Name ____

AP CHEM

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Collected AP Exam Essays for Chapter 16

1980 - #7

(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.

1983 - #2

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CO(g) + 2 H_2(g) \iff CH_3OH(l) \Delta H^\circ = -128.1 kilojoules
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Substance	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 ₃ OH(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 is 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?

1984 - #3

Substance	Standard Heat of Formation, ΔH_{f}°	Absolute Entropy, S° $(J \text{ mol}^{-1} \text{ K}^{-1})$
$\mathbf{C}(\mathbf{z})$	$(kJ mol^{-1})$	5 (0)
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	69.96
$O_2(g)$	0.00	205.0
C ₃ H ₇ COOH(l)	?	226.3

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

 $C_{3}H_{7}COOH(1) + 5O_{2}(g) \le 4CO_{2}(g) + 4H_{2}O(1)$

- (a) From the data above, calculate the standard heat of formation, ΔH_f° , for butyric acid at 25°C.
- (b) Write a correctly balanced equation for the formation of butyric acid from its elements.
- (c) Calculate the standard entropy change, ΔS_{f}° , for the formation of butyric acid at 25°C. The entropy change, ΔS° , for the combustion reaction above is -117.1 J K⁻¹ at 25°C.
- (d) Calculate the standard free energy of formation, ΔG_{f}° , for butyric acid at 25°C.

1985 - #6

(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 decrease. 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 your prediction.

1988 - #2

	Enthalpy of Combustion	Absolute Entropy, S°
Substance	ΔH° Kilojoules/mole	Joules/mole-K
C(s)	-393.5	5.740
$H_2(g)$	-285.8	130.6
$C_2H_5OH(1)$	-1366.7	160.7
$H_2O(1)$		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 $CO_2(g)$ 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, ΔH° , for the preparation of ethanol, as shown in the reaction above.

(c) Calculate the standard entropy change, ΔS° , 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).

1989 - #3

 $Br_2(l) \rightarrow Br_2(g)$

At 25 °C the equilibrium constant, K_p, for the reaction above is 0.281 atmosphere.

(a) What is ΔG°_{298} for this reaction?

(b) It takes 193 joules to vaporize 1.00 gram of $Br_2(l)$ at 25 °C and 1.00 atmosphere pressure. What are the values of ΔH°_{298} and of ΔS°_{298} for this reaction?

(c) Calculate the normal boiling point of bromine. Assume that ΔH° and ΔS° remain constant as the temperature is changed.

(d) What is the equilibrium vapor pressure of bromine at 25°C?

1990 - #3

Standard Free Energies of Formation at 298 K		Average Bond Dissociation Energies at 298 K	
Substance	ΔG_{f}° 298 K, kJ mol $^{-1}$	Bond	Energy, kJ mol ^{_1}
C ₂ H ₄ Cl ₂ (g)	- 80.3	C-H	414
C ₂ H ₅ Cl(g)	- 60.5	C-C	347
HCl(g)	-95.3	C-Cl	377
Cl ₂ (g)	0	Cl-Cl	243
		H-Cl	431

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

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

(a) Calculate ΔH° for the reaction above, using the table of average bond dissociation energies.

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

(c) Calculate the value for 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.

1991 - #5

 $BCl_3(g) + NH_3(g) \rightleftharpoons Cl_3BNH_3(s)$

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.

1992 - #3

 $Cl_2(g) + 3F_2(g) \rightarrow 2ClF_3(g)$

 ClF_3 can be prepared by the reaction represented by the equation above. For ClF_3 the standard enthalpy of formation, ΔH_f° is - 163.2 kilojoules/mole and the standard free energy of formation, ΔG_f° , is - 123.0 kilojoules/mole.

- (a) Calculate the value of the equilibrium constant for the reaction at 298 K.
- (b) Calculate the standard entropy change, ΔS° , for the reaction at 298 K.
- (c) If ClF₃ were produced as a liquid rather than as a gas, how would the sign and magnitude of ΔS for the reaction be affected? Explain.
- (d) At 298 K the absolute entropies of Cl₂(g) and ClF₃(g) are 222.96 joules per mole-Kelvin and 281.50 joules per mole-Kelvin, respectively.
 - (i) Account for the larger entropy of $ClF_3(g)$ relative to that of $Cl_2(g)$.
 - (ii) Calculate the value of the absolute entropy of $F_2(g)$ at 298 K.

1993 - #8

 $2 C_4 H_{10}(g) + 13 O_2(g) \rightarrow 8 CO_2(g) + 10 H_2 O(l)$

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 ΔS° for the reaction and justify your prediction.

