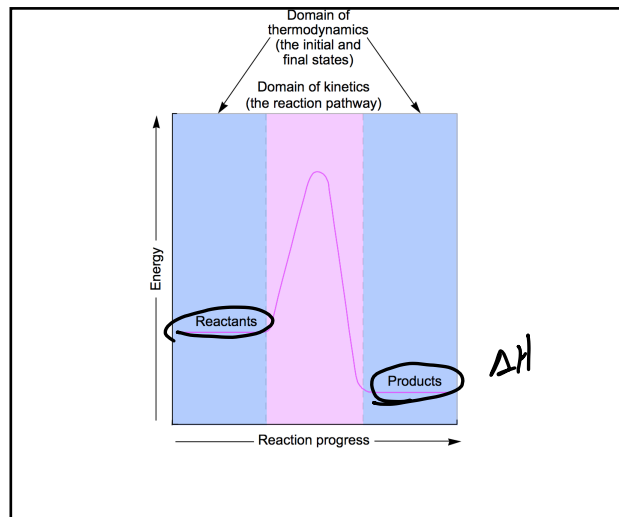# Thermodynamics

First Law of Thermodynamics

You will recall from Chapter 5 that energy cannot be created or destroyed.

Therefore, the total energy of the universe is a constant.

Energy can, however, be converted from one form to another or transferred from a system to the surroundings or vice versa.

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Spontaneous Processes and Entropy

Thermodynamics lets us predict whether a process will occur but gives no information about the amount of time required for the process.

A spontaneous process is one that occurs without outside intervention.

Spontaneous Processes

Spontaneous processes are those that can proceed without any outside intervention.

The gas in vessel B will spontaneously effuse into vessel A, but once the gas is in both vessels, it will *not* spontaneously return to vessel B.

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Spontaneous Processes

Processes that are spontaneous in one direction are nonspontaneous in the reverse direction.
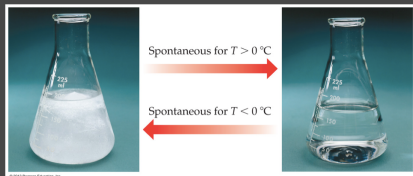
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Spontaneous Processes

Processes that are spontaneous at one temperature may be nonspontaneous at other temperatures.

Above 0 °C, it is spontaneous for ice to melt.

Below 0 °C, the reverse process is spontaneous.

Spontaneous for $T > 0\,°C$

Spontaneous for $T < 0\,°C$

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Reversible v. Irreversible Processes

Reversible: The universe is exactly the same as it was before the cyclic process.

Irreversible: The universe is different after the cyclic process.

All real processes are irreversible -- (some work is changed to heat).

The Second Law of Thermodynamics

. . . in any spontaneous process there is always an increase in the entropy of the universe.

$$\Delta S_{univ} > 0$$

for a spontaneous process.

Second Law of Thermodynamics

In other words:

For reversible processes:

$$\Delta S_{univ} = \Delta S_{system} + \Delta S_{surroundings} = 0$$

For irreversible processes:

$$\Delta S_{univ} = \Delta S_{system} + \Delta S_{surroundings} > 0$$

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Entropy

The driving force for a spontaneous process is an increase in the entropy of the universe.

Entropy, S, can be viewed as a measure of randomness, or disorder.

Entropy

Like total energy, E, and enthalpy, H, entropy is a state function.

Therefore,

$$\Delta S = S_{final} - S_{initial}$$
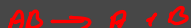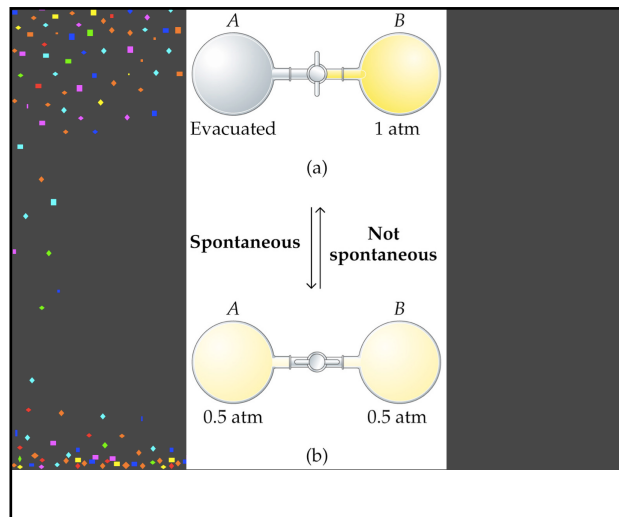
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Entropy on the Molecular Scale

