Thermochemistry

1) $2\ C_4H_{10}(g) + 13\ O_2(g) \text{------>} 8\ CO_2(g) + 10\ H_2O(l)$

The reaction represented above is spontaneous at 25 °C. Assume that all reactants and products are in their standard states.

(a) Predict the sign of $\Delta S°$ for the reaction and justify your prediction.

(b) What is the sign of $\Delta G°$ for the reaction? How would the sign and magnitude of $\Delta G°$ be affected by an increase in temperature to 50 °C? Explain your answer.

(c) What must be the sign of $\Delta H°$ for the reaction at 25°C? How does the total bond energy of the reactants compare to that of the products?

(d) When the reactants are placed together in a container, no change is observed even though the reaction is known to be spontaneous. Explain this observation.

2)

$$C_2H_2(g) + 2\ H_2(g) \text{--->} C_2H_6(g)$$

Information about the substances

Substance	S° (J/mol K)	$\Delta H°_f$ (kJ/mol)
$C_2H_2(g)$	200.9	226.7
$H_2(g)$	130.7	0
$C_2H_6(g)$	--------	-84.7

Bond	Bond Energy (kJ/mol)
C-C	347
C=C	611
C-H	414
H-H	436

(a) If the value of the standard entropy change, $\Delta S°$, for the reaction is -232.7 joules per mole Kelvin, calculate the standard molar entropy, S°, of C_2H_6 gas.

(b) Calculate the value of the standard free-energy change, $\Delta G°$, for the reaction. What does the sign of $\Delta G°$ indicate about the reaction above?

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

(d) Calculate the value of the C [triple bond] C bond energy in C_2H_2 in kilojoules per mole.

3) $C_6H_5OH(s) + 7\ O_2(g) \rightarrow 6\ CO_2(g) + 3H_2O(l)$

When a 2.000-gram sample of pure phenol, $C_6H_5OH(s)$, is completely burned according to the equation above, 64.98 kilojoules of heat is released. Use the information in the table below to answer the questions that follow.

Substance	Standard Heat of Formation, $\Delta H°_f$, at 25°C (kJ/mol)	Absolute Entropy, S°, at 25°C (J/mol-K)
C(graphite)	0.00	5.69
$CO_2(g)$	-395.5	213.6
$H_2(g)$	0.00	130.6
$H_2O(l)$	-285.85	69.91
$O_2(g)$	0.00	205.0
$C_6H_5OH(s)$	?	144.0

(a) Calculate the molar heat of combustion of phenol in kilojoules per mole at 25°C.

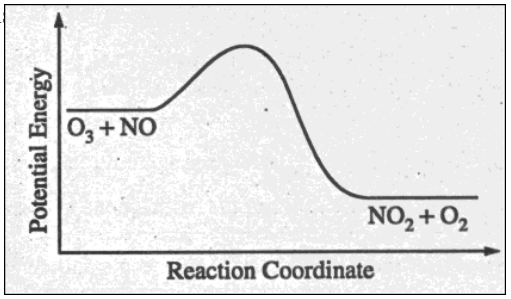
(b) Calculate the standard heat of formation, $\Delta H°_f$, of phenol in kilojoules per mole at 25°C.

(c) Calculate the value of the standard free-energy change, $\Delta G°$ for the combustion of phenol at 25°C.

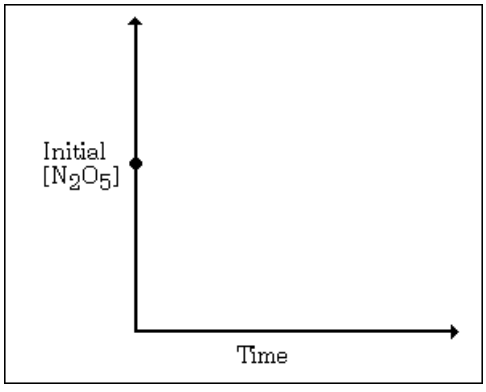
(d) If the volume of the combustion container is 10.0 liters, calculate the final pressure in the container when the temperature is changed to 110°C. (Assume no oxygen remains unreacted and that all products are gaseous.)

