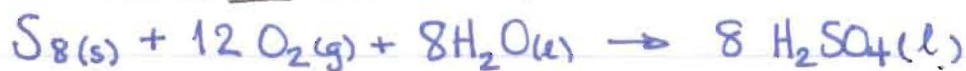


## CHEM - Thermodynamics (std state) Practice

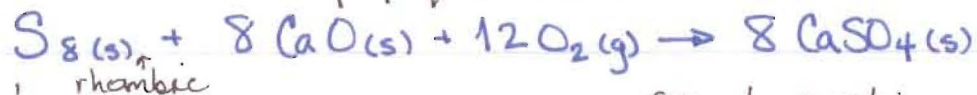
1. A major contributor to acid precipitation is solid sulfur (carried up as ash) when coal is burned; in air this reacts as:



Use the standard thermodynamic tables (A6 in our text - found in any first year text) to determine:

- $\Delta H^\circ_{rxn}$ : Is it exo or endothermic? Does this favour spontaneity?
- $\Delta S^\circ_{rxn}$ : Is entropy increasing or decreasing? " " " " ?
- Calculate  $\Delta G^\circ_{rxn}$  at 25°C. Is the process spontaneous at 25°C?
- A more realistic temperature in the atmosphere is -30°C. Calculate  $\Delta G^\circ(-30^\circ C)$ .  
Is the process spontaneous at -30°C.
- Determine the temperature range over which the process is spontaneous.

2. Sulfur can be removed from the output of coal burning by passing the effluent gas and ash through calcium oxide (in the presence of oxygen gas). The calcium sulfate that forms is called "gypsum" and can be sold to construction companies to make wall-board ("drywall"), so the process of cleaning up the sulfur can actually pay for itself! The reaction is:



- repeat questions a) to e) from Q1 for this reaction.

## CHEM - Thermodynamics (std. state) Practice

Q2  
cont'd.

	$\Delta H^\circ$ (kJ)	$\Delta S^\circ$ (J/K)
1. $S_8(s) + 8 O_2(g) \rightarrow 8 SO_2(g)$	-2374.4	-87
2. $CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(s)$	-64.5	-27
3. $CaSO_4(s) + 2 H_2O(l) \rightarrow H_2SO_4(aq) + Ca(OH)_2(s)$	110.1	-143
4. $2 SO_2(g) + 2 H_2O(l) + O_2(g) \rightarrow 2 H_2SO_4(l)$	-658.8	-607

SOLUTIONS

Q1.

$$\begin{aligned}
 a) \Delta H_{rxn}^\circ &= \sum \Delta H_f^\circ (\text{all products}) - \sum \Delta H_f^\circ (\text{all reagents}) \\
 &= [8 \text{ mol } (\Delta H_f^\circ (H_2SO_4(l)))] - [1 \text{ mol } (\Delta H_f^\circ (S_8(s))) + 12 \text{ mol } (\Delta H_f^\circ (O_2(g))) + 8 \text{ mol } (\Delta H_f^\circ (H_2O(l)))] \\
 &= [8 \text{ mol } (-814 \text{ kJ/mol})] - [8 \text{ mol } (-187.8 \text{ kJ/mol})] \\
 &= [-6512 \text{ kJ}] - [-1502.4 \text{ kJ}] = -5009.6 \text{ kJ} = \underline{\underline{-5010. \text{ kJ}}}
 \end{aligned}$$

\* Exothermic; favours spontaneity.

$$\begin{aligned}
 b) \Delta S_{rxn}^\circ &= [8 \text{ mol } (S^\circ (H_2SO_4(l)))] - [1 \text{ mol } (S^\circ (S_8(s))) + 12 \text{ mol } (S^\circ (O_2(g))) + 8 \text{ mol } (S^\circ (H_2O(l)))] \\
 &= [8 \text{ mol } (156.9 \text{ J/K.mol})] - [1 \text{ mol } (31.80 \text{ J/K.mol}) + 12 \text{ mol } (205.152 \text{ J/K.mol}) + 8 \text{ mol } (109.6 \text{ J/K.mol})] \\
 &= [1255.2 \text{ J/K}] - [3370.424 \text{ J/K}] = -2115.224 \text{ J/K} = \underline{\underline{-2115.2 \text{ J/K}}}
 \end{aligned}$$

Entropy is decreasing; favours non-spontaneity.



