**Thermodynamics Details**

Foundations are based on empirical observations

\[ \Rightarrow \text{Laws} \]

**1st Law**

\[ dE = dW + dQ \]

- **E** \( \Rightarrow \) total energy
- **W** \( \Rightarrow \) mechanical work
- **Q** \( \Rightarrow \) heat

**Conservation of Energy**

1st in any process energy is conserved

\[ dE \text{ variation of energy due by some process} \]

**Why** \( dE \) \& **SW**?

What is the difference between

**d(C) & d(C)**? Fundamental!

\[ E \text{ is a function of state of the system (X)} \]

\[ \Rightarrow \text{going from } x_0 \text{ to } x_1 (\text{states}) \]

is function only on final & initial position, not path!!!

\[ \Delta E = \int_{x_0}^{x_1} dE \]

\[ \Rightarrow \Delta E (\text{closed loop}) = \int_{x_0}^{x_0} dE = 0 \]

Change of a state function on a reversible process is **zero**
In mathematical terms

\[ dE = \text{Differential} \]

Example

\[ f(x, y) = \text{State Function} \]

Differential:

\[ df = \frac{\partial f}{\partial x} dx + \frac{\partial f}{\partial y} dy \]

\[ \frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x} \quad \text{are they identical?} \]

\[ \begin{align*}
\text{If } & \frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x} \implies f \text{ is called close form.} \\
\text{If only if } & \int dF = 0 \text{ integral on a loop } \Rightarrow \int_{(x_1, y_1)}^{(x_0, y_0)} df = \text{ does not depend on path} \\
\Rightarrow & \text{dE is differential of E} \\
\Rightarrow & \text{E is a function of state} \quad \text{(for the 1st law)}
\end{align*} \]
What about $S$? $S$ represents a tiny amount of something but it is not a differential !!!! $S \neq d$

**Example**

$SW = \text{tiny amount of work to go from close states}$

$$F \rightarrow \quad SW = F \, dl$$

$SW$ is not differential of $W$!! $\Rightarrow W = F \, L$

$$dW = d(FL) = F \, dl + L \, df$$

$$SW = F \, dl$$

Thus

$S$ (SOMETHING) symbol is applied when the variation depends on the path.

$$\alpha \quad SQ_1 \neq SQ_2 \quad \text{depends on the path, the way you go from 1 to 2}$$

So

$$df = \frac{\partial f}{\partial x} \, dx + \frac{\partial f}{\partial y} \, dy \Rightarrow \text{if } \frac{\partial^2 f}{\partial x \partial y} \neq \frac{\partial^2 f}{\partial y \partial x} \Rightarrow$$

PATH DEPENDENCE $\Rightarrow$

need $S$ & not $df$

**Usually called**

$d = \text{perfect differential, differential for state functions}$

$S = \text{delta, variation of, for non-state functions}$
We know \( SW = -pdV \)

\( V \) is a state function, \( \Rightarrow dV \)

Of course, \( V \) is a state by itself.

\[ dE = -pdV + SQ \]

comes from \(-pdV\)

\[ H = E + (-pv) = E + pv \]

\[ \Rightarrow dH = Vdp + SQ \]

**ENTHALPY**

**TRANSPORT**

\( dH = dQ - dW \)

**ENTHAPY, AT CONSTANT PRESSURE, CONTAIN HEAT VARIATION.**

\[ \frac{dH}{ dp} = SQ \]

\[ SQ = \frac{dH}{dp} = \frac{dE}{dv} \]

\[ c = \frac{SQ}{ST} \]

**SPECIFIC HEAT:**

\[ C_p = \frac{SQ}{ST} = \frac{dH}{dT}_{p} \]

\[ C_v = \frac{SQ}{ST} = \frac{dE}{dT}_{v} \]

\[ \text{USE } H \text{ TO DESCRIBE SYSTEM } \text{ AT } P = \text{CONST} \]

**NOTE**
II) SQ is not a function of state but

there is a state function, S, entropy, for which

for all reversible processes \( dS = \frac{\delta Q_{rev}}{T} \)

and all irreversible processes \( dS > \frac{\delta Q}{T} \)

Equilibra are not always reversible

Rev of EQ: small variation taken & given back brings to the same point

\[ \Rightarrow \] if in a close loop \( \bigcirc \)

I get some extra entropy \( \Rightarrow \) this measures degradation

(MORE HEAT EXCHANGE \( \Rightarrow \) MORE ENTROPY)

\[ \Rightarrow \]

\( dE = -p\delta V + TdS \)

\( dH = V\delta p + TdS \)

\( dA = -p\delta V + SdT \)

\( dG = -T\delta V - SdT \)

\( H = E + PV \) ENTHALPY

\( A = E - ST \) (HELMHOLTZ)

GOOD @ V, T constant

\( G = E + PV + ST \) (GIBBS)

GOOD @ P, T constant

Like normal life

(Total entropy of Universe \( \downarrow \))

TS
STABILITY? WHAT TO MINIMIZE?

