AP Questions: Thermodynamics

1970
Consider the first ionization of sulfurous acid:
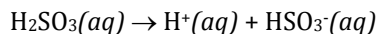
$$H_2SO_3(aq) \rightarrow H^+(aq) + HSO_3^-(aq)$$

Certain related thermodynamic data are provided below:

	$H_2SO_3(aq)$	$H^+(aq)$	$HSO_3^-(aq)$
ΔH_f° kcal/mole	-145.5	0	-151.9
S° cal/mole K	56	0	26

(a) Calculate the value of ΔG° at 25°C for the ionization reaction.

(b) Calculate the value of K at 25°C for the ionization reaction.

(c) Account for the signs of ΔS° and ΔH° for the ionization reaction in terms of the molecules and ions present.

1971
Given the following data for graphite and diamond at 298K.

$$S^\circ(\text{diamond}) = \quad 0.58 \text{ cal/mole deg}$$
$$S^\circ(\text{graphite}) = \quad 1.37 \text{ cal/mole deg}$$
$$\Delta H_f^\circ \text{ CO}_2(\text{from graphite}) = \ -94.48 \text{ kilocalories/mole}$$
$$\Delta H_f^\circ \text{ CO}_2(\text{from diamond}) = \ -94.03 \text{ kilocalories/mole}$$

Consider the change: C(graphite) = C(diamond) at 298K and 1 atmosphere.

(a) What are the values of ΔS° and ΔH° for the conversion of graphite to diamond.

(b) Perform a calculation to show whether it is thermodynamically feasible to produce diamond from graphite at 298K and 1 atmosphere.

(c) For the reaction, calculate the equilibrium constant K_{eq} at 298K

1975 D

$$2\text{ Cu} + S \rightarrow Cu_2S$$
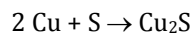
For the reaction above, ΔH°, ΔG°, and ΔS° are all negative. Which of the substances would predominate in an equilibrium mixture of copper, sulfur, and copper(I) sulfide at 298K? Explain how you drew your conclusion about the predominant substance present at equilibrium. Why must a mixture of copper and sulfur be heated in order to produce copper(I) sulfide?

1977 B

$$CH_3OH(l) + {}^3/_2 \ O_2(g) \rightarrow 2\ H_2O(l) + CO_2(g)$$
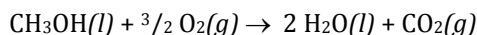
The value of ΔS° for the reaction is -19.3 cal/mol-degree at 25°C.

	ΔH_f° kcal/mole at 25°C	S° cal/mole-degree at 25°C
$CH_3OH(l)$	-57.0	30.3
$H_2O(l)$	-68.3	16.7
$CO_2(g)$	-94.0	51.1

(a) Calculate ΔG° for the complete combustion of methanol shown above at 25°C.

(b) Calculate the value for the equilibrium constant for this reaction at 25°C.

(c) Calculate the standard absolute entropy, S°, per mole of $O_2(g)$.

1980 D
(a) State the physical significance of entropy.

(b) From each of the following pairs of substances, choose the one expected to have the greater absolute entropy. Explain your choice in each case. Assume 1 mole of each substance.

  (1) Pb(s) or C(graphite) at the same temperature and pressure.
  (2) He(g) at 1 atmosphere or He(g) at 0.05 atmosphere, both at the same temperature.
  (3) $H_2O(l)$ or $CH_3CH_2OH(l)$ at the same temperature and pressure.
  (4) Mg(s) at 0°C or Mg(s) at 150°C both at the same pressure.

1978 B

Substance	Standard Entropy cal/deg mole
$N_2(g)$	45.8
$H_2(g)$	31.2
$NH_3(g)$	46.0

Ammonia can be produced by the following reaction:

$$N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$$
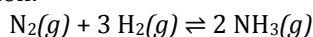
The Gibbs free energy of formation ΔG_f° of $NH_3(g)$ is -3.94 kilocalories per mole.

(a) Calculate the value for ΔH° for the reaction above 298K.

(b) Can the yield of ammonia be increased by raising the temperature? Explain.

(c) What is the equilibrium constant for the reaction above at 298K?

(d) If 235 milliliters of H_2 gas measured at 25°C and 570 millimeters Hg were completely converted to ammonia and the ammonia were dissolved in sufficient water to make 0.5000 liter of solution, what would be the molarity of the resulting solution?


