt bridge. (b) On the diagram label the anode and cathode half-cells, indicate the direction electron flows in the external circuit, and the flow of positive and negative ions in the salt bridge. (c) Write the net ionic equation for: (*i*) anode half-reaction; (*ii*) the cathode half-reaction, (*iii*) the overall cell reaction. (d) Calculate the standard cell potential ( $\mathcal{E}_{cell}$ ) and  $\Delta G^{\circ}$  for the overall reaction at 25 °C. (e) Calculate the cell potential ( $\mathcal{E}_{cell}$ ) at 25°C when the electrolyte concentrations are as follows: [Al<sup>3+</sup>] 0.10 *M* and [Cu<sup>2+</sup>] = 1.0 x 10<sup>-5</sup> *M*. (f) How much energy (in kJ) can be produced from a reaction that consumed 5.00 g of aluminum at an average cell potential of 2.00 V?

- 15. A copper concentration cell is set by placing a copper electrode in a  $1.0 M \operatorname{Cu(NO_3)_2}$  solution in one half-cell and another and another copper electrode in saturated solution of  $\operatorname{CuCO_3}$ , in which  $[\operatorname{Cu}^{2+}] \ll 1.0 M$ . The two half-cells are connected by KNO<sub>3</sub> salt bridge and the copper electrodes are connected to a voltmeter. If the concentration cell give a potential of 0.142 V, calculate  $[\operatorname{Cu}^{2+}]$  in the saturated solution and the  $K_{sp}$  of  $\operatorname{CuCO_3}$ ?
- 16. An aqueous solution containing a metal sulfate, MSO<sub>4</sub>, is electrolyzed using electrolytic cells that operate at 3.0 V and deliver a constant current of 25 A. Electrolysis was carried for 30.0 minutes, which produces 13.7 g of metal M at the cathode. Determine the atomic mass and identity of metal M.
- 17. Aluminum is produced by electrolysis of molten Al<sub>2</sub>O<sub>3</sub>-Na<sub>3</sub>AlF<sub>6</sub> mixture using a series of electrolytic cells that operates at a total voltage of 3.0 V and a constant current of 1.0 x 10<sup>6</sup> A.
  (a) How many kilograms of aluminum can be produced 1.00 hour of continuous electrolysis?
  (b) How much energy (in kWh) is consumed in 1.0 hour to produce the aluminum? (c) How many MJ of electrical energy is consumed per kg of Al produced?
- (a) Write a balanced equation for the reaction that occurs in a car battery when the ignition key is turned on. (b) Suppose that constant current of 450 A flowing through the engine for at least 5.0 seconds is needed to start a car. How many grams of lead are consumed during this time?
  (c) If the battery operates at 12 V of potential, how much energy (in kJ) is produced?
- 19. Write a balanced equation for the discharge reaction in an alkaline battery and in a non-alkaline battery, respectively.