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

(c) What must be the sign of ΔH° 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.

1994 - #6

 $2 H_2S(g) + SO_2(g) \iff 3 S(s) + 2 H_2O(g)$

At 298 K, the standard enthalpy change, ΔH° , for the reaction represented above is -145 kilojoules.

(a) Predict the sign of the standard entropy change, ΔS° , 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 ΔG° 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 nonspontaneous 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 - #8

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.

 $PbI_2(s) \le Pb^{2+} + 2I^{-}\Delta H = +46.5$ kilojoules

The solubility-product constant, K_{sp} , for PbI₂ is 7.1 x 10⁻⁹ at 25°C.

(a) How does the entropy of the system $PbI_2(s) + H_2O(1)$ 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 Γ in the solution? Explain.

(d) At equilibrium, $\Delta G = O$. What is the initial effect on the value of ΔG of adding a small amount of Pb(NO₃)₂ to the system at equilibrium? Explain.

1997 - #7

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.

 $PCl_{5}(g) \iff PCl_{3}(g) + Cl_{2}(g)$

(a) What is the sign of ΔS° for the reaction? Explain.

(b) What change, if any, will occur in ΔG° 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 Cl₂? Explain.

(d) If the volume of the original reaction 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.

1998 - #3

$$C_6H_5OH(s) + 7O_2(g) \rightarrow 6CO_2(g) + 3H_2O(1)$$

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.

	Standard Heat of Formation, ΔH°_{f} ,	Absolute Entropy, S°,
Substance	at 25°C (kJ/mol)	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
$H_2O(1)$	-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, ΔH°_{f} , of phenol in kilojoules per mole at 25°C.

(c) Calculate the value of the standard free-energy change, ΔG° 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.)

1999 - #6

Answer the following questions in terms of thermodynamic principles and concepts of kinetic molecular theory. (a) Consider the reaction represented below, which is spontaneous at 298 K.

 $\operatorname{CO}_2(g) + 2 \operatorname{NH}_3(g) \rightarrow \operatorname{CO}(\operatorname{NH}_2)_2(s) + \operatorname{H}_2\operatorname{O}(l) \Delta H^{\circ}_{298} = -134 \text{ kJ}$

(i) For the reaction, indicate whether the standard entropy change, ΔS°_{298} , is positive, or negative, or zero. Justify your answer.

(ii) Which factor, the change in enthalpy, ΔH°_{298} , or the change in entropy, ΔS°_{298} , provides the principal driving force for the reaction at 298 K? Explain.

(iii) For the reaction, how is the value of the standard free energy change, ΔG° , affected by an increase in temperature? Explain.

(b) Some reactions that are predicted by their sign of ΔG° to be spontaneous at room temperature do not proceed at a measurable rate at room temperature.

(i) Account for this apparent contradiction.

(ii) A suitable catalyst increases the rate of such a reaction. What effect does the catalyst have on ΔG° for the reaction? Explain.

2001 - #2

2 NO(g) + O₂(g) → 2 NO₂(g) $\Delta H^{\circ} = -114.1$ kJ, $\Delta S^{\circ} = -146.5$ J K-1

The reaction represented above is one that contributes significantly to the formation of photochemical smog.

(a) Calculate the quantity of heat released when 73.1 g of NO(g) is converted to $NO_2(g)$.

(b) For the reaction at 25°C, the value of the standard free-energy change, ΔG° is -70.4 kJ.

(i) Calculate the value of the equilibrium constant, K_{ea} , for the reaction at 25°C.

(ii) Indicate whether the value of ΔG° would become more negative, less negative, or remain unchanged as the temperature is increased. Justify your answer.

(c) Use the data in the table below to calculate the value of the standard molar entropy, S° for $O_2(g)$ at 25°C.

Standard Molar Entrop (J K ⁻¹ mol ⁻¹)	
NO(g)	210.8
$NO_2(g)$	240.1

(d) Use the data in the table below to calculate the bond energy, in kJ mol⁻¹, of the nitrogen-oxygen bond in NO₂. Assume that the bonds in the NO₂ molecule are equivalent (i.e., they have the same energy).

	Bond
	Energy
	(kJ mol ⁻¹)
Nitrogen-oxygen bond in NO	607
Oxygen-oxygen bond in O ₂	495
Nitrogen-oxygen bond in NO ₂	?

2002 - #8

$$C(s) + CO_2(g) \rightleftharpoons 2 CO(g)$$

Carbon (graphite), carbon dioxide, and carbon monoxide form an equilibrium mixture, as represented by the equation above.

