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:

$$S_{8(s)} + 12\,O_{2(g)} + 8H_2O_{(l)} \rightarrow 8\,H_2SO_{4(l)}$$

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

a) ΔH°_{rxn} : Is it exo or endothermic? Does this favour spontaneity?

b) ΔS°_{rxn} : is entropy increasing or decreasing? " " " ?

c) Calculate ΔG°_{rxn} at 25°C. Is the process spontaneous at 25°C?

d) A more realistic temperature in the atmosphere is −30°C. Calculate ΔG°(−30°C) Is the process spontaneous at −30°C.

e) 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:

$$\underset{\text{rhombic}}{S_{8(s)}} + 8\,CaO_{(s)} + 12\,O_{2(g)} \rightarrow 8\,CaSO_{4(s)}$$

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

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Q2 cont'd.

		$\Delta H°$ (kJ)	$\Delta S°$ (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. a) $\Delta H°_{rxn} = \sum \Delta H°_f(\text{all products}) - \sum \Delta H°_f(\text{all reagents})$

$$= \left[8\text{mol}\left(\Delta H°_f(H_2SO_{4}(l))\right)\right] - \left[1\text{mol}\left(\cancelto{\emptyset}{\Delta H°_f(S_{8(s)})}\right) + 12\text{mol}\left(\cancelto{\emptyset}{\Delta H°_f(O_{2(g)})}\right) + 8\text{mol}\left(\Delta H°_f(H_2O_{(l)})\right)\right]$$

$$= \left[8\cancel{\text{mol}}\left(-814\,\text{kJ}/\cancel{\text{mol}}\right)\right] - \left[8\cancel{\text{mol}}\left(-187.8\,\text{kJ}/\cancel{\text{mol}}\right)\right]$$

$$= \left[-6\,512\text{ kJ}\right] - \left[-1\,502.4\text{ kJ}\right] = -5009.6\text{kJ} = \underline{-5010.\text{ kJ}}$$

* Exothermic; favours spontenaety.

b) $\Delta S°_{rxn} = \left[8\text{mol}\left(S°(H_2SO_{4(l)})\right)\right] - \left[1\text{mol}\left(S°(S_{8(s)})\right) + 12\text{mol}\left(S°(O_{2(g)})\right) + 8\text{mol}\left(S°(H_2O_{(l)})\right)\right]$

$$= \left[8\cancel{\text{mol}}\left(156.9\,\text{J}/\text{K}\cdot\cancel{\text{mol}}\right)\right] - \left[1\cancel{\text{mol}}\left(31.80\,\text{J}/\text{K}\cdot\cancel{\text{mol}}\right) + 12\cancel{\text{mol}}\left(205.152\,\text{J}/\text{K}\cdot\cancel{\text{mol}}\right) + 8\cancel{\text{mol}}\left(109.6\,\text{J}|\text{K}\cdot\cancel{\text{mol}}\right)\right]$$

$$= \left[1\,255.2\text{ J}/\text{K}\right] - \left[3\,370.424\text{ J}|\text{K}\right] = -2115.224\text{J}|\text{K} = \underline{-2115.2\text{J}/\text{K}}$$

Entropy is decreasing; favours non-spontenaety.

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1c) 25°C + 273 = 298K $\quad \Delta G° = \Delta H° - T\Delta S°$

$$= (-5009.6\,kJ) - (298\cancel{K})(-2115.224\,J/\cancel{K})$$

$$= -5009.6\,\underline{\underline{kJ}} - (-630336.75\,\underline{\underline{J}})\ !$$

$\} \div 1000$

$$= -5009.\underset{x}{6}\,kJ - (-630.\underset{x}{3}3675\,\underline{kJ})$$

$$\Delta G° = -4379\,kJ \quad (\text{at } 25°C)$$

$\Delta G°$ is negative, so the rxn is spontaneous at 25°C

1d) −30°C + 273 = 243K ; $\Delta G° = \Delta H° - T\Delta S°$

already converted!