The number of microstates and, therefore, the entropy, tends to increase with increases in
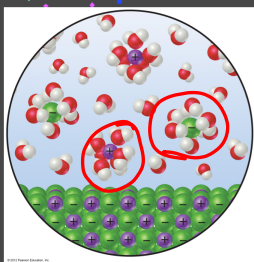
– Temperature

– Volume

$AB \longrightarrow A + B$

– The number of independently moving molecules.

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Evacuated   1 atm

(a)

Spontaneous ⇅ Not spontaneous

0.5 atm   0.5 atm

(b)

Solutions

Generally, when a solid is dissolved in a solvent, entropy increases.

$NaCl_{(s)} \rightarrow Na^+ + Cl^-$
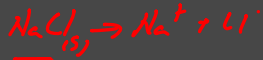
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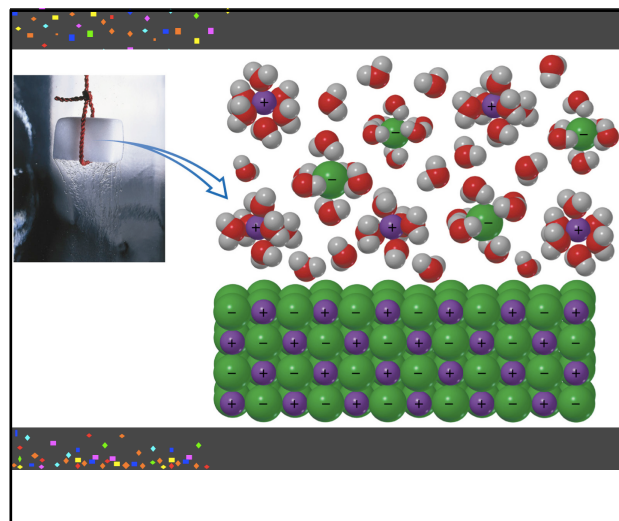
Positional Entropy

A gas expands into a vacuum because the expanded state has the highest positional probability of states available to the system.

Therefore,

(AC)

$$S_{solid} < S_{liquid} << S_{gas}$$

Entropy and Physical States

Entropy increases with the freedom of motion of molecules.

Therefore,

$$S(g) > S(l) > S(s)$$

Increasing entropy

Ice — Liquid water — Water vapor

Rigid, crystalline structure
Motion restricted to **vibration** only
Smallest number of microstates

Increased freedom with respect to **translation**
Free to **vibrate** and **rotate**
Larger number of microstates

Molecules spread out, essentially independent of one another
Complete freedom for **translation**, **vibration**, and **rotation**
Largest number of microstates

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Solid | Liquid | Gas

Absolute entropy, S

← Boiling

← Melting

Temperature (K) ⟶

Third Law of Thermodynamics

The entropy of a pure crystalline substance at absolute zero is 0.

ΔH   ΔG   S

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Standard Entropies

These are molar entropy values of substances in their standard states.

Standard entropies tend to increase with increasing molar mass.

TABLE 19.1 • Standard Molar Entropies of Selected Substances at 298 K

Substance	$S°$ (J/mol·K)
$H_2(g)$	130.6
$N_2(g)$	191.5
$O_2(g)$	205.0
$H_2O(g)$	188.8
$NH_3(g)$	192.5
$CH_3OH(g)$	237.6
$C_6H_6(g)$	269.2
$H_2O(l)$	69.9
$CH_3OH(l)$	126.8
$C_6H_6(l)$	172.8
$Li(s)$	29.1
$Na(s)$	51.4
$K(s)$	64.7
$Fe(s)$	27.23
$FeCl_3(s)$	142.3
$NaCl(s)$	72.3

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Standard Entropies

Larger and more complex molecules have greater entropies.

