Chapter 18: Thermodynamics

1. Which of these species would you expect to have the lowest standard entropy (S°)?
   A) $CH_4(g)$ B) $HF(g)$ C) $NH_3(g)$ D) $H_2O(g)$

3. Which of these species would you expect to have the lowest standard entropy (S°)?
   A) $Br_2(l)$ B) $Cl_2(g)$ C) $F_2(g)$ D) $H_2(g)$ E) $I_2(s)$

5. Which of these species has the highest entropy (S°) at 25°C?
   A) $CO(g)$ B) $CH_4(g)$ C) $NaCl(s)$ D) $H_2O(l)$ E) $Fe(s)$

7. Arrange the following substances in the order of increasing entropy at 25°C.
   $HF(g)$, $NaF(s)$, $SiF_4(g)$, $SiH_4(g)$, $Al(s)$
   lowest → highest
   A) $SiF_4(g) < SiH_4(g) < NaF(s) < HF(g) < Al(s)$
   B) $HF(g) < Al(s) < NaF(s) < SiF_4(g) < SiH_4(g)$
   C) $Al(s) < NaF(s) < HF(g) < SiH_4(g) < SiF_4(g)$
   D) $Al(s) < HF(g) < NaF(s) < SiF_4(g) < SiH_4(g)$
   E) $NaF(s) < Al(s) < HF(g) < SiF_4(g) < SiH_4(g)$

9. Which one of the following reactions would you expect to have highest $\Delta S°$?
   A) $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$
   B) $C_2H_2(g) + {}^5/_2O_2(g) \rightarrow 2CO_2(g) + H_2O(g)$
   C) $C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(g)$
   D) $C_2H_6(g) + {}^7/_2O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$

11. Which response includes *all* of the following processes that are accompanied by an *increase* in entropy?
    1. $I_2(s) \rightarrow I_2(g)$
    2. $2I(g) \rightarrow I_2(g)$
    3. $2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$
    4. $Mg^{2+}(aq) + 2OH^-(aq) \rightarrow Mg(OH)_2(s)$
    A) 1, 2 B) 1, 3 C) 3, 4 D) 3 E) 2, 4

13. Arrange these reactions according to *increasing* ΔS.
    1. $H_2O(g) \rightarrow H_2O(l)$
    2. $2NO(g) \rightarrow N_2(g) + O_2(g)$
    3. $MgCO_3(s) \rightarrow MgO(s) + CO_2(g)$

    A) 1 < 2 < 3 B) 2 < 3 < 1 C) 3 < 2 < 1 D) 2 < 1 < 3 E) 1 < 3 < 2

15. Sulfur can be separated from lead in the mineral galena, PbS(*s*), by "roasting" the ore in the presence of oxygen as shown in the following reaction:
    $2PbS(s) + 3O_2(g) \rightarrow 2PbO(s) + 2SO_2(g)$
    Calculate ΔS° for this reaction using the thermodynamic data provided below.

	S°(J/K·mol)
PbS(*s*)	91.2
$O_2(g)$	205.0
PbO(*s*)	69.45
$SO_2(g)$	248.5

    A) –410 J/K·mol
    B) –161.5 J/K·mol
    C) –47.7 J/K·mol
    D) 21.8 J/K·mol
    E) 43.5 J/K·mol

17. Calculate ΔS° for the reaction $SO_2(s) + NO_2(g) \rightarrow SO_3(g) + NO(g)$.

	S°(J/K·mol)
$SO_2(g)$	248.5
$SO_3(g)$	256.2
NO(g)	210.6
$NO_2(g)$	240.5

    A) 53.6 J/K·mol
    B) –53.6 J/K·mol
    C) –22.2 J/K·mol
    D) 474.8 J/K·mol
    E) –474.8 J/K·mol

19. HI has a normal boiling point of –35.4°C, and its ΔH_{vap} is 21.16 kJ/mol. Calculate the molar entropy of vaporization (ΔS_{vap}).
    A) 598 J/K·mol
    B) 68.6 J/K·mol
    C) 75.2 J/K·mol
    D) 0.068 J/K·mol
    E) 89.0 J/K·mol

21. A negative sign for ΔG indicates that, at constant T and P,
    A) the reaction is exothermic.
    B) the reaction is endothermic.
    C) the reaction is fast.
    D) the reaction is spontaneous.
    E) ΔS must be > 0.

