Spontaneous Processes

Which of the following processes are spontaneous?

(a) Separating a mixture of N_2 and O_2 into two separate samples

Non spontaneous

(b) Alignment of iron filings in a magnetic field

Spontaneous

(c) Dissolution of HCl(g) in water to form HCl(aq)

Spontaneous

(d) Sublimation of CO_2(s) at -100°C, 1 atm (CO_2 sublimation point is -78°C, 1 atm)

$-100°C < -78°C$ nonspontaneous

(e) Reaction of copper with oxygen to form CuO under typical environmental conditions in RI.

Spontaneous

Predicting Entropy Changes

Indicate whether the following produces an increase or decrease in the entropy of the system:

(a) $CO_2(s) \rightarrow CO_2(g)$ increase entropy

(b) $CaO(s) + CO_2(g) \rightarrow CaCO_3(s)$ decreasing entropy

(c) $NH_4Cl(s) \rightarrow HCl(g) + NH_3(g)$ increase entropy

1 molecule/particle

2 molecules/particles

(d) $NaCl(s) \xrightarrow{H_2O} NaCl(aq)$ increase entropy

Calculating Reaction Entropy from Standard Entropies

1. What is the molar change in entropy for water freezing at 25°C? A: -28.9 J/mol K

Process: $H_2O(\ell) \longrightarrow H_2O(s)$ $\quad \Delta S = \Sigma S^\circ_{prod} - \Sigma S^\circ_{react}$

69.9 J/mol K $\quad$ 41 J/mol K $\quad \Delta S = 41\ J/mol\ K - 69.9\ J/mol\ K$

$= -28.9\ J/mol$ = dec entropy (from neg)

2. What is the standard entropy change for the following reaction? A: 178.7 J/mol K

$$Al_2O_3(s) + 3H_2(g) \rightarrow 2\ Al(s) + 3H_2O(g)$$

S° $\quad$ 50.99 J/mol K $\quad$ 131.0 J/mol K $\quad$ 28.3 J/mol K $\quad$ 188.7 J/mol K

$\Delta S = \Sigma S^\circ_{prod} - \Sigma S^\circ_{reac}$

$\Delta S = [2(28.3\ J/mol K) + 3(188.7\ J/mol K)] - [1(50.99\ J/mol K) + 3(131.0\ J/mol K)]$

$= [56.6\ J/mol K + 566.1\ J/mol K] - [50.99\ J/mol K + 393.0\ J/mol K]$

$= 622.7\ J/mol K - 443.99\ J/mol K = 178.71\ J/mol K$

↳ 178.7 J/mol K increase entropy

entropically favored

Calculating Entropy (S) from ΔH

The normal boiling point of ethanol (C_2H_5OH, 46.07g/mol) is 78.3°C and its molar enthalpy of vaporization is 38.56 kJ/mol. What is the change in entropy in the system when 68.3g of gaseous ethanol at 1 atm condenses to liquid at the normal boiling point? A: -163 J/K

$S = \frac{\Delta H}{T}$ $\quad 78.3°C + 273.15 = 351.45K$

↖ opposite process
sign of ΔH changes
$\Delta H_{cond} = -38.56\ kJ/mol$

$$68.3g \left(\frac{1mol}{46.07g}\right) = 1.4825\ mol \left(\frac{-38.56\ kJ}{mol}\right) = -57.166\ kJ = \Delta H$$

$$S = \frac{\Delta H}{T} = \frac{-57.166\ kJ}{351.45K} = -0.163\ kJ/K \times \frac{1000\ J}{kJ}$$

$$= -163\ J/K$$

Gibbs Free Energy & Spontaneity

1. A certain reaction has $\Delta H^\circ = -19.5\text{kJ}$ and $\Delta S^\circ = 42.7\text{J/K}$.

(a) Is the reaction exothermic or endothermic? A: exothermic

$-\Delta H$ = exothermic

(b) Does the reaction lead to an increase or decrease in the randomness or disorder of the system? A: increase

entropy

$+\Delta S$ = increase entropy

(c) Calculate ΔG° at 298K A: -32.2kJ

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

$42.7\text{J/K}\left(\frac{1\text{kJ}}{1000\text{J}}\right) = 0.0427\text{ kJ/K}$

$= -19.5\text{ kJ} - 298\text{K}(0.0427\text{ kJ/K})$

$= -19.5\text{kJ} - 12.746\text{ kJ} = -32.2246\text{ kJ} \rightarrow \boxed{-32.2\text{ kJ}}$

