

15.2 Entropy & Spontaneity

- energy & matter tend to disperse & the universe becomes more disordered

Spontaneous change: occur naturally w/o need of work (reverse = work input)

Entropy (S): degree of disorder of a system (quant.)
(distribution of available energy among particles)

low S (entropy) $\xrightarrow{\text{time}}$ high S (entropy)
ordered disordered
widest energy distribution

an \uparrow in entropy (disorder) is favored

2nd law of thermodynamics: entropy of an isolated system never \downarrow , because isolated systems evolve towards thermodynamic equilibrium (a state of max entropy)

System changes:

S \rightarrow L ($\uparrow \Delta S$)

L \rightarrow G ($\uparrow \Delta S$)

S \rightarrow G ($\uparrow \Delta S$)

Solid dissolved in H₂O ($\uparrow \Delta S$)

Temp \downarrow ($\downarrow \Delta S$)

\downarrow # moles of gas ($\downarrow \Delta S$)

\uparrow # particles ($\uparrow \Delta S$)

pressure on gas \uparrow ($\downarrow \Delta S$)

Simple molecules ($\uparrow \Delta S$)

Complex molecules ($\downarrow \Delta S$)

Absolute entropy (S^\ominus)

measured off of a perfectly ordered crystal at 0 K

\therefore #'s always (+) b/c real substances are not perfect crystals

unit: $\frac{\text{J}}{\text{K mol}}$
(not kJ std)

S^\ominus is temp + pressure dependent (why?)

Calculating entropy changes (ΔS^\ominus)

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

example: $\text{C}_2\text{H}_4(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g})$
 $2 \text{ mol (g)} \rightarrow 1 \text{ mol (g)}$
more entropy \rightarrow less entropy = work

(Table 12) $(220) + (131) \rightarrow (230)$ $\downarrow \Delta S$

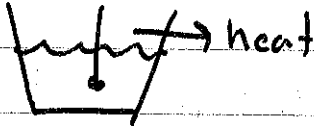
$$\Delta S^\ominus_{\text{rxn}} = 230 - (220 + 131)$$
$$= -121 \text{ J K}^{-1} \text{ mol}^{-1}$$

\downarrow

$$-0.121 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

Spontaneity: looking at total entropy (not just system)

total entropy change: look at change of substances in rxn + surroundings

example:  $S(\text{surr}) \uparrow$ as heat given out by rxn, \uparrow disorder of surroundings

$$\therefore \Delta S(\text{total}) = \Delta S(\text{surr}) + \Delta S(\text{sys})$$



$\Delta S(\text{surr})$ affected by ΔH_{sys} & $\text{Temp}(\text{surr})$
(exo/endo) (absolute (K))

$\Delta S(\text{surr}) \propto -\Delta H_{\text{sys}}$ (think $\Delta H_{\text{rxn}} = -\Delta H_{\text{sys}}$)
proportional

$\Delta S(\text{surr}) \propto 1/T$ (depends on surr. starting temp)
(hot, small Δ cold, big Δ)

$$\therefore \Delta S(\text{surr}) = \frac{-\Delta H_{\text{sys}}}{T} \quad (25^\circ\text{C} = 298\text{K})$$

Spontaneous change = $\Delta S_{(total)} = \Delta S_{(sys)} + \Delta S_{(sur)} > 0$

(endo rxn can occur if ΔS_{sys} can compensate for $-\Delta S_{sur}$ as heat flows into system) (255 ex)

$\Delta S_{(T)} = \Delta S_{(sys)} - \frac{\Delta H_{(sys)}}{T} > 0$ (substituted in as can be directly measured)

$T\Delta S_{(T)} = T\Delta S_{(sys)} - \Delta H_{(sys)} > 0$

$\boxed{-T\Delta S_{(T)}} = -T\Delta S_{(sys)} + \Delta H_{(sys)} < 0$

Gibbs Free energy

$\Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys} < 0$

ΔH : quantity of heat change

ΔG : quality of available energy

(measure of energy which is free to do useful work \rightarrow rather than heat loss)

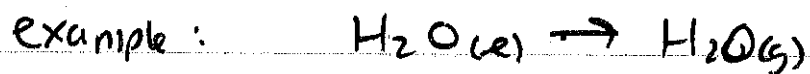
$\Delta G (-) = \text{spontaneous}$ ~~$\Delta G (-)$~~ $\Delta G = 0$ (eqm)

Predicting feasibility of change : ΔG affected by ΔT
play sign game

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

(-) - ? (+)

low $\Delta G (-)$ / high $\Delta G (+)$



predict sign of ΔS & ΔH , why?