(a) Predict the sign for the change in entropy, ΔS , for the reaction. Justify your prediction.

(b) In the table below are data that show the percent of CO in the equilibrium mixture at two different temperatures. Predict the sign for the change in enthalpy, ΔH ,

for the reaction. Justify your prediction.

Temperature	% CO
700°C	60
850°C	94

(c) Appropriately complete the potential energy diagram for the reaction by finishing the curve on the graph below. Also, clearly indicate ΔH for the reaction on the graph.

(d) If the initial amount of C(s) were doubled, what would be the effect on the percent of CO in the equilibrium mixture? Justify your answer.



2002B - #3

Nitrogen monoxide, NO(g), and carbon



monoxide, CO(g), are air pollutants generated by automobiles. It has been proposed that under suitable conditions these two gases could react to form $N_2(g)$ and $CO_2(g)$, which are components of unpolluted air.

(a) Write a balanced equation for the reaction described above. Indicate whether the carbon in CO is oxidized or whether it is reduced in the reaction. Justify your answer.

(b) Write the expression for the equilibrium constant, K_p , for the reaction.

(c) Consider the following thermodynamic data.

		CO	CO_2
$\Delta G_f^{\circ}(\text{kJ mol}^{-1})$	+86.55	-137.15	-394.36

(i) Calculate the value of ΔG° for the reaction at 298 K.

(ii) Given that ΔH° for the reaction at 298 K is -746 kJ per mole of N₂(g) formed, calculate the value of ΔS° for the reaction at 298 K. Include units with your answer.

(d) For the reaction at 298 K, the value of K_p is 3.3×10^{120} . In an urban area, typical pressures of the gases in the reaction are $P_{NO} = 5.0 \times 10^{-7}$ atm, $P_{CO} = 5.0 \times 10^{-5}$ atm, $P_{N2} = 0.781$ atm, and $P_{CO2} = 3.1 \times 10^{-4}$ atm.

(i) Calculate the value of ΔG for the reaction at 298 K when the gases are at the partial pressures given above.

(ii) In which direction (to the right or to the left) will the reaction be spontaneous at 298 K with these partial pressures? Explain.

2003 - #7

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) \rightarrow N₂(g)

Using the table of average bond energies below, determine the enthalpy change, ΔH , for the reaction.

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

(b) The reaction between nitrogen and hydrogen to form ammonia is represented below. $N_2(g) + 3 H_2(g) \rightarrow 2 NH_3(g) \Delta H^\circ = -92.2 kJ$

Predict the sign of the standard entropy change, ΔS° , for the reaction. Justify your answer. (c) The value of ΔG° 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 - #2

$$2 \operatorname{Fe}(s) + \frac{3}{2} \operatorname{O}_2(g) \xrightarrow{} \operatorname{Fe}_2 \operatorname{O}_3(s) \Delta H_f^{\circ} = -824 \text{ kJ mol}^{-1}$$

Iron reacts with oxygen to produce iron(III) oxide, as represented by the equation 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 begins.

- (i) Fe(*s*)
- (ii) $O_2(g)$

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

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

(d) The standard free energy of formation, ΔG_f° , of Fe₂O₃(s) is -740. kJ mol⁻¹ at 298 K.

(i) Calculate the standard entropy of formation, ΔS_f° , of Fe₂O₃(*s*) at 298 K. Include units with your answer.

(ii) Which is more responsible for the spontaneity of the formation reaction at 298 K, the standard enthalpy of formation, ΔH_f° , or the standard entropy of formation, ΔS_f° ? Justify your answer.

The reaction represented below also produces iron(III) oxide. The value of ΔH° for the reaction is -280. kJ per mole of Fe₂O₃(s) formed.

$$2 \operatorname{FeO}(s) + \frac{1}{2} \operatorname{O}_2(g) \rightarrow \operatorname{Fe}_2 \operatorname{O}_3(s)$$

(e) Calculate the standard enthalpy of formation, ΔH_f° , of FeO(*s*).

2004B - #7

 $N_2(g) + 2 H_2(g) \implies N_2 H_4(g) \Delta H_{298}^{\circ} = +95.4 \text{ kJ mol}^{-1}; \Delta S_{298}^{\circ} = -176 \text{ J K}^{-1} \text{ mol}^{-1}$

Answer the following questions about the reaction represented above using principles of thermodynamics. (a) On the basis of the thermodynamic data given above, compare the sum of the bond strengths of the reactants to the sum of the bond strengths of the product. Justify your answer.

(b) Does the entropy change of the reaction favor the reactants or the product? Justify your answer.

(c) For the reaction under the conditions specified, which is favored, the reactants or the product? Justify your answer.

