THERMODYNAMICS

Enthalpy, Entropy and Free Energy

General Notes:

ΔH°

S°

ΔG°

FRQ

2016 AP® CHEMISTRY FREE-RESPONSE QUESTIONS

$$NaHCO_3(s) + HC_2H_3O_2(aq) \rightarrow NaC_2H_3O_2(aq) + H_2O(l) + CO_2(g)$$

2. A student designs an experiment to study the reaction between $NaHCO_3$ and $HC_2H_3O_2$. The reaction is represented by the equation above. The student places 2.24 g of $NaHCO_3$ in a flask and adds 60.0 mL of 0.875 *M* $HC_2H_3O_2$. The student observes the formation of bubbles and that the flask gets cooler as the reaction proceeds.

(d) In thermodynamic terms, a reaction can be driven by enthalpy, entropy, or both.

(i) Considering that the flask gets cooler as the reaction proceeds, what drives the chemical reaction between $NaHCO_3(s)$ and $HC_2H_3O_2(aq)$? Answer by drawing a circle around one of the choices below.

Enthalpy only Entropy only Both enthalpy and entropy

(ii) Justify your selection in part (d)(i) in terms of ΔG°.

AP Retired 2018-1

$$Na_2S_2O_3(aq) + 4\ NaOCl(aq) + 2\ NaOH(aq) \rightarrow 2\ Na_2SO_4(aq) + 4\ NaCl(aq) + H_2O(l)$$

1. A student performs an experiment to determine the value of the enthalpy change, ΔH°_{rxn}, for the oxidation-reduction reaction represented by the balanced equation above.

   (a) Determine the oxidation number of Cl in NaOCl.

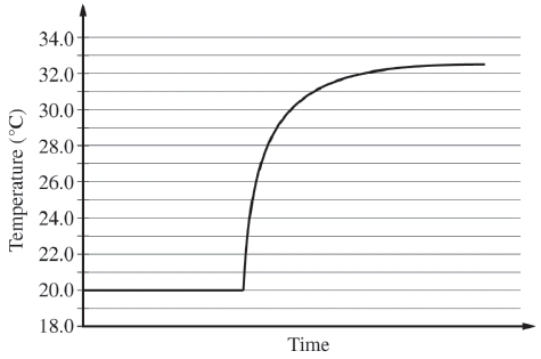
   (b) Calculate the number of grams of $Na_2S_2O_3$ needed to prepare 100.00 mL of 0.500 *M* $Na_2S_2O_3(aq)$.

   In the experiment, the student uses the solutions shown in the table below.

Solution	Concentration (*M*)	Volume (mL)
$Na_2S_2O_3(aq)$	0.500	5.00
$NaOCl(aq)$	0.500	5.00
$NaOH(aq)$	0.500	5.00

   (c) Using the balanced equation for the oxidation-reduction reaction and the information in the table above, determine which reactant is the limiting reactant. Justify your answer.

The solutions, all originally at 20.0°C, are combined in an insulated calorimeter. The temperature of the reaction mixture is monitored, as shown in the graph below.



(d) According to the graph, what is the temperature change of the reaction mixture?

(e) The mass of the reaction mixture inside the calorimeter is 15.21 g.

(i) Calculate the magnitude of the heat energy, in joules, that is released during the reaction. Assume that the specific heat of the reaction mixture is 3.94 J/(g·°C) and that the heat absorbed by the calorimeter is negligible.

(ii) Using the balanced equation for the oxidation-reduction reaction and your answer to part (c), calculate the value of the enthalpy change of the reaction, ΔH°_{rxn}, in kJ/mol$_{rxn}$. Include the appropriate algebraic sign with your answer.

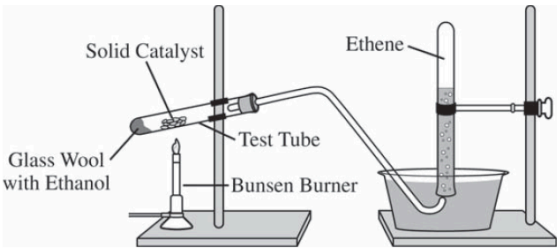
The student repeats the experiment, but this time doubling the volume of each of the reactants, as shown in the table below.