Chem Thermodynamics (std state)

$$Q2 a) \Delta H_{rxn}^{\circ} = [8 \text{ mol } (\Delta H_f^{\circ}(\text{CaSO}_4(s)))] - [1 \text{ mol } (\Delta H_f^{\circ}(\text{S}_8(s)) + 8 \text{ mol } (\Delta H_f^{\circ}(\text{CaO}(s)) + 12 \text{ mol } (\Delta H_f^{\circ}(\text{O}_2(g))))]$$

\* elements at  
std. state have  
 $\Delta H_f^{\circ} = \phi$

$$= [8 \text{ mol } (-1432.69 \text{ kJ/mol})] - [1 \text{ mol } (\phi)^* + 8 \text{ mol } (-635.6 \text{ kJ/mol}) + 12 \text{ mol } (\phi)^*]$$

$$= [-11461.52 \text{ kJ}] - [-5084.8 \text{ kJ}]$$

$$= -6376.72 \text{ kJ} \quad \text{Exothermic (ex!)}$$

$$= -6376.7 \text{ kJ} \quad \therefore \text{favour spontaneity.}$$

$$b) \Delta S_{rxn}^{\circ} = [8 \text{ mol } (S_{\text{CaSO}_4(s)})] - [1 \text{ mol } (S_{\text{S}_8(s)}) + 8 \text{ mol } (S_{\text{CaO}(s)}) + 12 \text{ mol } (S_{\text{O}_2(g)})]$$

$$= [8 \text{ mol } (106.69 \text{ J/K}\cdot\text{mol})] - [1 \text{ mol } (31.88 \text{ J/K}) + 8 \text{ mol } (39.8 \text{ J/K}\cdot\text{mol}) + 12 \text{ mol } (205.0 \text{ J/K}\cdot\text{mol})]$$

$$= [853.52 \text{ J/K}] - [2810.28 \text{ J/K}]$$

$$= -1956.76 \text{ J/K} = -1956.8 \text{ J/K}$$

Entropy is decreasing  $\Rightarrow$  Does NOT favour spontaneity

$\therefore \Delta H_{rxn}^{\circ} \& \Delta S_{rxn}^{\circ}$  are "pushing the rxn in opposite directions"

## Chem Thermodynamics (std. state)

$$\begin{aligned}
 2c) \quad \Delta G^\circ_{(25^\circ\text{C})} &= \Delta H^\circ - T \Delta S^\circ && \text{watch the units!} \\
 &= -6376.72 \text{ kJ} - (298 \text{ K})(-1.95676 \text{ kJ/K}) \\
 &= -6376.72 \text{ kJ} - (-583.1148 \text{ kJ}) = -5793.6 \text{ kJ}
 \end{aligned}$$

Over  $\Delta G^\circ$  at  $25^\circ\text{C} \Rightarrow$  Spontaneous at  $25^\circ\text{C} = -5794 \text{ kJ}$

$$d) -30^\circ\text{C} = 243 \text{ K}$$

$$\begin{aligned}
 \Delta G^\circ_{(-30^\circ\text{C})} &= \Delta H^\circ - T \Delta S^\circ \\
 &= -6376.72 \text{ kJ} - (243 \text{ K})(-1.95676 \text{ kJ/K}) \\
 &= -5901 \text{ kJ} \quad \text{more over} \Rightarrow \text{Even more spontaneous}
 \end{aligned}$$

$$e) \quad \Delta G^\circ \rightarrow \phi = \Delta H^\circ - T \Delta S^\circ$$

$$\phi = -6376.72 \text{ kJ} - T \Delta S^\circ (-1.95676 \text{ kJ/K})$$

$$T_{\neq} = 3258.81 \text{ K} = 3259 \text{ K} \quad (\text{or } 2986^\circ\text{C})$$

The reaction is spontaneous upto  $3259 \text{ K}$  ( $2986^\circ\text{C}$ )

It is non-spontaneous ABOVE this