Kinetics

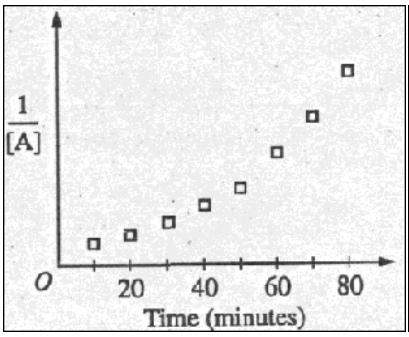
1) Answer the following questions regarding the kinetics of chemical reaction.
(a) The diagram below at right shows the energy pathway for the reaction: $O_3 + NO \rightarrow NO_2 + O_2$. Clearly label the following directly on the diagram.
(i) The activation energy (E_a) for the forward reaction
(ii) The enthalpy change (ΔH) for the reaction

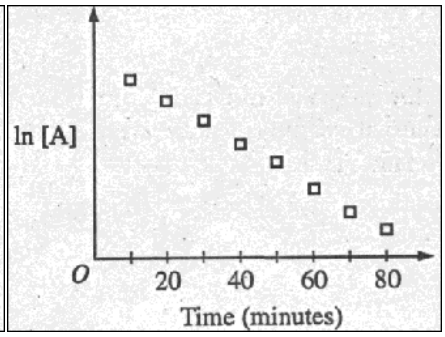


(b) The reaction $2\ N_2O_5 \rightarrow 4\ NO_2 + O_2$ is first order with respect to N_2O_5.
(i) Using the axes at right, complete the graph that represents the change in $[N_2O_5]$ over time as the reaction proceeds.
(ii) Describe how the graph in (i) could be used to find the reaction rate at a given time, t.
(iii) Considering the rate law and the graph in (i), describe how the value of the rate constant, k, could be determined.
(iv) If more N_2O_5 were added to the reaction mixture at constant temperature, what would be the effect on the rate constant, k? Explain.



(c) Data for the chemical reaction 2A → B + C were collected by measuring the concentration of A at 10-minute intervals for 80 minutes. The following graphs were generated from analysis of data.





Use the information in the graphs above to answer the following.
(i) Write the rate-law expression for the reaction. Justify your answer.
(ii) Describe how to determine the value of the rate constant for the reaction.

2) 2 A + B ---> C + D

The following results were obtained when the reaction represented above was studied at 25 °C

Experiment	Initial [A]	Initial [B]	Initial Rate of Formation of C (mol L^{-1} min^{-1})
1	0.25	0.75	4.3×10^{-4}
2	0.75	0.75	1.3×10^{-3}
3	1.50	1.50	5.3×10^{-3}
4	1.75	??	8.0×10^{-3}

a) Determine the order of the reaction with respect to A and B. Justify your answer.

b) Write the rate law for the reaction. Calculate the value of the rate constant, specifying units.

c) Determine the initial rate of change of [A] in Experiment 3.

d) Determine the initial value of [B] in Experiment 4.

e) Identify which of the reaction mechanisms represented below is consistent with the rate law developed in part (b). Justify your choice.

1	A + B ---> C + M	Fast
	M + A ---> D	Slow
2	B <===> M	Fast equilibrium
	M + A ---> C + X	Slow
	A + X ---> D	Fast
3	A + <===> M	Fast equilibrium
	M + A ---> C + X	Slow
	X ---> D	Fast

3) $2\ NO(g) + 2\ H_2(g) \rightarrow N_2(g) + 2\ H_2O(g)$

Experiments conducted to study the rate of the reaction represented by the equation above. Initial concentrations and rates of reaction are given in the table below.