$$= (-5009.6\,kJ) - (243\cancel{K})(-2.115224\,kJ/\cancel{K})$$

$$= -5009.\underset{x}{6}\,kJ - (-513.\underset{x}{9}99\,kJ)$$

$$= -4496\,kJ$$

$\Delta G°$ is (even more) ⊖ve, so the rxn is (even more) spontaneous at −30°C

1e) Entropy ($\Delta S°_{rxn}$) favours NON-spontaneous ⇒ Spontaneous at the LOWER temperatures.

$$T_{\neq}\ (\text{where } \Delta G° = 0):\ \frac{\Delta H°}{\Delta S°} = \frac{-5009.\underset{x}{6}\,kJ}{-2.115\underset{x}{2}24\,kJ/K} = 2368\,K$$

$$= 2095°C$$

Spontaneous at any temp BELOW 2368 K (or BELOW 2095°C)

Thd SS 4.
2014

Chem Thermodynamics (std state)

Q2 a) $\Delta H^\circ_{rxn} = [(8\text{ mol})(\Delta H^\circ_f(CaSO_{4(s)}))] - [1\text{ mol}(\Delta H^\circ_f(S_{8(s)}) +$

$8\text{ mol}(\Delta H^\circ_f(CaO_{(s)})) + 12\text{mol}(\Delta H^\circ_f(O_{2(g)}))]$

* elements at std. state have $\Delta H^\circ_f = \emptyset$

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

$+ 12\text{mol}(\emptyset)^{*}]$

$= [-11\,461.52\text{ kJ}] - [-5\,084.8\text{ kJ}]$

$= -6\,376.72\text{ kJ}$ Exothermic ($\ominus$ve!)

$= -6\,376.7\text{ kJ}$ ∴ favours spontenaety.

b) $\Delta S^\circ_{rxn} = [8\text{mol}(S_{CaSO_{4(s)}})] - [1\text{mol}(S_{S_{8(s)}}) + 8\text{mol}(S_{CaO_{(s)}}) + 12\text{ mol}(S_{O_{2(g)}})]$

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

$= [853.52\text{ J/K}] - [2\,810.28\text{ J/K}]$

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

Entropy is decreasing → Does NOT favour spontenaety

∴ ΔH°_{rxn} & ΔS°_{rxn} are "pushing the rxn in opposite directions"

Thd SS 5.

Chem Thermodynamics (std. state)

2 c) $\Delta G^\circ_{(25^\circ C)} = \Delta H^\circ - T\Delta S^\circ$ <u>watch</u> the units!

$\Delta S^\circ = -1956.\underset{-}{7}\underset{x}{6}\,J/K = -1.95676\,\frac{kJ}{K}$

$= -6376.\underset{-}{7}\underset{x}{2}\,kJ - (298\,\cancel{K})(-1.956\underset{-}{7}\underset{x}{6}\,kJ/\cancel{K})$

$= -6376.\underset{-}{7}\underset{x}{2}\,kJ - (-\underset{-}{5}\underset{-}{8}\underset{-}{3}.1448\,kJ) = -5793.6\,kJ$

−ve ΔG° at 25°C ⇒ <u>Spontaneous</u> at 25°C $= -5794\,kJ$

d) −30°C = 243 K

$\Delta G^\circ_{(-30^\circ C)} = \Delta H^\circ - T\Delta S^\circ$

$= -6376.\underset{-}{7}\underset{x}{2}\,kJ - (243\,\cancel{K})(-1.95676\,kJ/\cancel{K})$

$= -5901\,kJ$ <u>more</u> −ve ⇒ Even more spontaneous

e) $\Delta G^\circ_{rxn} \rightarrow 0 = \Delta H^\circ - T\Delta S^\circ$

$0 = -6376.72\,kJ - T_{\ddagger}(-1.\underset{.}{9}\underset{-}{5}\underset{-}{6}76\,kJ/\cancel{K})$

$T_{\ddagger} = \underset{-}{3}\underset{-}{2}\underset{-}{5}\underset{-}{8}.\underset{x}{8}1\,K = 3259\,K$ (or 2986°C)

The reaction is spontaneous <u>up to</u> 3259 K (2986°C)

<u>It</u> is <u>non-spontaneous</u> ABOVE this