

20 • Entropy & Free Energy

STUDY QUESTIONS

- Imagine tossing two coins in the air.
 - Predict the distribution of various combinations of heads and tails.
 - What is the probability of the result being two heads?
 - What is the most probable result?

Now imagine tossing three coins in the air.

- What is the probability of a three heads result?
 - Which system has the highest entropy, the two-coin system or the three-coin system?
- Which one of the following pairs of samples has the higher entropy?
 - $\text{Br}_2(\text{l})$ or $\text{Br}_2(\text{g})$
 - $\text{C}_2\text{H}_6(\text{g})$ or $\text{C}_3\text{H}_8(\text{g})$
 - $\text{MgO}(\text{s})$ or $\text{NaCl}(\text{s})$
 - $\text{KOH}(\text{s})$ or $\text{KOH}(\text{aq})$
 - Predict the entropy change for the following processes:
 - $\text{O}_2(\text{g}) \rightarrow 2\text{O}(\text{g})$
 - $2\text{O}_3(\text{g}) \rightarrow 3\text{O}_2(\text{g})$
 - $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$
 - $\text{NaCl}(\text{s}) \rightarrow \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq})$
 - $\text{C}_2\text{H}_5\text{OH}(\text{l}) \rightarrow \text{C}_2\text{H}_5\text{OH}(\text{g})$
 - $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{AgCl}(\text{s})$
 - Of the following reactions,

which are spontaneous at any temperature,
 which are never spontaneous regardless of the temperature,
 which are spontaneous only at a high temperature,
 and which are spontaneous only at low temperature?

	ΔH	ΔS
a. $\text{C}_8\text{H}_{18}(\text{l}) + \frac{25}{2}\text{O}_2(\text{g}) \rightarrow 8\text{CO}_2(\text{g}) + 9\text{H}_2\text{O}(\text{g})$	-	+
b. $\text{N}_2(\text{g}) + 2\text{F}_2(\text{g}) \rightarrow \text{N}_2\text{F}_4(\text{g})$	-	-
c. $\text{Cl}_2(\text{g}) \rightarrow 2\text{Cl}(\text{g})$	+	+
d. $2\text{O}_3(\text{g}) \rightarrow 3\text{O}_2(\text{g})$	-	+
e. $2\text{C}(\text{s}) + 2\text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_4(\text{g})$	+	-

Name: _____

Period: _____

Seat#: _____

STATION 1: ENTROPY CHANGE

For each of the following examples, decide whether the entropy is increasing or decreasing. Is ΔS + or -?

ΔS is _____ The electrolytic decomposition of water. $2\text{H}_2\text{O}(l) \rightarrow 2\text{H}_2(g) + \text{O}_2(g)$

ΔS is _____ The freezing of water. $\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(s)$

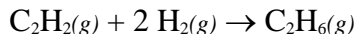
ΔS is _____ The reaction of sodium metal with water. $2\text{Na}(s) + 2\text{H}_2\text{O}(l) \rightarrow \text{H}_2(g) + 2\text{Na}^+(\text{aq}) + 2\text{OH}^-(\text{aq})$

ΔS is _____ The boiling of water. $\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(g)$

ΔS is _____ The reaction of OF_2 and water. $\text{OF}_2(g) + \text{H}_2\text{O}(g) \rightarrow \text{O}_2(g) + 2\text{HF}(g)$

Entropy and Free Energy

STATION 2: ΔH , ΔS , ΔG , GIBB'S FREE ENERGY



Substance	S° (J/mol·K)	ΔH°_f (kJ/mol)
$\text{C}_2\text{H}_2(g)$	200.9	226.7
$\text{H}_2(g)$	130.7	0
$\text{C}_2\text{H}_6(g)$	229.6	-84.7

Calculate ΔS , ΔH , and ΔG for this reaction at 298 K.

Entropy and Free Energy

STATION 3: EQUILIBRIUM

Consider the boiling of liquid bromine: $\text{Br}_2(l) \rightleftharpoons \text{Br}_2(g)$

At 25°C , $\Delta H^\circ = 30.84 \text{ kJ/mol}$ and $\Delta S^\circ = 92.9 \text{ J/mol}\cdot\text{K}$ for this reaction.

Calculate the value of ΔG° .

Assuming that ΔH and ΔS do not change at different temperatures, calculate the normal boiling point of liquid bromine.

Entropy and Free Energy

STATION 4: PREDICTING SPONTANEITY

Consider the reaction: $\text{MgO}(s) + \text{SO}_2(g) \rightarrow \text{MgSO}_3(s)$

What is the sign of ΔH for this reaction? _____ Justify your answer.

What is the sign of ΔS for this reaction? _____ Justify your answer.

This reaction will be:

- a) spontaneous at all temperatures
- b) spontaneous at high temperatures
- c) spontaneous at low temperatures
- d) non-spontaneous at all temperatures

Entropy and Free Energy

STATION 5: K_{eq} & ΔG

Consider the reaction: $C_2H_5Cl(g) + Cl_2(g) \rightarrow C_2H_4Cl_2(g) + HCl(g)$

Standard Free Energies of Formation at 298 K

Substance	ΔG_f° $\text{kJ}\cdot\text{mol}^{-1}$
$C_2H_4Cl_2(g)$	-80.3
$C_2H_5Cl(g)$	-60.5
$HCl(g)$	-95.3
$Cl_2(g)$	0

Calculate the value of ΔG° for this reaction.

Calculate the value of K_{eq} for the reaction at 298 K.

$$[\Delta G^\circ = -RT \ln K; R = 8.31 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}]$$

From the AP Exam:

THERMOCHEMISTRY/KINETICS

$$\Delta S^\circ = \sum S^\circ \text{ products} - \sum S^\circ \text{ reactants}$$

$$\Delta H^\circ = \sum \Delta H_f^\circ \text{ products} - \sum \Delta H_f^\circ \text{ reactants}$$

$$\Delta G^\circ = \sum \Delta G_f^\circ \text{ products} - \sum \Delta G_f^\circ \text{ reactants}$$

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

$$= -RT \ln K = -2.303 RT \log K$$

$$= -n\mathcal{F}E^\circ$$

$$\Delta G = \Delta G^\circ + RT \ln Q = \Delta G^\circ + 2.303 RT \log Q$$

$$q = mc\Delta T$$

$$C_p = \frac{\Delta H}{\Delta T}$$

$$\ln[A]_t - \ln[A]_0 = -kt$$

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$$

$$\ln k = \frac{-E_a}{R} \left(\frac{1}{T} \right) + \ln A$$

$$\text{Gas constant, } R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$= 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}$$

$$= 62.4 \text{ L torr mol}^{-1} \text{ K}^{-1}$$

$$= 8.31 \text{ volt coulomb mol}^{-1} \text{ K}^{-1}$$