***Chemistry***

**16: Thermodynamics**

**16.4: Free Energy**

31. A reactions has and . Is the reaction spontaneous at room temperature? If not, under what temperature conditions will it become spontaneous?

Solution





The , so the reaction is nonspontaneous at room temperature.

Δ*G* = Δ*H* – *T*Δ*S*



*T* = 400 K

Above 400 K, Δ*G* will become negative, and the reaction will become spontaneous.

33. Use the standard free energy of formation data in Appendix G to determine the free energy change for each of the following reactions, which are run under standard state conditions and 25 °C. Identify each as either spontaneous or nonspontaneous at these conditions.

(a) 

(b) 

(c) 

(d) 

(e) 

(f) 

Solution

(a) 



nonspontaneous

(b) 



spontaneous

(c) 

spontaneous

(d) 



spontaneous

(e) 



spontaneous

(f) 



spontaneous

35. Given:







(a) Determine the standard free energy of formation, , for phosphoric acid.

(b) How does your calculated result compare to the value in Appendix G? Explain.

Solution

(a) The standard free energy of formation is the standard free energy change for. We can use a Hess’s law-like approach. Note that adding the first reaction plus three times the second reaction plus the third reaction gives, after cancelling terms





Dividing this result by four gives the equation of interest. The standard free energy of formation is –1124.3kJ/mol. (b) The calculation agrees with the value in Appendix G because free energy is a state function (just like the enthalpy and entropy), so its change depends only on the initial and final states, not the path between them.

37. Consider the decomposition of red mercury(II) oxide under standard state conditions.



(a) Is the decomposition spontaneous under standard state conditions?

(b) Above what temperature does the reaction become spontaneous?

Solution

(a) Using the data in Appendix G, determine :



From its value at 298.15 K, the reaction is nonspontaneous; (b) requires the ratio of the standard enthalpy change to the standard entropy change:

= [2(0) + 0 – 2(–90.83)]kJ/mol = 181.66 kJ/mol



= [2(75.9) + 205.0 – 2(70.29)]J/K•mol = 216.42 J/K•mol



Above 566 °C the process is spontaneous.

39. Calculate Δ*G*° for each of the following reactions from the equilibrium constant at the temperature given.

(a) 

(b) 

(c) 

(d) 

(e) 

(f) 

Solution

(a) Δ*G*° = –*RT* ln *KP* = –(8.314 J K–1)(2273.15 K)(ln 4.1 × 10–4) = 147 kJ = 1.5 × 102 kJ; (b) Δ*G*° = –(8.314 J K–1)(673.15 K)(ln 50.0) = –21,893 J = 21.9 kJ; (c) Δ*G*° = –(8.314 J K–1)(1253.15 K)(ln 1.67) = –5.34 kJ; (d) Δ*G*° = –(8.314 J K–1)(1173.15 K)(ln 1.04) = –0.383 kJ; (e) Δ*G*° = –(8.314 J K–1)(298.15 K)(ln 7.2 × 10–4) = 17,937 J = 18 kJ; (f) Δ*G*° = –(8.314 J K–1)(298.15 K)(ln 3.3 × 10–13) = 71,240 J = 71 kJ

41. Calculate the equilibrium constant at 25°C for each of the following reactions from the value of Δ*G*° given.

(a) 

(b) 

(c) 

(d) 

(e) 

Solution

Equilibrium constants are calculated from . Note that *K* is a function of *T* and thus changes as *T* changes.

(a) , *K* = 41;

(b) , *K* = 0.053;

(c) , *K* = 6.9 × 1013;

(d) , *K* = 1.9;

(e) , *K* = 0.04

43. Calculate the equilibrium constant at the temperature given.

(a) 

(b) 

(c) 

(d) 

(e) 

Solution

In each of the following, the value of Δ*G* is not given at the temperature of the reaction. Therefore, we must calculate Δ*G* from the values Δ*H*° and Δ*S* and then calculate Δ*G* from the relation Δ*G* = Δ*H*° – *T*Δ*S*°.

(a) 

(b) 

(c) (d) ;

(e) 

45. Consider the following reaction at 298 K:



What is the standard free energy change at this temperature? Describe what happens to the initial system, where the reactants and products are in standard states, as it approaches equilibrium.