(d) Is the reaction spontaneous at 298K under standard conditions? A: yes

$+\Delta G$ non spontaneous

$-\Delta G$ spontaneous

-32.2 kJ

neg ΔG = is spontaneous

$-\Delta G$

2. Is the following process spontaneous at 25°C? at 75°C?

$$Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$$

A: no

$\Delta H^\circ = -4121\ kJ/mol$ $S^\circ = 236\ J/mol\,K$ $\Delta H^\circ = -542.96\ kJ/mol$ $S^\circ = -55.2\ J/mol\,K$ $\Delta H^\circ = -1277\ kJ/mol$ $S^\circ = -222\ J/mol\,K$

Step 1: Calculate ΔH

$\Delta H_{rxn} = \Sigma \Delta H_{prod} - \Sigma \Delta H_{reac}$

$\Delta H_{rxn} = [3(-542.96\ kJ/mol) + 2(-1277\ kJ/mol)] - [1(-4121\ kJ/mol)]$

$= -1628.88\ kJ/mol + (-2554\ kJ/mol) + (4121\ kJ/mol)$

$= -4182.88\ kJ/mol + 4121\ kJ/mol = -61.88\ kJ/mol$

Step 2: Calculate ΔS

$\Delta S_{rxn} = \Sigma S^\circ_{prod} - \Sigma S^\circ_{reac}$

$\Delta S_{rxn} = [3(-55.2\ J/mol\,K) + 2(-222\ J/mol\,K)] - [1(236\ J/mol\,K)]$

$= -165.6\ J/mol\,K - 444\ J/mol\,K - 236\ J/mol\,K$

$= -845.6\ J/mol\,K \left(\frac{1\ kJ}{1000\ J}\right) = -0.8456\ kJ/mol\,K$

Step 3: Calculate ΔG

$25°C + 273.15 = 298.15K$ $75°C + 273.15 = 348.15\,K$

@25°C $\Delta G = \Delta H - T\Delta S$

$\Delta G = -61.88\ kJ/mol - 298.15K(-0.8456\ kJ/mol\,K)$

$= -61.88\ kJ/mol + 252.16\ kJ/mol$

$= +190.24\ kJ/mol$ not spontaneous

@75°C

$\Delta G = -61.88\ kJ/mol - 348.15K(-0.8456\ kJ/mol\,K$

$= -61.88\ kJ/mol + 294.396\ kJ/mol$

$= +232.52\ kJ/mol$

Even less spontaneous!

3. At what temperature will the following process become spontaneous?

$$Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$$

From previous question!

$\Delta H°_{rxn} = -61.88\ kJ/mol$

$\Delta S°_{rxn} = -0.8456\ kJ/mol\,K$

$+\Delta G$ nonspontaneous

$-\Delta G$ spontaneous

transition $\Delta G = 0$

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

$$0\ kJ/mol = -61.88\ kJ/mol - T(-0.8456\ kJ/mol\,K)$$

$+61.88\ kJ/mol \quad +61.88\ kJ/mol$

$$\frac{61.88\ kJ/mol}{0.8456\ kJ/mol\,K} = \frac{(T)(0.8456\ kJ/mol\,K)}{0.8456\ kJ/mol\,K}$$

$$T = 73.18\ K - 273.15 = -199.97\ °C$$

A: -200°C

Free Energy & Equilibrium

1. Calculate ΔG° for the following reaction at 25°C.

$$Fe(OH)_2(s) \rightleftharpoons Fe^{2+}(aq) + 2OH^-(aq)$$

+ 273.15 = 298.15 K

K_{sp} for $Fe(OH)_2$ is 1.6×10^{-14}

A: 79kJ/mol

$\Delta G^\circ = -RT \ln K$

where $R = 8.314 \times 10^{-3}$ kJ/mol K

T = temp in K

K = equilibrium constant

$\Delta G = -(8.314 \times 10^{-3} \text{ kJ/molK})(298.15\text{K})(\ln 1.6 \times 10^{-14})$

$\Delta G = (2.4788 \text{ kJ/mol})(-31.766)$

$\Delta G = 78.742$ kJ/mol $\rightarrow$ 787 kJ/mol

$\hookrightarrow$ 79. kJ/mol

2. For the following reaction:

A: (a) -5.41 kJ/mol
(b) 0.295 kJ/mol

$$2NO_2(g) \longrightarrow N_2O_4(g)$$

(a) Using data from Appendix 2, calculate ΔG° at 298K
(b) Calculate ΔG at 298K if the partial pressure of NO_2 and N_2O_4 are 0.40atm and 1.60atm, respectively.

