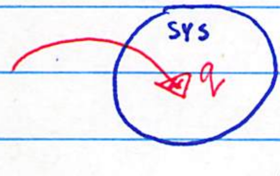
4/12/2019

How do we measure an entropy change, ΔS?

$$\left.\begin{array}{l}\Delta S \propto q \\ \quad\ \propto \frac{1}{T}\end{array}\right\} \boxed{\Delta S = \frac{q}{T}}$$



let's assume 100. J of heat enters system @ 50.0K

Q: what's ΔS?

$$\Delta S = \frac{+100.\,J}{50.0K} = 2.00\ J/K$$

units of S

(heat enters system, making it "disordered", increases its entropy)

let's say 25.0g water that freezes @ 0°C

$\Delta H^\circ_{fus} = +6.02\ kJ/mol$

What's ΔS for water? $\Delta S = \frac{q}{T}$ ← Kelvin / Abs. temp.

$0 + 273.15 = 273.15\,K$

fusion $H_2O(s) \rightarrow H_2O(l)$; $\Delta H^\circ = +6.02\,kJ$

$(s \rightarrow l)$ freezing: $H_2O(l) \rightarrow H_2O(s)$; $\Delta H^\circ = -6.02\,kJ$.

ΔH: $q \Leftrightarrow n$

$$q = 25.0\cancel{g\ H_2O} \times \frac{1\ mol\ H_2O}{18.02\cancel{g\ H_2O}} \times \frac{-6.02\,kJ}{1\ mol\ H_2O} = -8.352\,kJ$$

$$\Delta S = \frac{q}{T} = \frac{-8.352\cancel{kJ} \times \frac{10^3\,J}{\cancel{kJ}}}{273.15\,K} = -30.6\ J/K.$$

impossible?? NO! 2nd law: $\Delta S_{UNIV} \geq 0$

so, must account for surroundings!

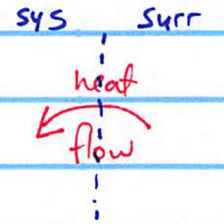
We must take into account the SURRoundings!

$$\Delta S_{UNIV} = \underbrace{\Delta S_{sys} + \Delta S_{surr}}_{\geq 0}$$

$\underline{\Delta S_{surr}}$

ice-cube: $\Delta S = -30.6\ J/K$

$\Rightarrow$ we know that $\Delta S_{surr} \geq 30.6\ J/K$!



So, how do we calculate ΔS_{surr}?

$$\Delta S_{surr} = \frac{q_{surr}}{T} \overset{1^{st}\ law}{=} \frac{-q_{sys}}{T}$$

1^{st} law: $q_{surr} = -q_{sys}$

$q = \Delta H$

$$\Delta S_{surr} = \frac{-\Delta H_{sys/rxn}}{T}$$

So, if we have an EXOTHERMIC process

$\Delta H < 0$ (-ve) so, system loses heat

$\Rightarrow$ surrounding gains heat

- creates entropy in surr!

(−) exothermic

$$\Delta S_{surr} = \frac{-\Delta H}{T}$$

So, presumably, the heat given off when water was frozen (exothermic), increased entropy of surr

$\Rightarrow \Delta S_{sys} + \Delta S_{surr} \geq 0$ ($\Delta S_{UNIV} \geq 0$)

Gibb's Free Energy

2nd law: $\underbrace{\Delta S_{UNIV} \geq 0}$ (spontaneous)

$$\Delta S_{sys} + \Delta S_{surr} \geq 0$$

$$\Delta S_{sys} - \frac{\Delta H_{sys}}{T} \geq 0$$

$\times(-T)$

$\times -1$ $\quad 9 > 8$ $\quad -9 < -8$

$$\Delta H_{sys} - T\Delta S_{sys} \leq 0$$

let's define: $G = H - TS$ $\qquad$ G = Gibb's free energy

free as in speech, not beer.

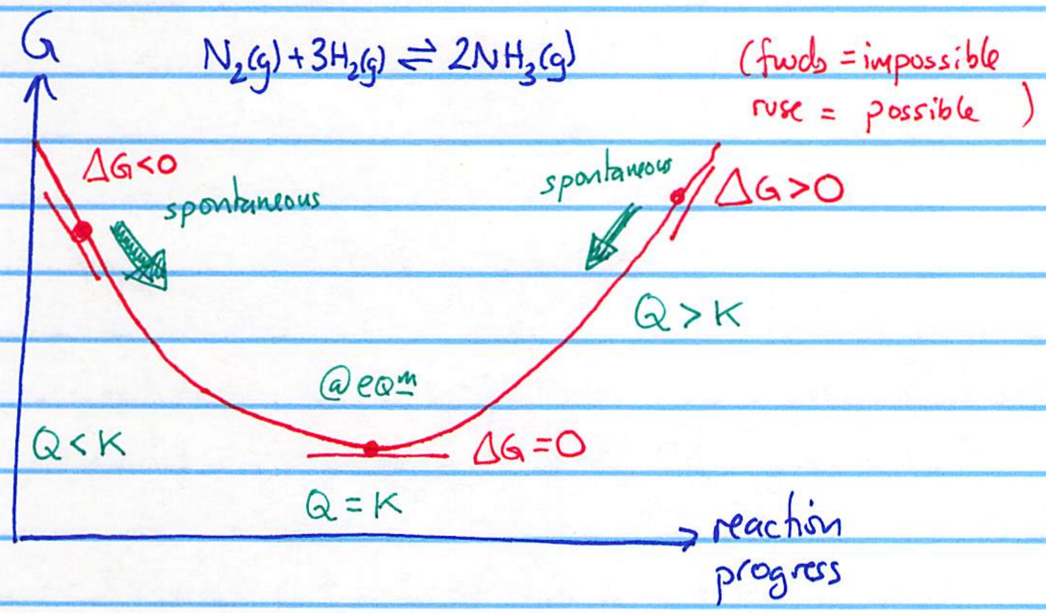
const T: $\boxed{\Delta G = \Delta H - T\Delta S}$

$\Rightarrow$ $\boxed{\Delta G_{sys} \leq 0}$ for a spontaneous process!

$\Delta G < 0$ (go)

$\Delta G = 0$ eQm

$\Delta G > 0$ (stop)



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

ΔH	ΔS	ΔG	
−	+	$\Delta G = \underbrace{\Delta H}_{\underbrace{(-)}_{-ve}} - \underbrace{T\Delta S}_{\underbrace{(+)}_{-ve}}$	always −ve always spont!
+	−	$\Delta G = \underbrace{\Delta H}_{(+)} - \underbrace{T\underbrace{\Delta S}_{-}}_{(+)}$	always +ve never spont! (non-spont)

Gibbs Free Energy Determines the Direction of Spontaneous Change