Solution

The standard free energy change is . When reactants and products are in their standard states (1 bar or 1 atm), *Q* = 1. As the reaction proceeds toward equilibrium, the reaction shifts left (the amount of products drops while the amount of reactants increases): *Q* < 1, and  becomes less positive as it approaches zero. At equilibrium, *Q* = *K*, and Δ*G* = 0.

47. Under what conditions is spontaneous?

Solution

This reaction will become spontaneous when Δ*G* goes from positive to negative, or at the point where Δ*G* = 0. 

Calculate Δ*H*° and Δ*S*°:



Thus this reaction is spontaneous at 298 K because Δ*G* is negative at this temperature, and because *T*Δ*S*° term is negative, Δ*G* will become progressively more negative as the temperature increases above 298 K. Thus the temperature at which Δ*G* first becomes negative must lie at a temperature lower than 298 K. We can find this temperature by substituting into .



The reaction will be spontaneous at temperatures greater than 287 K.

49. Hydrogen sulfide is a pollutant found in natural gas. Following its removal, it is converted to sulfur by the reaction. What is the equilibrium constant for this reaction? Is the reaction endothermic or exothermic?

Solution

Find Δ*G*° for the reaction, and from Δ*G*° find *K*.

The process is exothermic.

51. In the laboratory, hydrogen chloride (HCl(*g*)) and ammonia (NH3(*g*)) often escape from bottles of their solutions and react to form the ammonium chloride (NH4Cl(*s*)), the white glaze often seen on glassware. Assuming that the number of moles of each gas that escapes into the room is the same, what is the maximum partial pressure of HCl and NH3 in the laboratory at room temperature? (Hint: The partial pressures will be equal and are at their maximum value when at equilibrium.)

Solution

The equilibrium may be written as

to help simplify the mathematics. Use the standard free energy change to determine the equilibrium constant for the reaction: , K*P* = 1.1  10–16. At equilibrium, the partial pressures are equal so that . This is the maximum pressure of the gases under the stated conditions.

53. Carbon dioxide decomposes into CO and O2 at elevated temperatures. What is the equilibrium partial pressure of oxygen in a sample at 1000 °C for which the initial pressure of CO2 was 1.15 atm?

Solution

The reaction is .

Δ*H*° = (2 mol)(–110.52 kJ mol–1) + (1 mol)(0) – (2 mol)(–393.51 kJ mol–1) = 565.98 kJ;

Δ*S*° = (2 mol)(197.56 J K–1mol–1) + (1 mol)(205.03 J K–1mol–1) – (2 mol)(–393.51 kJ mol–1) = 172.95 J K–1;

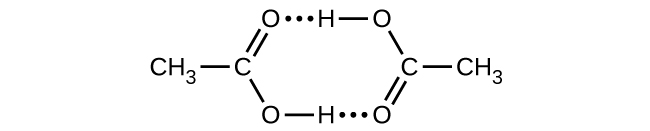
Δ*G*° = (565,980 J) – (1273 K)(172.95 J K–1) = 345,810 J;



55. Acetic acid, CH3CO2H, can form a dimer, (CH3CO2H)2, in the gas phase.



The dimer is held together by two hydrogen bonds with a total strength of 66.5 kJ per mole of dimer.



At 25 °C, the equilibrium constant for the dimerization is 1.3  103 (pressure in atm). What is Δ*S*° for the reaction?

Solution

The equilibrium constant allows the calculation of .The strength of the bond (66.5 kJ) means that it requires 66.5 kJ to pull 1 mol of bonds apart. In other words, . The values of  and  allow us to calculate Δ*S*° by use of the equation



57. Determine Δ*G*° for the following reactions.

(a) Antimony pentachloride decomposes at 448 °C. The reaction is:



An equilibrium mixture in a 5.00 L flask at 448 °C contains 3.85 g of SbCl5, 9.14 g of SbCl3, and 2.84 g of Cl2.

(b) Chlorine molecules dissociate according to this reaction:



1.00% of Cl2 molecules dissociate at 975 K and a pressure of 1.00 atm.