23. Calculate $\Delta G°$ for the reaction $3NO_2(g) + H_2O(l) \rightarrow 2HNO_3(l) + NO(g)$.

	$\Delta G°_f$ (kJ/mol)
$H_2O(l)$	–237.2
$HNO_3(l)$	–79.9
$NO(g)$	86.7
$NO_2(g)$	51.8

    A) 8.7 kJ/mol
    B) 192 kJ/mol
    C) –414 kJ/mol
    D) –192 kJ/mol
    E) –155 kJ/mol

25. Sodium carbonate can be made by heating sodium bicarbonate:
    $2NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(g)$
    Given that $\Delta H° = 128.9$ kJ/mol and $\Delta G° = 33.1$ kJ/mol at 25°C, above what minimum temperature will the reaction become spontaneous under standard state conditions?
    A) 0.4 K B) 3.9 K C) 321 K D) 401 K E) 525 K

27. For the reaction $H_2(g) + S(s) \rightarrow H_2S(g)$, $\Delta H° = –20.2$ kJ/mol and $\Delta S° = +43.1$ J/K·mol. Which of these statements is *true*?
    A) The reaction is only spontaneous at low temperatures.
    B) The reaction is spontaneous at all temperatures.
    C) $\Delta G°$ becomes less favorable as temperature increases.
    D) The reaction is spontaneous only at high temperatures.
    E) The reaction is at equilibrium at 25°C under standard conditions.

29. Hydrogen peroxide (H_2O_2) decomposes according to the equation
    $H_2O_2(l) \rightarrow H_2O(l) + {}^1/_2O_2(g)$.
    Calculate K_p for this reaction at 25°C. ($\Delta H° = –98.2$ kJ/mol, $\Delta S° = 70.1$ J/K·mol)
    A) 1.3×10^{-21} B) 20.9 C) 3.46×10^{17} D) 7.5×10^{20} E) 8.6×10^4

31. Calculate K_p at 298 K for the reaction $SO_2(g) + NO_2(g) \rightarrow SO_3(g) + NO(g)$.

	$\Delta G°_f$
$SO_2(g)$	–300.4 kJ/mol
$SO_3(g)$	–370.4 kJ/mol
$NO(g)$	86.7 kJ/mol
$NO_2(g)$	51.8 kJ/mol

A) 6.99×10^{-7} B) 5.71×10^{-8} C) 14.2 D) 475 E) 1.42×10^{6}

33. Determine the equilibrium constant K_p at 25°C for the reaction $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$
[$\Delta G°_f$ ($NH_3(g)$) = –16.6 kJ/mol].
A) 1.52×10^{-6} B) 6.60×10^{5} C) 8.28×10^{-2} D) 2.60 E) 13.4

35. Nitrosyl chloride (NOCl) decomposes at elevated temperatures according to the equation $2NOCl(g) \rightarrow 2NO(g) + Cl_2(g)$. Calculate K_p for this reaction at 227°C. ($\Delta H° = 81.2$ kJ/mol, $\Delta S° = 128$ J/K·mol)
A) 1.59×10^{-2} B) 2.10×10^{-7} C) 62.8 D) 4.90×10^{6} E) 3.20×10^{9}