Methane, CH_4
$S° = 186.3$ J/mol·K

Ethane, C_2H_6
$S° = 229.6$ J/mol·K

Propane, C_3H_8
$S° = 270.3$ J/mol·K

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20.8   Which of these processes are spontaneous? (a) Water evaporates from a puddle. (b) A lion chases an antelope. (c) An isotope undergoes radioactive disintegration. [A]

20.10   Which of these processes are spontaneous? (a) Methane burns in air. (b) A teaspoonful of sugar dissolves in a cup of hot coffee. (c) A soft-boiled egg becomes raw. [A]

20.12   Predict the sign of ΔS_{sys} for each process: (a) A piece of wax melts. (b) Silver chloride precipitates from solution. (c) Dew forms on a lawn in the morning. [A]

20.14   Predict the sign of ΔS_{sys} for each process: (a) Alcohol evaporates. (b) A solid explosive converts to a gas. (c) Perfume vapors diffuse through a room. [A]

20.16   Without using **Appendix B**, predict the sign of $\Delta S°$ for [A]
(a) $2K(s) + F_2(g) \longrightarrow 2KF(s)$ $\Delta S° < 0$
(b) $NH_3(g) + HBr(g) \longrightarrow NH_4Br(s)$
(c) $NaClO_3(s) \longrightarrow Na^+(aq) + ClO_3^-(aq)$

20.20   Predict the sign of ΔS for each process: [A]
(a) $C_2H_5OH(g)$ (350 K and 500 torr) $\longrightarrow C_2H_5OH(g)$ (350 K and 250 torr)
(b) $N_2(g)$ (298 K and 1 atm) $\longrightarrow N_2(aq)$ (298 K and 1 atm)
(c) $O_2(aq)$ (303 K and 1 atm) $\longrightarrow O_2(g)$ (303 K and 1 atm)

20.22   Predict which substance has greater molar entropy. Explain. [A]
(a) Butane $CH_3CH_2CH_2CH_3(g)$ or 2-butene CH_3CH=$CHCH_3(g)$
(b) $Ne(g)$ or $Xe(g)$
(c) $CH_4(g)$ or $CCl_4(l)$

20.28 Without consulting **Appendix B** 🔗, arrange each group in order of *decreasing* standard molar entropy ($S°$). Explain. Ⓐ

(a) $ClO_4^-(aq)$, $ClO_2^-(aq)$, $ClO_3^-(aq)$

(b) $NO_2(g)$, $NO(g)$, $N_2(g)$

(c) $Fe_2O_3(s)$, $Al_2O_3(s)$, $Fe_3O_4(s)$

$Fe_3O_4 \qquad Fe_2O_3 \qquad Al_2O_3$

20.29 Without consulting **Appendix B** 🔗, arrange each group in order of *decreasing* standard molar entropy ($S°$). Explain.

(a) Mg metal, Ca metal, Ba metal

(b) Hexane (C_6H_{14}), benzene (C_6H_6), cyclohexane (C_6H_{12})

(c) $PF_2Cl_3(g)$, $PF_5(g)$, $PF_3(g)$

Entropy Changes

Entropy changes for a reaction can be estimated in a manner analogous to that by which ΔH is estimated:

$$\Delta S° = \Sigma n \Delta S°(\text{products}) - \Sigma m \Delta S°(\text{reactants})$$

where n and m are the coefficients in the balanced chemical equation.