Solution	Concentration (M)	Volume (mL)
$Na_2S_2O_3(aq)$	0.500	10.0
NaOCl(aq)	0.500	10.0
NaOH(aq)	0.500	10.0

(f) The magnitude of the enthalpy change, ΔH°_{rxn}, in kJ/mol$_{rxn}$, calculated from the results of the second experiment is the same as the result calculated in part (e)(ii). Explain this result.

(g) Write the balanced net ionic equation for the given reaction.

2015 AP® CHEMISTRY FREE-RESPONSE QUESTIONS



2. Ethene, $C_2H_4(g)$ (molar mass 28.1 g/mol), may be prepared by the dehydration of ethanol, $C_2H_5OH(g)$ (molar mass 46.1 g/mol), using a solid catalyst. A setup for the lab synthesis is shown in the diagram above. The equation for the dehydration reaction is given below.

$$\underset{\text{ethanol}}{C_2H_5OH(g)} \xrightarrow{\text{catalyst}} \underset{\text{ethene}}{C_2H_4(g)} + \underset{\text{water}}{H_2O(g)} \quad \Delta H^\circ_{298} = 45.5 \text{ kJ/mol}_{rxn};\ \Delta S^\circ_{298} = 126 \text{ J/(K·mol}_{rxn})$$

Because the dehydration reaction is not observed to occur at 298 K, the student claims that the reaction has an equilibrium constant less than 1.00 at 298 K.

(c) Do the thermodynamic data for the reaction support the student's claim? Justify your answer, including a calculation of ΔG°_{298} for the reaction.

AP Retired 2018-2

The student reads in a reference text that $NO(g)$ and $NO_2(g)$ will react as represented by the equation below. Thermodynamic data for the reaction are given in the table below the equation.

$$NO(g) + NO_2(g) \rightleftarrows N_2O_3(g)$$

ΔH°_{298}	ΔS°_{298}	ΔG°_{298}
-40.4 kJ/mol$_{rxn}$	-138.5 J/(K·mol$_{rxn}$)	0.87 kJ/mol$_{rxn}$

(b) The student begins with an equimolar mixture of $NO(g)$ and $NO_2(g)$ in a rigid reaction vessel and the mixture reaches equilibrium at 298 K.

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

(ii) If both P_{NO} and P_{NO_2} in the vessel are initially 1.0 atm, will $P_{N_2O_3}$ at equilibrium be equal to 1.0 atm? Justify your answer.

(c) The student hypothesizes that increasing the temperature will increase the amount of $N_2O_3(g)$ in the equilibrium mixture. Indicate whether you agree or disagree with the hypothesis. Justify your answer.

AP Retired 2017-2

Fulminic acid can convert to isocyanic acid according to the equation below.

$$HCNO(g) \rightleftarrows HNCO(g)$$

fulminic acid *isocyanic acid*

Fulminic Acid	Isocyanic Acid
H—C≡N—Ö:	H—N̈=C=Ö:

(b) Using the Lewis electron-dot diagrams of fulminic acid and isocyanic acid shown in the boxes above and the table of average bond enthalpies below, determine the value of ΔH° for the reaction of $HCNO(g)$ to form $HNCO(g)$.

Bond	Enthalpy (kJ/mol)	Bond	Enthalpy (kJ/mol)	Bond	Enthalpy (kJ/mol)
N–O	201	C=N	615	H–C	413
C=O	745	C≡N	891	H–N	391

(c) A student claims that ΔS° for the reaction is close to zero. Explain why the student's claim is accurate.

(d) Which species, fulminic acid (HCNO) or isocyanic acid (HNCO), is present in higher concentration at equilibrium at 298 K? Justify your answer in terms of thermodynamic favorability and the equilibrium constant.

7. A student wants to determine the concentration of H_2O_2 in a solution of $H_2O_2(aq)$. The student can use one of two titrants, either dichromate ion, $Cr_2O_7^{2-}(aq)$, or cobalt(II) ion, $Co^{2+}(aq)$. The balanced chemical equations for the two titration reactions are shown below.

Dichromate as titrant: $Cr_2O_7^{2-}(aq) + 3\ H_2O_2(aq) + 8\ H^+(aq) \rightarrow 2\ Cr^{3+}(aq) + 3\ O_2(g) + 7\ H_2O(l)$

Cobalt(II) as titrant: $2\ Co^{2+}(aq) + H_2O_2(aq) + 2\ H^+(aq) \rightarrow 2\ Co^{3+}(aq) + 2\ H_2O(l)$

The half-reactions and the $E°$ values for the systems related to the titrations above are given in the following table.

