RAFFLES INSTITUTION
Year 5 H2 CHEMISTRY 2023
Tutorial 5b – Chemical Energetics 2

Suggested Solutions to Tutorial 5b: Chemical Energetics 2

6. **(a)** **Entropy increases.** There are **more ways** for the molecules to **arrange themselves in the larger volume**, resulting in an increase in the disorder and hence entropy of the system.

(b) **Entropy increases.** This is because the **increase in temperature** causes the **broadening of the Maxwell-Boltzmann energy distribution** of the particles. Thus, there are **more possible energy states** in which the molecules can adopt at a high temperature, which increases disorder in the system.

(c) **Entropy decreases.** This is because the reaction results in a **decrease in the number of moles of gaseous particles** (from 1 mole to 0 mole) in the system, causing a decrease in disorder and hence a decrease in entropy.

(d) **Entropy increases.** This is because the reaction results in an **increase in the number of moles of gaseous particles** (from 1 mole to 2 moles). With more particles, there are **more ways to arrange the particles** and more ways to **distribute the energy** in the system, and hence creating greater disorder and higher entropy in the system.

7. **(a)** **(i)** $C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g)$

$\Delta G_f^\ominus = \Delta H_f^\ominus - T\Delta S_f^\ominus$

$-137.2 = -110.5 - (298)\ \Delta S_f^\ominus$

Hence, $\Delta S_f^\ominus[CO(g)] = [(137.2 - 110.5) \times 1000]/298 =$ **+89.6 J mol^{-1} K^{-1}**

$C(s) + O_2(g) \longrightarrow CO_2(g)$

$\Delta G_f^\ominus = \Delta H_f^\ominus - T\Delta S_f^\ominus$

$-394.4 = -393.5 - (298)\ \Delta S_f^\ominus$

Hence, $\Delta S_f^\ominus[CO_2(g)] = [(394.4 - 393.5) \times 1000]/298 =$ **+3.0 J mol^{-1} K^{-1}**

(ii) $C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g)$

The reaction results in an **increase in the number of moles of gaseous molecules**, causing an increase in entropy. Hence the $\Delta S_f^\ominus$ value should be **large and positive**.

$C(s) + O_2(g) \longrightarrow CO_2(g)$

The reaction does not result in any **change in the number of moles of gaseous molecules** in the system. Hence the $\Delta S_f^\ominus$ value is small and **near to zero**.

(b) $C(s) + CO_2(g) \longrightarrow 2CO(g)$

$\Delta G^\ominus_{(298K)} = 2\Delta G_f^\ominus(CO) - \Delta G_f^\ominus(CO_2) = 2(-137.2) - (-394.4) =$ **+120 kJ mol^{-1}**

Since $\Delta G^\ominus_{(298K)} > 0$, the above reaction is **not** feasible at 298 K.

Since $\Delta H_r^\theta = \sum m\Delta H_f^\theta(\text{products}) - \sum n\Delta H_f^\theta(\text{reactants})$

$\Delta H_r^\ominus = 2(-110.5) - (-393.5) = +172.5$ kJ mol^{-1}

Convert from kJ to J

Now $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$

So $\Delta S^\ominus_{(298K)} = (\Delta H^\ominus_{(298K)} - \Delta G^\ominus_{(298K)}) / 298 = (172.5 - 120)(10^3) / 298$

$= +176.2$ J mol^{-1} K^{-1}

At **1000 K**,

Using $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$

$\Delta G^{\ominus}_{(1000K)} = (172.5 \times 10^3) - (1000)(176.2) =$ **-3.7 kJ mol^{-1}**

Since now $\Delta G^{\ominus}_{(1000K)} < 0$, the reaction has now become **feasible**.

[Assumption: $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ remain constant over the temperature range from 298 K to 1000 K.]

8. **(a)** $\Delta H^{\theta} = (-8.37) - (62.43) = -70.8 \text{ kJ mol}^{-1}$

$$\Delta G^{\theta} = \Delta H^{\theta} - T\Delta S^{\theta} = (-70.8) - (273+350)\left(-\frac{43.1}{1000}\right) = \mathbf{-43.9\ kJ\ mol^{-1}}$$

(b) Consider the decomposition reaction.

$$\mathbf{WI_2(g) \longrightarrow W(s) + I_2(g)}$$

For the above decomposition reaction, $\Delta H^{\ominus}$ = +70.8 kJ mol^{-1}

$\Delta S^{\ominus}$ = +0.0431 kJ mol^{-1} K^{-1}

$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$

For the reaction to be spontaneous, **$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus} < 0$**

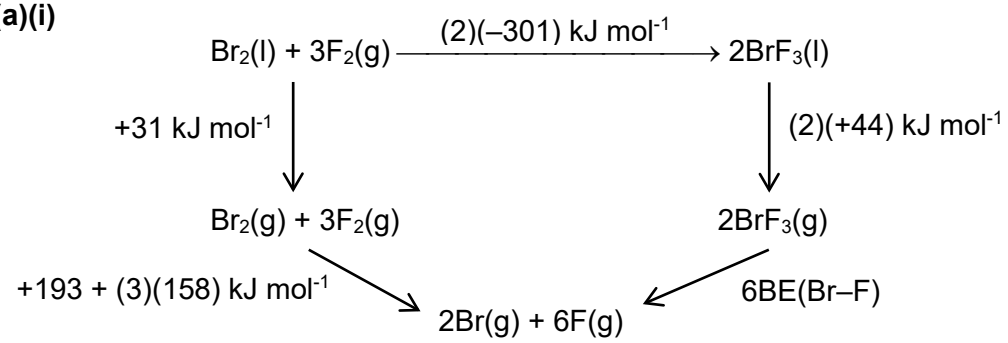
$70.8 - (T)(0.0431) < 0$

$T > 70.8/0.0431$

$T > 1643$ K

Hence the temperature of the filament above which WI_2 will decompose is **1643 K** (4 sig. fig.) (NOT 1640K)