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$$\Delta H_{Rxn} = \Sigma n_p \Delta H_0° - \Sigma n_r \Delta H_i°$$

20.33 For each reaction, predict the sign and find the value of $\Delta S°_{rxn}$: Ⓐ

(a) $3NO(g) \longrightarrow N_2O(g) + NO_2(g)$

(b) $3H_2(g) + Fe_2O_3(s) \longrightarrow 2Fe(s) + 3H_2O(g)$

(c) $P_4(s) + 5O_2(g) \longrightarrow P_4O_{10}(s)$

a.) $\Delta S < 0$

$$\Delta S_{Rxn} = \Sigma n_p S_p° - \Sigma n_r S_r°$$

$$= \left[1 \, mol \, N_2O_{(g)}\left(219.7 \tfrac{J}{mol \cdot k}\right) + 1 \, mol \, NO_{2(g)}\left(239.9\right)\right]$$

$$- \left[3 \, mol \, NO_{(g)}\left(210.65 \tfrac{J}{mol \cdot k}\right)\right] = -172 \tfrac{J}{K}$$

20.35 Find ΔS_{rxn} for the combustion of ethane (C_2H_6) to carbon dioxide and gaseous water. Is the sign of ΔS_{rxn} as expected? Ⓐ

$$2 \, C_2H_{6(g)} + 7 \, O_{2(g)} \longrightarrow 4 \, CO_{2(g)} + 6 \, H_2O_{(g)}$$

$$\Delta S_{Rxn} = \left[4 \, mol \, CO_2\left(188.7 \tfrac{J}{mol \cdot k}\right) + 6 \, mol \, H_2O_{(g)}\left(213.7 \tfrac{J}{k \cdot mol}\right)\right]$$

$$- \left[2 \, mol \, C_2H_6\left(229.5 \tfrac{J}{mol \cdot k}\right) + 7 \, mol \, O_2\left(205.0 \tfrac{J}{mol \cdot k}\right)\right]$$

$$= 93 \tfrac{J}{K}$$

Entropy Changes in Surroundings

Heat that flows into or out of the system changes the entropy of the surroundings.

For an isothermal process:

$$\Delta S_{surr} = \frac{-q_{sys}}{T}$$

- At constant pressure, q_{sys} is simply $\Delta H°$ for the system.

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$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$$

$$(-T) \Delta S_{univ} = \Delta S_{sys}(-T) + \frac{-\Delta H_{sys}}{T}(-T)$$

$$-T \Delta S_{univ} = \Delta H_{sys} - T \Delta S_{sys}$$

Free Energy

$$\Delta G = -T \Delta S$$

$$\Delta S_{univ} = -\frac{\Delta G}{T}$$

$$\boxed{\Delta G = \Delta H - T \Delta S}$$

The Second Law of Thermodynamics

. . . in any spontaneous process there is always an **increase in the entropy of the universe.**

$$\Delta S_{univ} > 0$$

for a spontaneous process.

Entropy Change in the Universe

The universe is composed of the system and the surroundings.

Therefore,

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}$$

For spontaneous processes
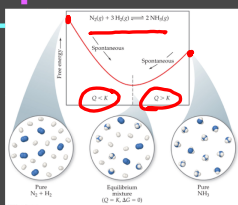
$$\Delta S_{universe} > 0$$

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Free Energy

$\Delta G = \Delta H - T\Delta S$ (from the standpoint of the system)

A process (at constant T, P) is spontaneous in the direction in which free energy decreases:

$$-\Delta G \ means \ +\Delta S_{univ}$$

Gibbs Free Energy

1. If ΔG is negative, the forward reaction is spontaneous.

2. If ΔG is 0, the system is at equilibrium.   Q = K

3. If ΔG is positive, the reaction is spontaneous in the reverse direction.

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Free Energy and Temperature

sys.

There are two parts to the free energy equation:

$\Delta H°$ — the enthalpy term

$- T\Delta S°$ — the entropy term

Exo = Enth +

The temperature dependence of free energy then comes from the entropy term.