Experiment	Initial Concentration (mol/L) [NO]	[H_2]	Initial Rate of Formation of N_2 (mol/L min)
1	0.0060	0.0010	1.8×10^{-4}
2	0.0060	0.0020	3.6×10^{-4}
3	0.0010	0.0060	0.30×10^{-4}
4	0.0020	0.0060	1.2×10^{-4}

(a)

(i) Determine the order for each of the reactants, NO and H_2, from the data given and show your reasoning.
(ii) Write the overall rate law for the reaction.

(b) Calculate the value of the rate constant, k, for the reaction. Include units.

(c) For experiment 2, calculate the concentration of NO remaining when exactly one-half of the original amount of H_2 has been consumed.

(d) The following sequence of elementary steps is a proposed mechanism for the reaction.

I. $NO + NO \leftrightarrows N_2O_2$
II. $N_2O_2 + H_2 \rightarrow H_2O + N_2O$
III. $N_2O + H_2 \rightarrow N_2 + H_2O$

Based on the data present, which of the above is the rate-determining step? Show that the mechanism is consistent with: (i) the observed rate law for the reaction, and (ii) the overall stoichiometry of the reaction.

Electrochemistry

1) $Sr(s) + Mg^{2+} \leftrightarrows Sr^{2+} + Mg(s)$

Consider the reaction represented above that occurs at 25°C. All reactants and products are in their standard states. The value of the equilibrium constant, K_{eq}, for the reaction is 4.2×10^{17} at 25°C.

(a) Predict the sign of the standard cell potential, E°, for a cell based on the reaction. Explain your prediction.

(b) Identify the oxidizing agent for the spontaneous reaction.

(c) If the reaction were carried out at 60°C instead of 25°C, how would the cell potential change? Justify your answer.

(d) How would the cell potential change if the reaction were carried out at 25°C with a 1.0-molar solution of $Mg(NO_3)_2$ and a 0.10-molar solution of $Sr(NO_3)_2$? Explain.

(e) When the cell reaction in (d) reaches equilibrium, what is the cell potential?

2) $M(s) + Cu^{2+}(aq) \text{ ---> } M^{2+}(aq) + Cu(s)$

For the reaction above, $E° = 0.740$ volt at 25 °C.

(a) Determine the standard electrode potential for the reaction half-reaction $M^{2+}(aq) + 2\ e^- \text{ ---> } M(s)$.

(b) A cell is constructed in which the reaction above occurs. All substances are initially in their standard states, and equal volumes of the solutions are used. The cell is then discharged. Calculate the value of the cell potential, E, when $[Cu^{2+}]$ has dropped to 0.20 molar.

(c) Find the ratio $[M^{2+}]_{aq} / [Cu^{2+}]_{aq}$ when the cell reaction above reaches equilibrium.

3) A solution of $CuSO_4$ was electrolyzed using platinum electrodes by passing a current through the solution. As a result, there was a decrease in both $[Cu^{2+}]$ and the solution pH; one electrode gained in weight and a gas was evolved at the other electrode.

(a) Write the cathode half-reaction that is consistent with the observation above.

(b) Write the anode half-reaction that is consistent with the observations above.

(c) Sketch an apparatus that can be used for such an experiment and label its necessary components.

(d) List the experimental measurement that would be needed in order to determine from such an experiment the value of the faraday.

4) A direct current of 0.125 ampere was passed through 200 milliliters of a 0.25-molar solution of $Fe_2(SO_4)_3$ between platinum electrodes for a period of 1.100 hours. Oxygen gas was produced at the anode. The only change at the cathodes was a slight change in the color of the solution. At the end of the electrolysis, the electrolyte was acidified with sulfuric acid and was titrated with an aqueous solution of potassium permanganate. The volume of the $KMnO_4$ solution required to reach the end point was 24.65 milliliters.

(a) How many faradays were passed through the solution?

(b) Write a balanced half-reaction for the process that occurred at the cathode during the electrolysis.

(c) Write a balanced net ionic equation for the reaction that occurred during the titration with potassium permanganate.

(d) Calculate the molarity of the $KMnO_4$ solution.