Half-Reaction	$E°$ (V) at 298 K
$Co^{3+}(aq) + e^- \rightarrow Co^{2+}(aq)$	1.84
$H_2O_2(aq) + 2\ H^+(aq) + 2\ e^- \rightarrow 2\ H_2O(l)$	1.77
$Cr_2O_7^{2-}(aq) + 14\ H^+(aq) + 6\ e^- \rightarrow 2\ Cr^{3+}(aq) + 7\ H_2O(l)$	1.33
$O_2(g) + 2\ H^+(aq) + 2\ e^- \rightarrow H_2O_2(aq)$	0.70

(a) Use the information in the table to calculate the following.

(i) $E°$ for the reaction between $Cr_2O_7^{2-}(aq)$ and $H_2O_2(aq)$ at 298 K

(ii) $E°$ for the reaction between $Co^{2+}(aq)$ and $H_2O_2(aq)$ at 298 K

(b) Based on the calculated values of $E°$, the student must choose the titrant for which the titration reaction is thermodynamically favorable at 298 K.

(i) Which titrant should the student choose? Explain your reasoning.

(ii) Calculate the value of $\Delta G°$, in kJ/mol$_{rxn}$, for the reaction between the chosen titrant and $H_2O_2(aq)$.

Multiple Choice:

1. Based on the following reaction, the information provided and your knowledge of thermodynamic properties, which statement is correct regarding the reaction?

$$\text{Heat} + CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

	ΔH°	ΔS°
A)	Negative	Positive
B)	Positive	Negative
C)	Negative	Negative
D)	Positive	Positive

2. Which of the following systems is expected to have the greatest increase in entropy?
   A) $Na^+(g) + Cl^-(g) \rightarrow NaCl(s)$
   B) $SO_2(g) + H_2O(l) \rightarrow H_2SO_3(aq)$
   C) $NH_4Cl(s) \rightarrow HCl(g) + NH_3(g)$
   D) $CO_2(g) \rightarrow CO(g) + \frac{1}{2} O_2(g)$

3. For which of the following reaction are ΔH°_{rxn} and ΔG°_{rxn} about the same?
   A) $4Fe(s) + 3O_2(g) \rightarrow Fe_2O_3(s)$
   B) $2Na(s) + 2H_2O(l) \rightarrow 2Na^+(aq) + 2OH^-(aq) + H_2(g)$
   C) $N_2O_4(g) \rightarrow 2NO_2(g)$
   D) $Fe_2O_3(s) + 2Al(s) \rightarrow Al_2O_3(s) + 2Fe(s)$

4. $CH_3OH(g) \rightarrow CO(g) + 2H_2(g) \qquad \Delta H^\circ = +91 \text{ kJ mol}^{-1}$

The reaction takes place in a rigid, insulated vessel that is initially at 600 K. At this temperature the reaction represented above goes left to right, essentially to completion.

What can be inferred about the ΔS° for the reaction at 600 K?

   A) ΔS° must be positive, since the reaction is thermodynamically unfavorable at 600 K.
   B) ΔS° must be negative, since there are more moles of products than reactants.
   C) ΔS° must be positive, since ΔG° is negative and ΔH° is positive.
   D) ΔS° must be negative, since ΔG° is positive and ΔH° is positive.

5. For the reaction

$$H_2O(g) \rightarrow H_2(g) + 1/2\ O_2(g)$$

$\Delta H°$ is +242 kJ mol^{-1} and $\Delta S°$ is +45 J mol^{-1} K^{-1}.

A) $\Delta G°$ is always positive.
B) $\Delta G°$ is always negative.
C) $\Delta G°$ is negative at low temperature.
D) $\Delta G°$ is negative at high temperature.

6. The reaction

$$N_2(g) + 3\ H_2(g) \rightarrow 2\ NH_3(g)$$

is thermodynamically spontaneous at 298 K, but becomes nonspontaneous at higher temperatures. Which of the following is true at 298 K?

A) ΔG, ΔH, and ΔS are all positive.
B) ΔG, ΔH, and ΔS are all negative.
C) ΔG and ΔH are negative, but ΔS is positive.
D) ΔG and ΔS are negative, but ΔH is positive.