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Effect of ΔH and ΔS on Spontaneity

ΔH	ΔS	Result
Exo −	+	spontaneous at all temps
Endo +	+	spontaneous at high temps
Exo −	−	spontaneous at low temps
+	−	not spontaneous at any temp

$$\Delta G = \Delta H - \ominus \Delta S$$
+   (−χ−)   shift left
          +

TABLE 19.4   Effect of Temperature on the Spontaneity of Reactions

ΔH	ΔS	$-T\Delta S$	$\Delta G = \Delta H - T\Delta S$	Reaction Characteristics	Example
−	+	−	Always negative	Spontaneous at all temperatures	$2O_3(g) \longrightarrow 3O_2(g)$
+	−	+	Always positive	Nonspontaneous at all temperatures; reverse reaction always spontaneous	$3O_2(g) \longrightarrow 2O_3(g)$
−	−	+	Negative at low T; positive at high T	Spontaneous at low T; becomes nonspontaneous at high T	$H_2O(l) \longrightarrow H_2O(s)$
+	+	−	Positive at low T; negative at high T	Nonspontaneous at low T; becomes spontaneous at high T	$H_2O(s) \longrightarrow H_2O(l)$

Free Energy Change and Chemical Reactions

ΔG° = standard free energy change that occurs if reactants in their standard state are converted to products in their standard state.

$$\Delta G^\circ = \Sigma n_p \Delta G_f^\circ(\text{products}) - \Sigma n_r \Delta G_f^\circ(\text{reactants})$$

$CH_4(g) + \frac{1}{2} O_2(g) \rightarrow CH_3OH(g)$

Methanol can be made by controlling the oxidation of methane:

1. Calculate ΔH and ΔS for this reaction.
2. How is ΔG for this reaction expected to vary with temp.
3. Calculate ΔG at 298 K and standard conditions. Is the reaction spontaneous at this temperature?
4. Is there a temperature at which the reaction would be at equilibrium under standard conditions and is low enough so that compounds involved are likely to be stable?

	ΔH kJ/mol	ΔG kJ/mol	S J/mol K
$CH_4(g)$	-74.8	-50.8	186.3
$O_2(g)$	0	0	205.0
$CH_3OH(g)$	-201.2	-161.9	237.6

$\Delta H = \Sigma n_p \Delta H_p^\circ - \Sigma n_r \Delta H_r^\circ = -126.4$ kJ exo

$\Delta S_{rxn} = -51.2 \frac{J}{K}$

$\Delta G_{rxn} = \Sigma n_p \Delta G_p^\circ - \Sigma n_r \Delta G_r^\circ = -111.1$ kJ

$\Delta G = \Delta H - T\Delta S = -126.4$ kJ $- (298K)(-51.2 \times 10^{-3}\frac{kJ}{K}) = -111$ kJ

At Equil

$\Delta G = \Delta H - T\Delta S = 0$

$T = \frac{\Delta H}{\Delta S} = \frac{-126.4kJ}{-51.2 \times 10^{-3}\frac{kJ}{K}} = 2469K$

$P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$

std cont.

Use data in Appendix C to calculate ΔH°, ΔS°, and ΔG° at 25°C for each of the following reactions. In each case show that:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

App. C Data	ΔH kJ/mol	ΔG kJ/mol	S J/mol K
$P_4O_{10}(s)$	-2940.1	-2675.2	228.9
$H_2O(l)$	-285.83	-237.13	69.91
$H_3PO_4(aq)$	-1288.3	-1142.6	158.2

20.59 One reaction used to produce small quantities of pure H_2 is
$$CH_3OH(g) \rightleftharpoons CO(g) + 2H_2(g)$$

(a) Determine ΔH° and ΔS° for the reaction at 298 K. (H = 90.7 kJ and S = 221 J/K)

(b) Assuming that these values are relatively independent of temperature, calculate ΔG° at 28°C, 128°C, and 228°C.

(c) What is the significance of the different values of ΔG°?