(d) Explain how to determine the value of the equilibrium constant, K_{eq} , for the reaction. (Do not do any calculations.)

(e) Predict whether the value of K_{eq} for the reaction is greater than 1, equal to 1, or less than 1. Justify your answer.

2005 - #8

 $\operatorname{AgNO}_3(s) \rightarrow \operatorname{Ag}^+(aq) + \operatorname{NO}_3^-(aq)$

The dissolving of $AgNO_3(s)$ in pure water is represented by the equation above.

(a) Is ΔG for the dissolving of AgNO₃(s) positive, negative, or zero? Justify your answer.

(b) Is ΔS for the dissolving of AgNO₃(s) positive, negative, or zero? Justify your answer.

(c) The solubility of $AgNO_3(s)$ increases with increasing temperature.

- (i) What is the sign of ΔH for the dissolving process? Justify your answer.
- (ii) Is the answer you gave in part (a) consistent with your answers to parts (b) and (c) (i)? Explain.

2005B - #7

Answer the following questions about thermodynamics.

		Enthalpy of Combustion,
Substance	Combustion Reaction	ΔH°_{comb} , at 298 K (kJ mol ⁻¹)
$H_2(g)$	$H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l)$	-290
C(s)	$C(s) + O_2(g) \rightarrow CO_2(g)$	-390
$CH_3OH(l)$		-730

(a) In the empty box in the table above, write a balanced chemical equation for the complete combustion of one mole of CH₃OH(1). Assume products are in their standard states at 298 K. Coefficients do not need to be whole numbers.

(b) On the basis of your answer to part (a) and the information in the table, determine the enthalpy change for the reaction $C(s) + H_2(g) + H_2O(l) \rightarrow CH_3OH(l)$.

(c) Write the balanced chemical equation that shows the reaction that is used to determine the enthalpy of formation for one mole of $CH_3OH(l)$.

(d) Predict the sign of ΔS° for the combustion of $H_2(g)$. Explain your reasoning.

(e) On the basis of bond energies, explain why the combustion of $H_2(g)$ is exothermic.

2006 - #2

 $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$

The combustion of carbon monoxide is represented by the equation above.

(a) Determine the value of the standard enthalpy change, ΔH_{rm} , for the combustion of CO(g) at 298 K using the following information.

C(s) + ¹/₂ O₂(g) → CO(g) $\Delta H_{298} = -110.5 \text{ kJ mol}^{-1}$ C(s) + O₂(g) → CO₂(g) $\Delta H_{298} = -393.5 \text{ kJ mol}^{-1}$

(b) Determine the value of the standard entropy change, ΔS_{rxn} , for the combustion of CO(g) at 298 K using the information in the following table.

D 298
$(J \text{ mol}^{-1} \text{ K}^{-1})$
197.7
213.7
205.1

(c) Determine the standard free energy change, ΔG_{rxn} , for the reaction at 298 K. Include units with your answer.

(d) Is the reaction spontaneous under standard conditions at 298 K? Justify your answer.

(e) Calculate the value of the equilibrium constant, K_{eq} , for the reaction at 298 K.

2006B - #3

Answer the following questions about the thermodynamics of the reactions represented below.

Reaction X: $\frac{1}{2}I_2(s) + \frac{1}{2}Cl_2(g) \implies ICl(g) \quad \Delta H_f^{\circ} = 18 \text{ kJ mol}^{-1}, \Delta S_{298}^{\circ} = 78 \text{ J K}^{-1} \text{ mol}^{-1}$

Reaction Y: $\frac{1}{2}I_2(s) + \frac{1}{2}Br_2(l) \rightleftharpoons IBr(g)$ $\Delta H_f^{\circ} = 41 \text{ kJ mol}^{-1}, \Delta S_{298}^{\circ} = 124 \text{ J K}^{-1} \text{ mol}^{-1}$

(a) Is reaction X, represented above, spontaneous under standard conditions? Justify your answer with a calculation.

(b) Calculate the value of the equilibrium constant, K_{eq} , for reaction X at 25°C.

(c) What effect will an increase in temperature have on the equilibrium constant for reaction X? Explain your answer.

(d) Explain why the standard entropy change is greater for reaction Y than for reaction X.

(e) Above what temperature will the value of the equilibrium constant for reaction *Y* be greater than 1.0? Justify your answer with calculations.