1981 D

$$PCl_5(g) \rightleftharpoons PCl_3(g)\ +\ Cl_2(g)$$
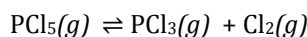
For the reaction above, ΔH° = +22.1 kilocalories per mole at 25°C

(a) Does the tendency of reactions to proceed to a state of minimum energy favor the formation of the products of this reaction? Explain

(b) Does the tendency of reactions to proceed to a state of maximum entropy favor the formation of the products of this reaction? Explain.

(c) State whether an increase in temperature drives this reaction to the right, to the left, or has no effect. Explain.

(d) State whether a decrease in the volume of the system at constant temperature drives this reaction to the right, to the left or has no effect. Explain?

1983 B

$$CO(g) + 2\ H_2(g) \rightarrow CH_3OH(l) \quad \Delta H^\circ = -128.1\ kJ$$
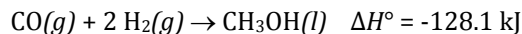
	ΔH_f° (kJ mol^{-1})	ΔG_f° (kJ mol^{-1})	S° (J mol^{-1} K^{-1})
$CO(g)$	-110.5	-137.3	+197.9
$CH_3OH(l)$	-238.6	-166.2	+126.8

The data in the table above were determined at 25°C.

(a) Calculate ΔG° for the reaction above at 25°C.

(b) Calculate K_{eq} for the reaction above at 25°C.

(c) Calculate ΔS° for the reaction above at 25°C.

(d) In the table above, there are no data for H_2. What are the values of ΔH_f°, ΔG_f°, and of the absolute entropy, S°, for H_2 at 25°C?


1985 D

(a) When liquid water is introduced into an evacuated vessel at 25°C, some of the water vaporizes. Predict how the enthalpy, entropy, free energy, and temperature change in the system during this process. Explain the basis for each of your predictions.

(b) When a large amount of ammonium chloride is added to water at 25°C, some of it dissolves and the temperature of the system decreases. Predict how the enthalpy, entropy, and free energy change in the system during this process. Explain the basis for each of your predictions.

(c) If the temperature of the aqueous ammonium chloride system in part (b) were to be increased to 30°C, predict how the solubility of the ammonium chloride would be affected. Explain the basis for each of your predictions.

1984 B

Substance	Standard Heat of Formation, $\Delta H_f°$, in kJ mol⁻¹	Absolute Entropy, S°, in J mol⁻¹ K⁻¹
C(s)	0.00	5.69
$CO_2(g)$	-393.5	213.6
$H_2(g)$	0.00	130.6
$H_2O(l)$	-285.85	69.91
$O_2(g)$	0.00	205.0
$C_3H_7COOH(l)$	?	226.3

The enthalpy change for the combustion of butyric acid at 25°C, $\Delta H°_{comb}$, is -2,183.5 kilojoules per mole. The combustion reaction is

$$C_3H_7COOH(l) + 5\,O_2(g) \rightarrow 4\,CO_2(g) + 4\,H_2O(l)$$
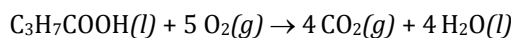
(a) From the above data, calculate the standard heat of formation, $\Delta H_f°$, for butyric acid.

(b) Write a correctly balanced equation for the formation of butyric acid from its elements.

(c) Calculate the standard entropy change, $\Delta S_f°$, for the formation of butyric acid at 25°C. The entropy change, $\Delta S°$, for the combustion reaction above is -117.1 J K⁻¹ at 25°C.

(d) Calculate the standard free energy of formation, $\Delta G°_f$, for butyric acid at 25°C.

1986 D
The first ionization energy of sodium is +496 kilojoules per mole, yet the standard heat of formation of sodium chloride from its elements in their standard state is -411 kilojoules per mole.

(a) Name the factors that determine the magnitude of the standard heat of formation of solid sodium chloride. Indicate whether each factor makes the reaction for the formation of sodium chloride from its elements more or less exothermic.

(b) Name the factors that determine whether the reaction that occurs when such a salt dissolves in water is exothermic or endothermic and discuss the effect of each factor on the solubility.