Solution

(a) Find the equilibrium constant by first calculating the number of moles of each component.

molar masses: SbCl5 = 299.11 g mol–1

SbCl3 = 228.11 g mol–1

Cl2 = 70.9054 g mol–1





At 448 °C = 721.15 K,



(b) Determine the value of *K* and then determine the value of Δ*G*° from the value of *K*. Molar concentrations are required to find *K*. The concentration of Cl2 at 1.00 atm and 975 K is determined from the ideal gas law, *PV* = *nRT*



Since the Cl2 gas is 1.00% dissociated, the concentration of Cl2 is 0.9900  0.0125 *M* = 0.0124 *M*. The concentration of Cl2 is 2  0.0100  0.0124 = 0.000250 *M* (we have to use the factor of two since each dissociated Cl2 molecule produces two Cl particles).



Using this result, Δ*G*o = –*RT* ln*K* = –8.314 J/mol K  975 K ln(0.000504) = 61,500 J/mol = 61.5 kJ/mol.

59. Determine the standard free energy change, , for the formation of S2–(*aq*) given that the  for Ag+(*aq*) and Ag2S(*s*) are 77.1 kJ/mole and –39.5 kJ/mole respectively, and the solubility product for Ag2S(*s*) is 8  10–51.

Solution

The reaction of interest is: 







61. The evaporation of one mole of water at 298 K has a standard free energy change of 8.58 kJ.



(a) Is the evaporation of water under standard thermodynamic conditions spontaneous?

(b) Determine the equilibrium constant, *KP*, for this physical process.

(c) By calculating ∆*G*, determine if the evaporation of water at 298 K is spontaneous when the partial pressure of water, , is 0.011 atm.

(d) If the evaporation of water were always nonspontaneous at room temperature, wet laundry would never dry when placed outside. In order for laundry to dry, what must be the value of  in the air?

Solution

(a) Under standard thermodynamic conditions, the temperature is 298 K, and the pressure of water vapor would be 1 atm (or 1 bar). Under these conditions, the evaporation is nonspontaneous as indicated by . (b) , 8.58  103 = –8.314  2981.15 ln *K*, *Kp* = 0.031; (c) , , Δ*G* = 8.58  103 + (8.314  298  ln0.011) = –2.6 kJ, Under these conditions, the evaporation of water is spontaneous; (d)  must always be less than *KP* or less than 0.031 atm. 0.031 atm represents air saturated with water vapor at 25 °C, or 100% humidity.

63. One of the important reactions in the biochemical pathway glycolysis is the reaction of glucose-6-phosphate (G6P) to form fructose-6-phosphate (F6P):



(a) Is the reaction spontaneous or nonspontaneous under standard thermodynamic conditions?

(b) Standard thermodynamic conditions imply the concentrations of G6P and F6P to be 1 *M*, however, in a typical cell, they are not even close to these values. Calculate Δ*G* when the concentrations of G6P and F6P are 120 μ*M* and 28 μ*M* respectively, and discuss the spontaneity of the forward reaction under these conditions. Assume the temperature is 37 °C.

Solution

(a) Nonspontaneous as ; (b) ΔG = ΔG° + RT ln*Q*, . The forward reaction to produce F6P is spontaneous under these conditions.

65. When ammonium chloride is added to water and stirred, it dissolves spontaneously and the resulting solution feels cold. Without doing any calculations, deduce the signs of Δ*G*, Δ*H*, and Δ*S* for this process, and justify your choices.

Solution

Δ*G* is negative as the process is spontaneous. Δ*H* is positive as with the solution becoming cold, the dissolving must be endothermic. Δ*S* must be positive as this drives the process, and it is expected for the dissolution of any soluble ionic compound.

67. What happens to (becomes more negative or more positive) for the following chemical reactions when the partial pressure of oxygen is increased?

(a) 

(b) 

(c) 

Solution

(a) Increasing will shift the equilibrium toward the products, which increases the value of *K*.  therefore becomes more negative.

(b) Increasing will shift the equilibrium toward the products, which increases the value of *K*.  therefore becomes more negative.

(c) Increasing will shift the equilibrium the reactants, which decreases the value of *K*.  therefore becomes more positive.

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