(f) For the vaporization of solid iodine, $I_2(s) \rightarrow I_2(g)$, the value of ΔH_{298}° is 62 kJ mol⁻¹. Using this information, calculate the value of ΔH_{298}° for the reaction represented below.

$$I_2(g) + Cl_2(g) \rightleftharpoons 2 ICl(g)$$

2007 - #2

$$\mathrm{N}_{2}(g) \ + \ 3 \ \mathrm{F}_{2}(g) \ \rightarrow \ 2 \ \mathrm{NF}_{3}(g) \qquad \Delta H^{\circ}_{298} \ = \ - \ 264 \ \mathrm{kJ} \ \mathrm{mol}^{-1}; \ \Delta S^{\circ}_{298} \ = \ - \ 278 \ \mathrm{J} \ \mathrm{K}^{-1} \ \mathrm{mol}^{-1}$$

The following questions relate to the synthesis reaction represented by the chemical equation in the box above. (a) Calculate the value of the standard free energy change, ΔG_{298}° , for the reaction.

(b) Determine the temperature at which the equilibrium constant, K_{eq} , for the reaction is equal to 1.00. (Assume that ΔH° and ΔS° are independent of temperature.)

(c) Calculate the standard enthalpy change, ΔH° , that occurs when a 0.256 mol sample of NF₃(g) is formed from N₂(g) and F₂(g) at 1.00 atm and 298 K.

The enthalpy change in a chemical reaction is the difference between energy absorbed in breaking bonds in the reactants and energy released by bond formation in the products.

(d) How many bonds are formed when two molecules of NF_3 are produced according to the equation in the box above?

(e) Use both the information in the box above and the table of average bond enthalpies below to calculate the average enthalpy of the F - F bond.

Bond	Average Bond Enthalpy (kJ mol ⁻¹)		
N≡N	946		
N–F	272		
F-F	?		

2008B - #6

Use principles of thermodynamics to answer the following questions.

(a) The gas N₂O₄ decomposes to form the gas NO₂ according to the equation below.



(i) Predict the sign of ΔH° for the reaction. Justify your answer.

(ii) Predict the sign of ΔS° for the reaction. Justify your answer.

(b) One of the diagrams below best represents the relationship between ΔG° and temperature for the reaction given in part (a). Assume that ΔH° and ΔS° are independent of temperature.



Draw a circle around the correct graph. Explain why you chose that graph in terms of the relationship $\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ}$.

2009 - #5d-f

Reaction	Equation	ΔH_{298}°	ΔS°_{298}	ΔG_{298}°
X	$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$	+131 kJ mol ⁻¹	+134 J mol ⁻¹ K ⁻¹	+91 kJ mol ⁻¹
Y	$\operatorname{CO}_2(g) + \operatorname{H}_2(g) \rightleftharpoons \operatorname{CO}(g) + \operatorname{H}_2\operatorname{O}(g)$	+41 kJ mol ⁻¹	+42 J mol ⁻¹ K ⁻¹	+29 kJ mol ⁻¹
Z	$2 \operatorname{CO}(g) \rightleftharpoons \operatorname{C}(s) + \operatorname{CO}_2(g)$?	?	?

Answer the following questions using the information related to reactions X, Y, and Z in the table above. (d) For reaction Y at 298 K, which is larger: the total bond energy of the reactants or the total bond energy of the products? Explain.

(e) Is the following statement true or false? Justify your answer.

"On the basis of the data in the table, it can be predicted that reaction Y will occur more rapidly than reaction X will occur."

(f) Consider reaction Z at 298 K.

(i) Is ΔS° for the reaction positive, negative, or zero? Justify your answer.

(ii) Determine the value of ΔH° for the reaction.

(iii) A sealed glass reaction vessel contains only CO(g) and a small amount of C(s). If a reaction occurs and the temperature is held constant at 298 K, will the pressure in the reaction vessel increase, decrease, or remain the same over time? Explain.

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(b) Calculate the standard free-energy change, ΔG° , that occurs when 12.0 g of H₂(g) reacts with excess N₂(g) at 298 K according to the reaction represented below.

 $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \Delta G_{298} = -34 \text{ kJ mol}^{-1}$

(c) Given that ΔH_{298} for the reaction is -92.2 kJ mol⁻¹, which is larger, the total bond dissociation energy of the reactants or the total bond dissociation energy of the products? Explain.

(d) The value of the standard entropy change, ΔS_{298} , for the reaction is -199 J mol⁻¹K⁻¹. Explain why the value of ΔS_{298} is negative.

(e) Assume that ΔH° and ΔS° for the reaction are independent of temperature.

(i) Explain why there is a temperature above 298 K at which the algebraic sign of the value of ΔG° changes.

(ii) Theoretically, the best yields of ammonia should be achieved at low temperatures and high pressures. Explain.