## Answers:

1.	(a) Rate = $k[H_2SeO_3][H^+]^2[\Gamma]; k = 2.1 \times 10^2 L^3.mol^{-3}.s^{-1};$ (b) Rate = 2.1 x 10 <sup>-8</sup> mol/L.s
2.	(a) half-life = $210 \text{ s}$ ; (b) $0.014 M$ ; (c) $420 \text{ s}$
3.	(a) $t_{1/2}$ (at 40°C) = 2.57 x 10 <sup>3</sup> s; $t_{1/2}$ (at 60°C) = 239 s; (b) $E_a = 103$ kJ/mol; (c) $k_{298K} = 3.68 \times 10^{-5} \text{ s}^{-1}$ ; (d) $A = 4.18 \times 10^{13} \text{ s}^{-1}$ ;
4.	(a) $k = 0.012 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ ; (b) 420 s; (c) $[\text{Br}_2] = 0.059 M$
5.	(a) $2NO + Br_2 \rightarrow 2NOBr$ ; (b) Intermediate = $NOBr_2$ ; (c) $Rate = k[NO]^2[Br_2]$
6.	(a) spontaneous at low temperature; (b) spontaneous at high temperature; (c) not spontaneous at all temperature; (d) spontaneous at all temperature.
7.	$\Delta G^{\circ} = -35.2 \text{ kJ};  K_{\rm p} = 1.48 \text{ x } 10^{6}.$ Spontaneous at 25°C under standard condition)
8.	(a) $\Delta H^{\circ} = 206.2 \text{ kJ};  \Delta S^{\circ} = 214.7 \text{ J/K};  \Delta G^{\circ} = 142.2 \text{ kJ}; \text{ (not spontaneous)};  K_{\rm p} = 1.185 \text{ x } 10^{-25};$ (b) $\Delta G^{\circ}_{1220\rm K} = -55.7 \text{ kJ}$ (reaction is spontaneous); $K_{\rm p} = 2.43 \text{ x } 10^2$ (at 1220 K); (c) $T_{\rm tr} = 960$ . K (687°C); under standard condition, reaction is spontaneous above this temperature.
9.	(a) $\Delta H^{\circ} = -90.5 \text{ kJ};  \Delta S^{\circ}_{298} = -219.2 \text{ J/K};  \Delta G^{\circ}_{298} = -25.2 \text{ kJ} \text{ (spontaneous)};  K_{\rm p} = 2.61 \text{ x } 10^4;$ (b) $\Delta G^{\circ}_{473} = 13.2 \text{ kJ} \text{ (not spontaneous under standard condition)};  K_{\rm p(473K)} = 0.0349;$ (c) $\Delta G_{473} = -21.3 \text{ kJ} \text{ (reaction is spontaneous)}$
10.	(a) $\Delta G^{\circ} = 298 \text{ kJ}$ (not spontaneous); (b) $\Delta G^{\circ} = -31 \text{ kJ}$ (spontaneous);
11.	(a) Spontaneous ( $\mathcal{E}_{cell}^{o} = 0.16 \text{ V}$ ); (b) Not spontaneous ( $\mathcal{E}_{cell}^{o} = -0.34 \text{ V}$ ); (c) Spontaneous ( $\mathcal{E}_{cell}^{o} = 0.80 \text{ V}$ ); (d) Spontaneous ( $\mathcal{E}_{cell}^{o} = 1.10 \text{ V}$ ); (e) Spontaneous ( $\mathcal{E}_{cell}^{o} = 0.20 \text{ V}$ );
12.	(a) $2MnO_4^{-}(aq) + 5H_2C_2O_4(aq) + 6H^{+}(aq) \rightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(l);$ (b) $Cr_2O_7^{2-}(aq) + 3H_2O_2(aq) + 8H^{+}(aq) \rightarrow 2Cr^{3+}(aq) + 3O_2(g) + 7H_2O(l)$
13.	(a) $2Al(s) + 6H_2O(l) + 2OH^{-}(aq) \rightarrow 2Al(OH)_4^{-}(aq) + 3H_2(g)$ (b) $4Zn(s) + NO_3^{-}(aq) + 6H_2O(l) + 7OH^{-}(aq) \rightarrow 4Zn(OH)_4^{-}(aq) + NH_3(aq)$
14.	(c) ( <i>i</i> ) Al(s) $\rightarrow$ Al <sup>3+</sup> (aq) + 3e <sup>-</sup> ; ( <i>ii</i> ) Cu <sup>2+</sup> (aq) + 2e <sup>-</sup> $\rightarrow$ Cu(s); ( <i>iii</i> ) 2Al(s) + 3Cu <sup>2+</sup> (aq) $\rightarrow$ 2Al <sup>3+</sup> (aq) + 3Cu(s); (d) $\mathcal{E}^{o}_{cell} = 2.00 \text{ V};  \Delta G^{o} = -1.16 \text{ x } 10^{3} \text{ kJ};$ (e) $\mathcal{E}_{cell} = 1.87 \text{ V};$ (f) 107 kJ;
15.	$[Cu^{2+}] = 1.6 \text{ x } 10^{-5} M; K_{sp} \text{ of } CuCO_3 = 2.5 \text{ x } 10^{-10}$
16.	Atomic mass = 58.7 g/mol; M = nickel (Ni)
17.	(a) $340 \text{ kg/hr}$ ; (b) $3.0 \times 10^3 \text{ kW-hr}$ (c) $32 \text{ MJ/kg of Al}$ ;
18.	(b) 2.4 g of Pb; (c) 27 kJ
19.	For alkaline battery: $Zn(s) + 2MnO_4(s) \rightarrow ZnO(s) + Mn_2O_3(s);$

Non-alkaline battery:  $Zn(s) + 2MnO_2(s) + 2NH_4^+(aq) \rightarrow Zn^{2+}(aq) + Mn_2O_3(s) + NH_3(aq) + H_2O;$