1987 D
When crystals of barium hydroxide, $Ba(OH)_2·8H_2O$, are mixed with crystals of ammonium thiocyanate, NH_4SCN, at room temperature in an open beaker, the mixture liquefies, the temperature drops dramatically, and the odor of ammonia is detected. The reaction that occurs is the following:
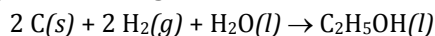$$Ba(OH)_2·8H_2O(s) + 2\,NH_4SCN(s) \rightarrow Ba^{2+} + 2\,SCN^- + 2\,NH_3(g) + 10\,H_2O(l)$$
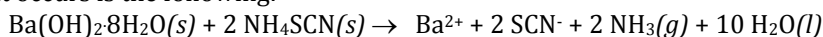
(a) Indicate how the enthalpy, the entropy, and the free energy of this system change as the reaction occurs. Explain your predictions.

(b) If the beaker in which the reaction is taking place is put on a block of wet wood, the water on the wood immediately freezes and the beaker adheres to the wood. Yet the water inside the beaker, formed as the reaction proceeds, does not freeze even though the temperature of the reaction mixture drops to -15°C. Explain these observations.

1988 B

Substance	Enthalpy of Combustion, $\Delta H°$ (kiloJoules/mol)	Absolute Entropy, S° (Joules/mol-K)
C(s)	-393.5	5.740
$H_2(g)$	-285.8	130.6
$C_2H_5OH(l)$	-1366.7	160.7
$H_2O(l)$	- -	69.91

(a) Write a separate, balanced chemical equation for the combustion of each of the following: C(s), $H_2(g)$, and $C_2H_5OH(l)$. Consider the only products to be CO_2 and/or $H_2O(l)$.

(b) In principle, ethanol can be prepared by the following reaction:
$$2\,C(s) + 2\,H_2(g) + H_2O(l) \rightarrow C_2H_5OH(l)$$
Calculate the standard enthalpy change, $\Delta H°$, for the preparation of ethanol, as shown in the reaction above.

(c) Calculate the standard entropy change, $\Delta S°$, for the reaction given in part (b).

(d) Calculate the value of the equilibrium constant at 25°C for the reaction represented by the equation in part (b).

1988 D

An experiment is to be performed to determine the standard molar enthalpy of neutralization of a strong acid by a strong base. Standard school laboratory equipment and a supply of standardized 1.00 molar HCl and standardized 1.00 molar NaOH are available.

(a) What equipment would be needed?

(b) What measurements should be taken?

(c) Without performing calculations, describe how the resulting data should be used to obtain the standard molar enthalpy of neutralization.

(d) When a class of students performed this experiment, the average of the results was -55.0 kilojoules per mole. The accepted value for the standard molar enthalpy of neutralization of a strong acid by a strong base is -57.7 kilojoules per mole. Propose two likely sources of experimental error that could account for the result obtained by the class.
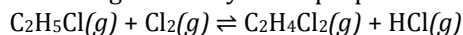

1990 B

Standard Free Energies of Formation at 298 K	
Substance	$\Delta G°_f$ 298 K, kJ mol^{-1}
$C_2H_4Cl_2(g)$	-80.3
$C_2H_5Cl(g)$	-60.5
$HCl(g)$	-95.3
$Cl_2(g)$	0

Average Bond Dissociation Energies at 298 K	
Bond	Energy, kJ mol^{-1}
C-H	414
C-C	347
C-Cl	377
Cl-Cl	243
H-Cl	431

The tables above contain information for determining thermodynamic properties of the reaction below.

$$C_2H_5Cl(g) + Cl_2(g) \rightleftharpoons C_2H_4Cl_2(g) + HCl(g)$$

(a) Calculate the $\Delta H°$ for the reaction above, using the table of average bond dissociation energies.

(b) Calculate the $\Delta S°$ for the reaction at 298 K, using data from either table as needed.

(c) Calculate the value of K_{eq} for the reaction at 298 K.

(d) What is the effect of an increase in temperature on the value of the equilibrium constant? Explain your answer.

1991 D (Required)

$$BCl_3(g) + NH_3(g) \rightleftharpoons Cl_3BNH_3(s)$$
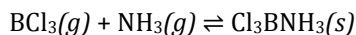
The reaction represented above is a reversible reaction.

(a) Predict the sign of the entropy change, ΔS, as the reaction proceeds to the right. Explain your prediction.

(b) If the reaction spontaneously proceeds to the right, predict the sign of the enthalpy change, ΔH. Explain your prediction.

(c) The direction in which the reaction spontaneously proceeds changes as the temperature is increased above a specific temperature. Explain.