(d) At what temperature (in K) does the reaction become spontaneous?

b. $\Delta G = \Delta H - T\Delta S$
$= 90.7$ kJ $- (273+28K)(221\times10^{-3}\frac{kJ}{K})$

$\Delta G_{28}^\circ = 24.2$ kJ

$\Delta G_{128}^\circ = 2.1$ kJ

$\Delta G_{228}^\circ = -20$ kJ

d. $\Delta G = \Delta H - T\Delta S = 0$
$T = 410$ K

Free Energy and Equilibrium

Under any conditions, standard or nonstandard, the free energy change can be found this way:
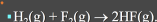
$$\Delta G = \Delta G^\circ + RT \ln Q$$

(Under standard conditions, all concentrations are 1 M, so $Q = 1$ and $\ln Q = 0$; the last term drops out.)

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At $K = Q$
$\Delta G = 0$
$0 = \Delta G^\circ + RT \ln K$
$\Delta G^\circ = -RT \ln K$

Problem

Consider the reaction of
$H_2(g) + F_2(g) \rightarrow 2HF(g)$.

a. Calculate ΔG° at 298K.

b. Calculate ΔG at 298 K if the reaction mixture consists of 8.0 atm H_2, 4.5 atm F_2, and 0.36 atm of HF.

	ΔH kJ/mol	ΔG kJ/mol	S J/mol K
$H_2(g)$		0	
$F_2(g)$		0	
HF(g)		-270.70	

$\Delta G^\circ = \Sigma n_p \Delta G_p^\circ - \Sigma n_r \Delta G_r^\circ$
$\Delta G^\circ = -541.4$ kJ

$Q = \frac{(P_{HF})^2}{(P_{H_2})(P_{F_2})}$

$\Delta G = \Delta G^\circ + RT \ln Q$
$= (-541.4$ kJ$) + (8.314\times10^{-3}\frac{kJ}{K})(298K) \ln \frac{(0.36)^2}{(8.0)(4.5)}$

$\Delta G = -555$ kJ

	H_2	F_2	$= 2HF$
I	8.0	4.5	0.36
C	-x	-x	+2x

Free Energy and Equilibrium

$\Delta G° = -RT \ln(K)$

K = equilibrium constant

This is so because $\Delta G = 0$ and $Q = K$ at equilibrium.

20.79 The equilibrium constant for the reaction

$$2Fe^{3+}(aq) + Hg_2^{2+}(aq) \rightleftharpoons 2Fe^{2+}(aq) + 2Hg^{2+}(aq)$$

is $K_c = 9.1 \times 10^{-6}$ at 298 K.

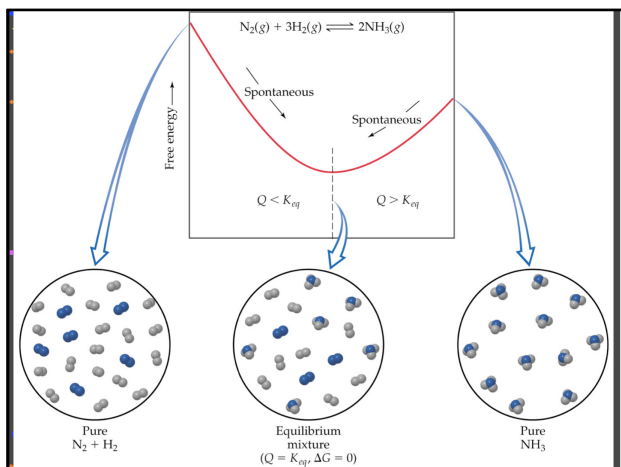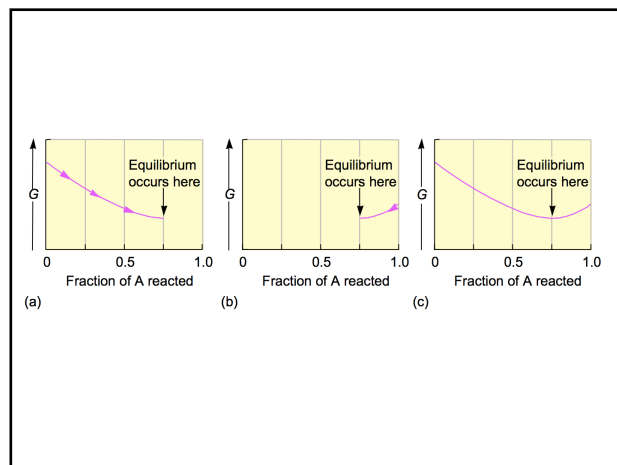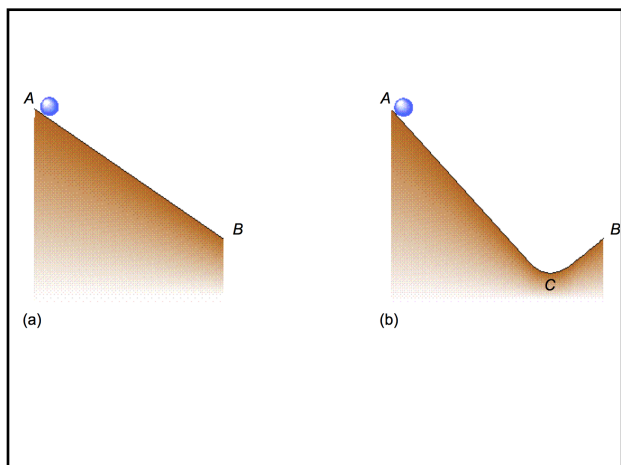(a) What is $\Delta G°$ at this temperature?

