

**20 • Entropy and Free Energy****STATION 1: ENTROPY CHANGE**

For each of the following examples, decide whether the entropy is increasing or decreasing. Is  $\Delta S$  + or -?

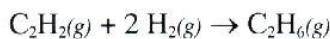
$\Delta S$  is + The electrolytic decomposition of water.  $2\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{H}_2(\text{g}) + \text{O}_2(\text{g})$

$\Delta S$  is - The freezing of water.  $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{s})$

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

$\Delta S$  is + The boiling of water.  $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{g})$

$\Delta S$  is + The reaction of  $\text{OF}_2$  and water.  $\text{OF}_2(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{O}_2(\text{g}) + 2\text{HF}(\text{g})$   
*2 mol gas                      3 mol gas*

**20 • Entropy and Free Energy****STATION 2:  $\Delta H$ ,  $\Delta S$ ,  $\Delta G$ , GIBB'S FREE ENERGY**

Substance	$S^\circ$ (J/mol K)	$\Delta H^\circ_f$ (kJ/mol)
$\text{C}_2\text{H}_2(\text{g})$	200.9	226.7
$\text{H}_2(\text{g})$	130.7	0
$\text{C}_2\text{H}_6(\text{g})$	229.6	-84.7

Calculate  $\Delta S$ ,  $\Delta H$ , and  $\Delta G$  for this reaction at 298 K.

$$\begin{aligned} \Delta S_{\text{rxn}} &= \Delta S(\text{C}_2\text{H}_6) - (\Delta S(\text{C}_2\text{H}_2) + 2\Delta S(\text{H}_2)) \\ &= 229.6 - (200.9 + 2(130.7)) = \boxed{-232.7 \text{ J/mol}\cdot\text{K}} \\ \Delta H_{\text{rxn}} &= \Delta H(\text{C}_2\text{H}_6) - \Delta H(\text{C}_2\text{H}_2) - 2\Delta H(\text{H}_2) = \boxed{-311.4 \text{ kJ/mol}} \\ \Delta G &= \Delta H - T\Delta S = -311.4 \frac{\text{kJ}}{\text{mol}} - (298\text{K})(-232.7 \frac{\text{J}}{\text{mol}\cdot\text{K}}) \left(\frac{1\text{kJ}}{1000\text{J}}\right) \\ &= -311.4 - (-69.3) = \boxed{-242.1 \text{ kJ/mol}} \end{aligned}$$

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### STATION 3: EQUILIBRIUM

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

At <sup>298 K</sup>  $25^\circ\text{C}$ ,  $\Delta H^\circ = 30.84 \text{ kJ/mol}$  and  $\Delta S^\circ = 92.9 \text{ J/mol}\cdot\text{K}$  for this reaction.  
Calculate the value of  $\Delta G^\circ$ .

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ = 30.84 \frac{\text{kJ}}{\text{mol}} - (298\text{K}) \left( \frac{92.9 \text{ J}}{\text{mol}\cdot\text{K}} \right) \left( \frac{1 \text{ kJ}}{1000 \text{ J}} \right) \\ &= 30.84 - 27.68 = \boxed{3.16 \text{ kJ/mol}}\end{aligned}$$

Assuming that  $\Delta H$  and  $\Delta S$  do not change at different temperatures, calculate the normal boiling point of liquid bromine.

Equilibrium;  $\Delta G = 0$

$$\begin{aligned}0 &= \Delta H - T\Delta S \\ \Delta H &= T\Delta S \\ T &= \frac{\Delta H}{\Delta S} = \frac{30.84 \text{ kJ/mol}}{92.9 \text{ J/mol}\cdot\text{K} \times \frac{1 \text{ kJ}}{1000 \text{ J}}} = 331.96986 \\ &= \boxed{332 \text{ K}}\end{aligned}$$

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### STATION 4: PREDICTING SPONTANEITY

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

What is the sign of  $\Delta H$  for this reaction? — Justify your answer.

Heat is needed to decompose  $\text{MgSO}_3(s)$  into  $\text{MgO} + \text{SO}_2(g)$   
 $\therefore$  Heat is released when they combine.

What is the sign of  $\Delta S$  for this reaction? — Justify your answer.

gas  $\rightarrow$  solid less disorder.

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

$\Delta H$   $\Delta S$   
 $\ominus$   $\ominus$  Spontaneous at low Temp

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### STATION 5: $K_{eq}$ & $\Delta G$

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	$\Delta G_f^\circ$ $\text{kJ}\cdot\text{mol}^{-1}$
$C_2H_4Cl_2(g)$	-80.3
$C_2H_5Cl(g)$	-60.5
$HCl(g)$	-95.3
$Cl_2(g)$	0

Calculate the value of  $\Delta G^\circ$  for this reaction.

$$\begin{aligned} \Delta G_{rxn} &= \Delta G(C_2H_4Cl_2) + \Delta G(HCl) - \Delta G(C_2H_5Cl) \\ &= -80.3 \frac{\text{kJ}}{\text{mol}} + (-95.3) - (-60.5) = \boxed{-115.1 \text{ kJ/mol}} \end{aligned}$$

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

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

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

$$\left(\frac{1000 \text{ J}}{1 \text{ kJ}}\right) (-115.1 \frac{\text{kJ}}{\text{mol}}) = - (8.31 \frac{\text{J}}{\text{mol}\cdot\text{K}}) (298 \text{ K}) \ln K$$

$$\ln K = \frac{-115,100}{-2476.38} = 46.479$$

$$\begin{aligned} K &= e^{46.479} \\ &= \boxed{1.53 \times 10^{20}} \end{aligned}$$

From the AP Exam:

#### THERMOCHEMISTRY/KINETICS

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

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

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

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

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

$$= -nFE^\circ$$

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

$$q = mc\Delta T$$

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

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

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

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

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

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

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

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