(a) $NO_2(g)$ $\Delta H_f^\circ = 33.85\ kJ/mol$ $S^\circ = 240.46\ J/mol\,K$

$N_2O_4(g)$ $\Delta H_f^\circ = 9.66\ kJ/mol$ $S^\circ = 304.3\ J/mol\,K$

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

$\Delta H_{rxn} = 9.66\ kJ/mol - 2(33.85\ kJ/mol)$

$9.66\ kJ/mol - 67.7\ kJ/mol = -58.04\ kJ/mol$

$\Delta S_{rxn} = 304.3\ J/mol\,K - 2(240.46\ J/mol\,K) =$

$304.3\ J/mol\,K - 480.92\ J/mol\,K = -176.62\ J/mol\,K \left(\frac{1kJ}{1000\ J}\right) = -0.17662\ kJ/mol\,K$

$\Delta G^\circ = -58.04\ kJ/mol - 298K(-0.17662\ kJ/mol\,K)$

$-58.04\ kJ/mol + 52.63\ kJ/mol = \boxed{-5.41\ kJ/mol} = \Delta G^\circ$

(b) $\Delta G = \Delta G^\circ + RT\ln Q = -5.41\ kJ/mol + (8.314 \times 10^{-3}\ kJ/mol\,K)(298K)\left(\frac{\ln\left[\frac{1.60}{0.40^2}\right]}{\ln(10)} = 2.3026\right)$

$\Delta G = -5.41\ kJ/mol + 5.705\ kJ/mol$

$= \boxed{0.295\ kJ/mol}$

3. Compare the molar solubility of lead chloride at 25°C and 90°C.

$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$ (X, 2X)

K_{sp} for $PbCl_2$ is 1.6×10^{-5} at 25°C

From Table:

	ΔH°_f (kJ/mol)	S° (J/molK)
$PbCl_2(s)$	-359	136
$Pb^{2+}(aq)$	-1.7	10.5
$Cl^-(aq)$	-167.2	56.5

@ 25°C → regular molar solubility

$K_{sp} = [Pb^{2+}][Cl^-]^2 = [X][2X]^2 = 1.6 \times 10^{-5}$

$4X^3 = 1.6 \times 10^{-5}$ $X^3 = 4.0 \times 10^{-6}$ $X = 1.59 \times 10^{-2}$ M @ 25°C

90 + 273.15 = 363.15K

@ 90°C $\Delta G = -RT \ln K$ $\Delta G = \Delta H - T\Delta S$

$\Delta H = [-1.7 \text{ kJ/mol} + 2(-167.2 \text{ kJ/mol})] - [-359 \text{ kJ/mol}] = 22.9 \text{ kJ/mol}$

$\Delta S = [10.5 \text{ J/molK} + 2(56.5 \text{ J/molK})] - 136 \text{ J/molK} = -12.5 \text{ J/molK} \rightarrow -0.0125 \text{ kJ/molK}$

$\Delta G = 22.9 \text{ kJ/mol} - (363.15\text{K})(-0.0125 \text{ kJ/molK})$

$22.9 \text{ kJ/mol} + 4.54 \text{ kJ/mol} = 27.44 \text{ kJ/mol}$

$\frac{3.05 \times 10^{-2} \text{M}}{1.59 \times 10^{-2} \text{M}} = 1.9$

$\Delta G = -RT \ln K$

$27.44 \text{ kJ/mol} = (-8.314 \times 10^{-3} \text{ kJ/molK})(363.15\text{K})(\ln K)$

$\frac{27.44 \text{ kJ/mol}}{-3.02 \text{ kJ/mol}} = \frac{-3.02 \text{ kJ/mol} \times \ln K}{-3.02 \text{ kJ/mol}}$ $\ln K = -9.086$

$K = e^{-9.086} = 1.13 \times 10^{-4} = K_{sp}$ @ 90°C

$1.13 \times 10^{-4} = 4X^3$

$X^3 = 2.83 \times 10^{-5}$

$X = 3.05 \times 10^{-2}$ M @ 90°C

A: solubility at 90°C about double the solubility at 25°C