(b) If standard-state concentrations of the reactants and products are mixed, in which direction does the reaction proceed?

(c) Calculate ΔG when $[Fe^{3+}] = 0.20\ M$, $[Hg_2^{2+}] = 0.010\ M$, $[Fe^{2+}] = 0.010\ M$, and $[Hg^{2+}] = 0.025\ M$. In which direction will the reaction proceed to achieve equilibrium?

a.) $\Delta G° = -RT \ln K$

$\Delta G° = -\left(\frac{8.314 J}{K \cdot mol}\right)(298k) \ln(9.1 \times 10^{-6})$

$\Delta G° = 2.9 \times 10^4\ J$ ←

c.) $\Delta G = \Delta G° + RT \ln Q$ $\qquad Q = \frac{[Fe^{2+}]^2 [Hg^{2+}]^2}{[Fe^{3+}]^2 [Hg_2^{2+}]}$

$\Delta G = 7.0 \times 10^3\ J$ ←

(a) (b)

(a) (b) (c)

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

Free energy

Spontaneous Spontaneous

$Q < K_{eq}$ $Q > K_{eq}$

Pure $N_2 + H_2$ Equilibrium mixture ($Q = K_{eq}$, $\Delta G = 0$) Pure NH_3

Problem

Write the equilibrium-constant expression and calculate the value of the equilibrium constant for the following reaction at 298 K.

$2HBr(g) + Cl_2(g) \rightarrow 2HCl(g) + Br_2(g)$

$K = \frac{[HCl]^2 [Br_2]}{[HBr]^2 [Cl_2]} = 1.6 \times 10^{14}$

	ΔG kJ/mol
$HBr(g)$	-53.22
$Cl_2(g)$	0
$HCl(g)$	-95.27
$Br_2(g)$	3.14

$\Delta G° = -RT \ln K$

$\Delta G° = -80.96\ kJ$

$\ln K = -\frac{\Delta G°}{RT}$

$K = e^{-\left(\frac{\Delta G°}{RT}\right)} = e^{-\left(\frac{-8.096 \times 10^4 J}{\left(8.314 \frac{J}{K}\right)(298k)}\right)}$

$K = 1.6 \times 10^{14}$

Problem

Consider the reaction of

$BaCO_3(s) \leftrightarrow BaO(s) + CO_2(g)$
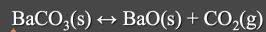
1. Calculate the change in Enthalpy, Entropy, and Free Energy for the reaction.

   a. Is the reaction favored at high or low temperature?

2. Calculate the equilibrium pressure of CO_2 at:

   a. 298 K

   b. 1100 K

	ΔH	S
	kJ/mol	J/mol K
BaCO₃(s)	-1216.3	112.1
CO₂(g)	-393.5	213.6
BaO(s)	-553.5	70.42

END