9. **(a)(i)**



By Hess' law, 6BE(Br–F) = – (2)(+44) – (2)(–301) + 31 + 193 + (3)(158)

BE(Br–F) = +1212/6 = +202 kJ mol^{-1}

Average bond energy of the Br–F bond in BF_3 = **+202 kJ mol^{-1}**

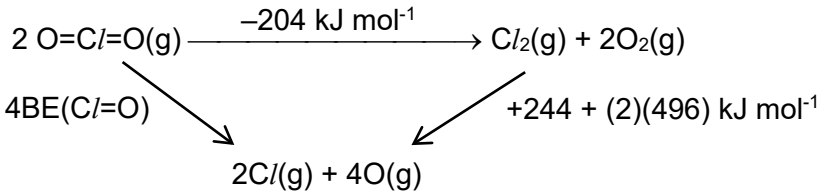
(a)(ii) $\Delta G^{\ominus}_f = \Delta H^{\ominus}_f - T\Delta S^{\ominus}_f$

$-241 = -301 - 298(\Delta S^{\ominus}_f)$

$\Delta S^{\ominus}_f = \frac{-301+241}{298}$ = **-0.201 kJ mol^{-1} K^{-1}**

$\Delta S^{\ominus}_f$ is negative which is expected as the reaction results in a decrease in the number of moles of gas particles, which reduces entropy.

(b)(i)



By Hess' law, 4BE(C*l*=O) = –204 + 244 + (2)(496)
BE(C*l*=O) = +1032/4 = +258 kJ mol^{-1}

Hence C*l*=O bond energy in C*l*O$_2$ = **+258 kJ mol^{-1}**

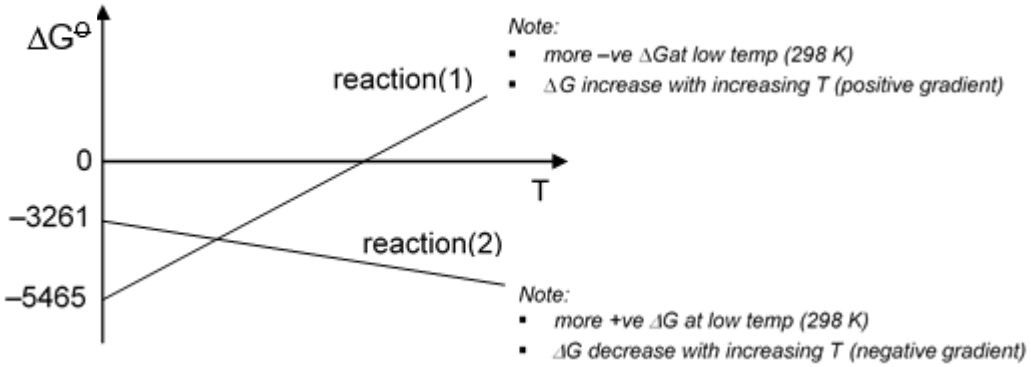
(b)(ii) $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$
$\Delta H^\ominus < 0$
$\Delta S^\ominus > 0 \Rightarrow -T\Delta S^\ominus < 0$

Since both $\Delta H^\ominus$ and $-T\Delta S^\ominus$ are negative, the sign of $\Delta G^\ominus$ is negative.
Since both $\Delta H^\ominus$ and $-T\Delta S^\ominus$ are negative, the value of $\Delta G^\ominus$ is more negative than $\Delta H^\ominus$.

10 **(a)** $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$
At 298 K,
Reaction (1): $\Delta G^\ominus$ = – 5465 – (298)(–553/1000) = **–5300 kJ mol^{-1}**
Reaction (2): $\Delta G^\ominus$ = – 3261 – (298)(138/1000) = **–3300 kJ mol^{-1}**

(b) Since **$\Delta G^\ominus$ (1) is more negative**, **reaction (1)** takes places predominantly.

(c)



(d) At high temperatures, **$\Delta G^\ominus$ (2) will be more negative than $\Delta G^\ominus$ (1)** or **reaction (2) is more exergonic than reaction (1)** and **CO** will be produced in greater proportion.

11. **(a)** The magnitude of hydration energy is dependent on the charge density of the cation. Mg^{2+} has a **higher charge** and **smaller ionic size** than Na^{+} and hence has a higher charge density.

(b) $\Delta H_{soln} = -L.E. + \Sigma\Delta H_{hyd}$

For NaOH: $-44 = 896 + (-390) + \Delta H_{hyd}\ (OH^{-})$

$\Delta H_{hyd}(OH^{-}) = -550\ kJ\ mol^{-1}$

For $Mg(OH)_2$: $x = 2995 - 1890 + \mathbf{2}(-550) = \mathbf{+5\ kJ\ mol^{-1}}$

(c) Although the disruption of crystal lattice during dissolution in both cases increases disorder, the hydration process **decreases disorder** about the Na^{+} and Mg^{2+} ions because it puts the hydrating water molecules into an orderly arrangement about the ions. So, there is a decrease in entropy in the hydration process.

Due to the higher charge and smaller size of Mg^{2+} ion, more water molecules are attached to (or ordered around) the Mg^{2+} ion. Hence, on the average, the entropy change in the hydration process decreases more than that of Na^{+}.

Hence the net entropy changes of solution of $Mg(OH)_2$ is likely to be more negative (or less positive) than that of NaOH.

(d) $Mg(OH)_2$ dissolves with the **formation of more mobile aqueous ions**; so the entropy (of the system) increases (or ΔS is positive).