(d) What is the value of the equilibrium constant at the temperature referred to in (c); that is, the specific temperature at which the direction of the spontaneous reaction changes? Explain.
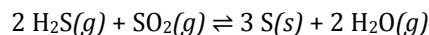
1994 D
$$2 H_2S(g) + SO_2(g) \rightleftharpoons 3 S(s) + 2 H_2O(g)$$
At 298 K, the standard enthalpy change, $\Delta H°$ for the reaction represented above is -145 kilojoules.

(a) Predict the sign of the standard entropy change, $\Delta S°$, for the reaction. Explain the basis for your prediction.

(b) At 298 K, the forward reaction (*i.e.*, toward the right) is spontaneous. What change, if any, would occur in the value of $\Delta G°$ for this reaction as the temperature is increased? Explain your reasoning using thermodynamic principles.

(c) What change, if any, would occur in the value of the equilibrium constant, K_{eq}, for the situation described in (b)? Explain your reasoning.

(d) The absolute temperature at which the forward reaction becomes <u>nonspontaneous</u> can be predicted. Write the equation that is used to make the prediction. Why does this equation predict only an approximate value for the temperature?

1995 B
Propane, C_3H_8, is a hydrocarbon that is commonly used as fuel for cooking.

(a) Write a balanced equation for the complete combustion of propane gas, which yields $CO_2(g)$ and $H_2O(l)$.

(b) Calculate the volume of air at 30°C and 1.00 atmosphere that is needed to burn completely 10.0 grams of propane. Assume that air is 21.0 percent O_2 by volume.

(c) The heat of combustion of propane is -2,220.1 kJ/mol. Calculate the heat of formation, $\Delta H_f°$, of propane given that $\Delta H_f°$ of $H_2O(l)$ = -285.3 kJ/mol and $\Delta H_f°$ of $CO_2(g)$ = -393.5 kJ/mol.

(d) Assuming that all of the heat evolved in burning 30.0 grams of propane is transferred to 8.00 kilograms of water (specific heat = 4.18 J/g·K), calculate the increase in temperature of water.


1995 D
Lead iodide is a dense, golden yellow, slightly soluble solid. At 25°C, lead iodide dissolves in water forming a system represented by the following equation.
$$PbI_2(s) \rightleftharpoons Pb^{2+} + 2 I^- \qquad \Delta H = +46.5 \text{ kilojoules}$$

(a) How does the entropy of the system $PbI_2(s) + H_2O(l)$ change as $PbI_2(s)$ dissolves in water at 25°C? Explain

(b) If the temperature of the system were lowered from 25°C to 15°C, what would be the effect on the value of K_{sp}? Explain.

(c) If additional solid PbI_2 were added to the system at equilibrium, what would be the effect on the concentration of I^- in the solution? Explain.

(d) At equilibrium, $\Delta G = 0$. What is the initial effect on the value of ΔG of adding a small amount of $Pb(NO_3)_2$ to the system at equilibrium? Explain.
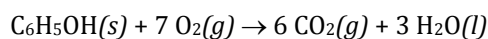

1998 B
$$C_6H_5OH(s) + 7 O_2(g) \rightarrow 6 CO_2(g) + 3 H_2O(l)$$
When a 2.000-gram sample of pure phenol, $C_6H_5OH(s)$, is completely burned according to the equation above, 64.98 kilojoules of heat is released. Use the information in the table below to answer the questions that follow.

Substance	Standard Heat of Formation, $\Delta H°_{â}$ at 25°C (kJ/mol)	Absolute Entropy, $S°$, at 25°C (J/molòK)
C(*graphite*)	0.00	5.69
$CO_2(g)$	-393.5	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, $\Delta H°_{â}$, 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.)

1996 B

$$C_2H_2(g) + 2 H_2(g) \rightleftharpoons C_2H_6(g)$$
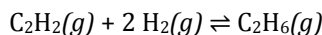
Information about the substances involved in the reaction represented above is summarized in the following tables.

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≡C bond energy in C_2H_2 in kilojoules per mole.

2002 D Required

A student is asked to determine the molar enthalpy of neutralization, ΔH_{neut}, for the reaction represented above. The student combines equal volumes of 1.0 M HCl and 1.0 M NaOH in an open polystyrene cup calorimeter. The heat released by the reaction is determined by using the equation $q = mc\Delta T$.

Assume the following.

- Both solutions are at the same temperature before they are combined.
- The densities of all the solutions are the same as that of water.
- Any heat lost to the calorimeter or to the air is negligible.
- The specific heat capacity of the combined solutions is the same as that of water.

(a) Give appropriate units for each of the terms in the equation $q = mc\Delta T$.