37. For the reaction $2C(\text{graphite}) + H_2(g) \rightarrow C_2H_2(g)$, $\Delta G° = +209.2$ kJ/mol at 25°C. If $P(H_2) = 100.$ atm, and $P(C_2H_2) = 0.10$ atm, calculate ΔG for this reaction.
A) +207.8 kJ/mol
B) +226.3 kJ/mol
C) +192.1 kJ/mol
D) +17.3 kJ/mol
E) –16.9 kJ/mol

39. K_w for the auto-ionization of water, $H_2O(l) \rightarrow H^+(aq) + OH^-(aq)$, is 1.0×10^{-14}. What are the signs (+/–) of $\Delta S°$ and $\Delta H°$ for the reaction at 25°C?
A) $\Delta S°$ = (+) and $\Delta H°$ = (+)
B) $\Delta S°$ = (+) and $\Delta H°$ = (–)
C) $\Delta S°$ = (–) and $\Delta H°$ = (+)
D) $\Delta S°$ = (–) and $\Delta H°$ = (–)

41. The reaction rates of many spontaneous reactions are actually very slow. Which of these statements is the best explanation for this observation?
A) K_p for the reaction is less than one.
B) The activation energy of the reaction is large.
C) $\Delta G°$ for the reaction is positive.
D) Such reactions are endothermic.
E) The entropy change is negative.

43. Calculate $\Delta G°$ for the combustion of ethanol vapor, $C_2H_5OH(g)$, at 750°C in oxygen to form carbon dioxide and water vapor. The following data is valid at 25°C:

	$\Delta H°_f$ (kJ/mol)	$\Delta G°_f$ (kJ/mol)
$C_2H_5OH(g)$	–234.8	–167.9
$O_2(g)$	0	0
$H_2O(g)$	–241.8	–228.6
$CO_2(g)$	–393.5	–394.4

A) –1407 kJ/mol
B) –2151 kJ/mol
C) –1307 kJ/mol
D) –4486 kJ/mol
E) –1377 kJ/mol

45. Predict the normal boiling point of triethylborane ($C_6H_{15}B$) using the following data:

	$\Delta H°_f$ (25°C)	$\Delta G°_f$ (25°C)
$C_6H_{15}B(l)$	–194.6 kJ/mol	9.4 kJ/mol
$C_6H_{15}B(g)$	–157.7 kJ/mol	16.1 kJ/mol

A) 92°C B) –21°C C) 21°C D) 365°C E) 256°C

47. The standard free energy of formation of gaseous hydrogen iodide is 1.30 kJ/mol at 25°C. Find K_p for the reaction $H_2(g) + I_2(s) \rightarrow 2HI(g)$ at this temperature.
A) 7.0 B) 7100 C) 1.0 D) 2.4 E) 2.9

49. Find the temperature at which $K_p = 42.0$ for the reaction $H_2(g) + I_2(g) \rightarrow 2HI(g)$. [Given: at 25°C, for $H_2(g)$, $\Delta H°_f = 0$, $S° = 131.0$ J/mol·K; for $I_2(g)$, $\Delta H°_f = 62.26$ kJ/mol, $S° = 260.6$ J/mol·K; for HI(g), $\Delta H°_f = 25.9$ kJ/mol, $S° = 206.3$ J/mol·K; assume that $\Delta H°$ and $\Delta S°$ are independent of temperature.]
A) 1040 K B) 168 K C) 539 K D) 1400 K E) 34,200 K

51. In the gas phase, formic acid forms a dimmer, $2HCOOH(g) \rightarrow (HCOOH)_2(g)$. For this reaction, $\Delta H° = –60.1$ kJ/mol and $\Delta G° = –13.9$ kJ/mol at 25°C. Find the equilibrium constant (K_p) for this reaction at 75 °C.
A) 8960 B) 273 C) 0.120 D) 8.33 E) 1.12×10^{-4}

53. Which species will have the greatest absolute entropy at 25°C?
A) Ne(g) B) $C_2H_2(g)$ C) $H_2O(l)$ D) $C_2H_5OH(l)$ E) $C_4H_{10}(g)$