

THIRD LAW OF THERMODYNAMICS

→ The entropy of a pure crystal is 0 J/mK at 0 Kelvin

⇒ as $T \uparrow$ motion \uparrow , $S \uparrow$

* all "real world" substances have a (+)S
(ΔS can be (-))

SECOND LAW OF THERMODYNAMICS

The entropy of the universe INCREASES with any SPONTANEOUS PROCESS, and remains UNCHANGED for an EQ process

UNIVERSE = SYSTEM + SURROUNDINGS

$$\text{SPONT. } \Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{sur}} > 0$$

$$\text{EQ } \Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{sur}} = 0$$

ΔS_{univ} is (-) → nonspontaneous as written
reverse is spontaneous

If the system $-\Delta H$, the heat released causes a $+\Delta S$ for the surroundings

$$\Delta S_{\text{sur}} \propto -\Delta H_{\text{sys}} \Rightarrow \frac{\text{at}}{T} \text{ const.}$$

$$\Delta S_{\text{sur}} = \frac{-\Delta H_{\text{sys}}}{T}$$

THIRD LAW OF THERMODYNAMICS

→ The entropy of a pure crystal is 0 J/mol K at 0 Kelvin

⇒ as $T \uparrow$, motion \uparrow , $S \uparrow$

* all "real world" substances have a (+) S
(ΔS can be \leftarrow)

SECOND LAW OF THERMODYNAMICS

The entropy of the universe INCREASES with any SPONTANEOUS PROCESS, and remains UNCHANGED for an EQ process

UNIVERSE = SYSTEM + SURROUNDINGS

$$\text{SPONT. } \Delta S_{\text{UNI}} = \Delta S_{\text{SYS}} + \Delta S_{\text{SURR}} > 0$$

$$\text{EQ } \Delta S_{\text{UNI}} = \Delta S_{\text{SYS}} + \Delta S_{\text{SURR}} = 0$$

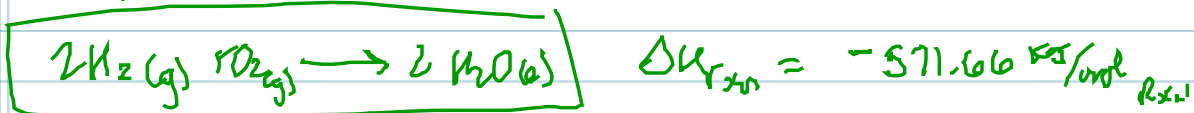
ΔS_{UNI} is \leftarrow → nonspontaneous as written
reverse is spontaneous

If the system $-\Delta H$, the heat released causes a $+\Delta S$ for the surroundings

$$\Delta S_{\text{SURR}} \propto -\Delta H_{\text{SYS}} \Rightarrow \frac{\text{at}}{T},$$

$$\Delta S_{\text{SURR}} = \frac{-\Delta H_{\text{SYS}}}{T}$$

$$\Delta H_f^\circ \text{H}_2\text{O (l)} = -285.83 \text{ kJ/mol}$$



$$\begin{aligned} \Delta S_{\text{sys}}^\circ &= \sum S_{\text{products}}^\circ - \sum S_{\text{reactants}}^\circ \\ &= [2 \times 69.91 \text{ J/mol}\cdot\text{K}] - [(2 \times 130.68 \text{ J/mol}\cdot\text{K}) + (205.14 \text{ J/mol}\cdot\text{K})] \end{aligned}$$

$$\Delta S_{\text{sys}}^\circ = -326.68 \text{ J/mol}\cdot\text{K}$$

$$\Delta S_{\text{surroundings}}^\circ = - \frac{(\Delta H_{\text{sys}})}{T} = - \frac{(-571.66 \times 10^3 \text{ J/mol})}{298 \text{ K}}$$

$$\Delta S_{\text{surroundings}}^\circ = 1918.3 \text{ J/mol}\cdot\text{K}$$

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}}^\circ + \Delta S_{\text{surroundings}}^\circ = -326.68 \text{ J/mol}\cdot\text{K} + 1918.3 \text{ J/mol}\cdot\text{K}$$

$$\Delta S_{\text{univ}} = \oplus 1591.6 \text{ J/mol}\cdot\text{K}$$



but slow... ..

large activation E

SPONTANEOUS
"thermodynamically favored"

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surroundings}} > 0$$

$$T \left(\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \frac{-\Delta H_{\text{sys}}}{T} > 0 \right)$$

$$\rightarrow T \Delta S_{\text{univ}} = T \Delta S_{\text{sys}} - \Delta H_{\text{sys}} > 0$$

ΔG
change in free energy

$$\left(-T \Delta S_{\text{univ}} \right) = \Delta H_{\text{sys}} - T \Delta S_{\text{sys}} < 0$$

"free energy"
↳ do useful work

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

Gibbs Equation

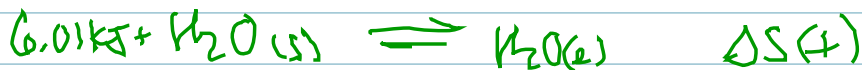
$\Delta G (-) \Rightarrow$ spontaneous as written

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

- | | |
|---|--|
| - | spontaneous forward |
| + | non spontaneous forward
spontaneous rev |
| 0 | @ EQ |

ΔH	ΔS	$\Delta G = \Delta H - T\Delta S$
-	+	- @ any T
+	-	+
-	-	- $\Delta H > T\Delta S$ $\downarrow T$ low
+	+	- $T\Delta S > \Delta H$ $\uparrow T$ high

ice cube on table \rightarrow melt $\Delta G (-)$



ΔH_{fus}

$$\Delta G = 0 \text{ @ EQ}$$

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

$$T = \frac{\Delta H}{\Delta S}$$

$$\Delta S = \frac{\Delta H_{fus}}{T_{mp}}$$