(b) List the measurements that must be made in order to obtain the value of q.

(c) Explain how to calculate each of the following.

   (i)   The number of moles of water formed during the experiment

   (ii) The value of the molar enthalpy of neutralization, ΔH_{neut}, for the reaction between HCl(aq) and NaOH(aq)

(d) The student repeats the experiment with the same equal volumes as before, but this time uses 2.0 M HCl and 2.0 M NaOH.

   (i)   Indicate whether the value of q increases, decreases, or stays the same when compared to the first experiment. Justify your prediction.

   (ii) Indicate whether the value of the molar enthalpy of neutralization, ΔH_{neut}, increases, decreases, or stays the same when compared to the first experiment. Justify your prediction.

(e) Suppose that a significant amount of heat were lost to the air during the experiment. What effect would this have on the calculated value of the molar enthalpy of neutralization, ΔH_{neut}? Justify your answer.

1997 D

For the gaseous equilibrium represented below, it is observed that greater amounts of PCl_3 and Cl_2 are produced as the temperature is increased.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$
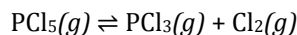
(a) What is the sign of $\Delta S°$ for the reaction? Explain.

(b) What change, if any, will occur in $\Delta G°$ for the reaction as the temperature is increased? Explain your reasoning in terms of thermodynamic principles.

(c) If He gas is added to the original reaction mixture at constant volume and temperature, what will happen to the partial pressure of Cl_2? Explain.

(d) If the volume of the reaction mixture is decreased at constant temperature to half the original volume, what will happen to the number of moles of Cl_2 in the reaction vessel? Explain.

2003 D

Answer the following questions that relate to the chemistry of nitrogen.

(a) Two nitrogen atoms combine to form a nitrogen molecule, as represented by the following equation.

$$2\,N(g) \rightleftharpoons N_2(g)$$
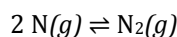
Using the table of average bond energies below, determine the enthalpy change, ΔH, for the reaction.

Bond	Average Bond Energy (kJ mol^{-1})
N–N	160
N=N	420
N≡N	950

(b) The reaction between nitrogen and hydrogen to form ammonia is represented below.

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g) \qquad \Delta H° = -92.2\ kJ$$
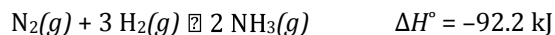
Predict the sign of the standard entropy change, $\Delta S°$, for the reaction. Justify your answer.

(c) The value of $\Delta G°$ for the reaction represented in part (b) is negative at low temperatures but positive at high temperatures. Explain.

(d) When $N_2(g)$ and $H_2(g)$ are placed in a sealed container at a low temperature, no measurable amount of $NH_3(g)$ is produced. Explain.

2004 B

$$2\,Fe(s) + \frac{3}{2}\,O_2(g) \rightarrow Fe_2O_3(s) \qquad \Delta H_f° = -824\ kJ\ mol^{-1}$$
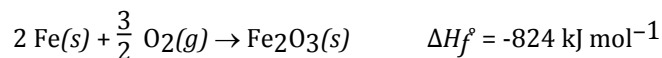
Iron reacts with oxygen to produce iron(III) oxide as represented above. A 75.0 g sample of $Fe(s)$ is mixed with 11.5 L of $O_2(g)$ at 2.66 atm and 298 K.

(a) Calculate the number of moles of each of the following before the reaction occurs.

 (i) $Fe(s)$

 (ii) $O_2(g)$

(b) Identify the limiting reactant when the mixture is heated to produce Fe_2O_3. Support your answer with calculations.

 (c) Calculate the number of moles of Fe_2O_3 produced when the reaction proceeds to completion.

(d) The standard free energy of formation, $\Delta G_f°$ of Fe_2O_3 is –740. kJ mol^{-1} at 298 K.

 (i) Calculate the standard entropy of formation $\Delta S_f°$ of Fe_2O_3 at 298 K. Include units with your answer.

 (ii) Which is more responsible for the spontaneity of the formation reaction at 298K, the standard enthalpy or the standard entropy?

The reaction represented below also produces iron(III) oxide. The value of $\Delta H°$ for the reaction is –280 kJ per mol.

$$2\,FeO(s) + \frac{1}{2}\,O_2(g) \rightarrow Fe_2O_3(s)$$
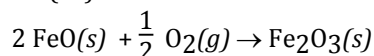
(e) Calculate the standard enthalpy of formation, $\Delta H_f°$ of $FeO(s)$.