$$\begin{aligned}\Delta S_{\text{rxn}} &= \sum S(p) - \sum S(r) \\ &= +188.8 - +70.0 = +118.8 \text{ J K}^{-1} \text{ mol}^{-1} \\ &\quad + 0.1188 \text{ kJ K}^{-1} \text{ mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta H_{\text{rxn}} &= \sum \Delta H_f(p) - \sum \Delta H_f(r) \\ &= -242 - (-286) = +44 \text{ kJ mol}^{-1}\end{aligned}$$

$\Delta G = 0$ @ ? Temp

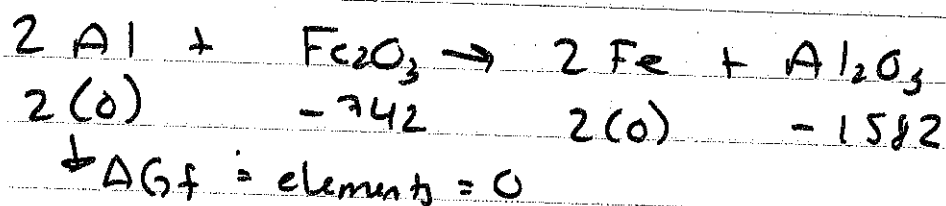
$$\begin{aligned}\Delta G &= \Delta H - T\Delta S = 0 \\ (+44) - (T)(+0.1188) &= 0 \\ \frac{+44}{+0.1188} &= T \\ 370 \text{ K} &= \end{aligned}$$

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Calculating ΔG values

1) ΔG_{rxn} from ΔG_f (rxn @ 298 K only)

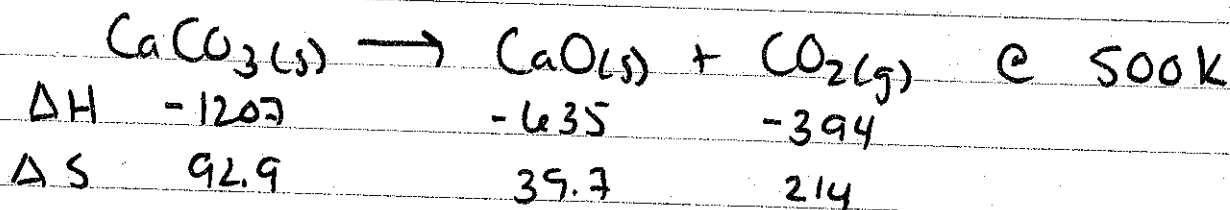
$$\Delta G_{\text{rxn}} = \sum \Delta G_f(\text{p}) - \sum \Delta G_f(\text{r})$$



$$\begin{aligned} \Delta G_{\text{rxn}} &= -1582 - (-742) \\ &= -840 \text{ kJ mol}^{-1} \text{ (spontaneous)} \end{aligned}$$

2) ΔG @ varying temps (extremely temp sensitive)

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



$$\begin{aligned} \text{Calc. } \Delta H: \quad \Delta H_{\text{rxn}} &= \sum \Delta H_f(\text{p}) - \sum \Delta H_f(\text{r}) \\ &= (-635 + -394) - (-1207) \\ &= +178 \text{ kJ mol}^{-1} \end{aligned}$$

$$\begin{aligned}
 \text{Calc } \Delta S: \quad \Delta S_{\text{rxn}} &= \sum \Delta S_{\text{(p)}} - \sum \Delta S_{\text{(r)}} \\
 &= (39.7 + 214) - 92.9 \\
 &= +160.8 \text{ J K}^{-1} \text{ mol}^{-1} \\
 &= +0.1608 \text{ kJ K}^{-1} \text{ mol}^{-1}
 \end{aligned}$$

$$\begin{aligned}
 \text{Calc } \Delta G = \Delta G &= \Delta H - T\Delta S \\
 &= +178 - (500)(+0.1608) \\
 &= +97.6 \text{ kJ mol}^{-1} \quad (\text{not spont})
 \end{aligned}$$

What temp is spontaneous?

$$0 = \Delta H - T\Delta S$$

$$T = \frac{\Delta H}{\Delta S} = \frac{(+178)}{(+0.1608)} = 1106 \text{ K}$$

spontaneous above temp

ΔG & equilibrium (extent of reaction: complete/incomp.)

$$\Delta G > +30 \text{ kJ mol}^{-1} \quad \text{no rxn} \quad \frac{[P]}{[R]} \ll 1$$

$$0 < \Delta G < +30 \quad \text{eqm mixture} \quad \frac{[P]}{[R]} < 1$$

$$\Delta G = 0 \quad \text{eqm mix} \quad \frac{[P]}{[R]} = 1$$

$$0 > \Delta G > -30 \quad \text{eqm mix} \quad \frac{[P]}{[R]} > 1$$

$$\Delta G < -30 \quad \text{complete rxn} \quad \frac{[P]}{[R]} \gg 1$$