SECOND LAW IRREV. REV. $T \Delta S \geq \Delta Q$ IF IRR

$\Delta Q \leq T \Delta S$ IF REV.

A VARIATION $S$ (NOT A DIFFERENTIAL)

$\Delta E = \Delta S W + \Delta Q \leq \Delta S W + T \Delta S$

$\Rightarrow \Delta E - \Delta S W - T \Delta S \leq 0$ suppose $\Delta S W = -p \Delta V$

for much work

$\Delta E + p \Delta V - T \Delta S < 0$ for all irreversible processes

PROCESS = SOMETHING MOVING $\Delta Q \leq T \Delta S$, IRR $\Delta Q < T \Delta S$

IF EQUILIBRIUM, NO PROCESS $\Rightarrow \Delta Q \geq T \Delta S$

$\Rightarrow$ ad equilibrium (variation back/forth does not change) Virtual

if you vary $S \rightarrow SS$, you need to violate THE irreversible process

(because you need to come back)

$SS \leq \Delta Q / T$

VIRTUAL VARIATION

APPLIES TO STATE FUNCTIONS TO

$\Rightarrow \Delta S E - T \Delta S S + P \Delta S V \geq 0 \Rightarrow$

$SZ = \Delta S E - T \Delta S S + P \Delta S V \geq 0$

EQUILIBRIUM
At $T=0$, constant volume, equilibrium is $SE \geq 0 \Rightarrow$ the point where every variation of $E_i \geq 0$ is $\text{MIN}(E)$.

What about $H^2$? Enthalpy (if no extra heat moves $SQ=0$; $TDS=0$)

\[ dH = dE + VdP + TdS \]
\[ dH|_S = VdP \Rightarrow dH|_{S,P} = 0 \]

\[ (\text{SOL}) \]
\[ SE|_{S,P} = (SE - TSS + PSV)|_{SP} = (SE + PSV)|_{SP} = 0 \text{ always} \]

At constant $P$, $VSP = 0 \Rightarrow$
\[ (SE + PSV + VSP)|_{SP} = (SE + PV)|_{SP} = S|_{SP} \]
\[ \Rightarrow \text{S|}_{SP} \geq 0 \Rightarrow S|_{H_{SP}} \geq 0 \]

For $G$

\[ dG = VdP - SDT \Rightarrow S\geq 0 \Rightarrow SG_{SP,T} \geq 0 \]

If you like at $T,P constant \Rightarrow$ need to $\text{MIN}(G)$, not $E$!!
Melting ⇒ Where the Heat of Melting Goes?

\[ T = 0 \quad \boxed{\text{SOLID}} \quad \text{Const Pressure!} \]

\[ Q \Rightarrow \boxed{\text{SOLID}} \quad T \text{ const} \]

\[ Q \Rightarrow \boxed{\text{LIQUID}} \quad T \text{ const} \]

\[ \Delta Q \to \text{MELT?} \]

\[ \text{Melt happens at const } T \]

\[ \Delta E = -p \Delta V + T \Delta S = \Delta Q \]

\[ dH = VdT + \Delta Q \quad \text{at } P = \text{const} \quad d\mathcal{H}_p = \Delta Q \]

\[ \Rightarrow \Delta Q_{\text{Melting}} = \Delta \mathcal{H}_p \text{, meaningful} \]

\[ T_m \Delta S_m = \Delta H_m \Rightarrow \Delta S_m = \frac{\Delta H_m}{T_m} \]

\[ \Rightarrow \text{H} \]

\[ \Delta H_{\text{melt}} \]

\[ \Delta T \]
WHERE S COMES FROM?

F, L, P, V, T, W, are all easy to measure!
where S comes from? What is it? It's functional slope?
2nd law tells that $S$ is function of state
\[ \frac{dS}{dQ} = \frac{\delta Q}{T} \tag{1} \]

**INTENSIVE PROPERTIES:**

$T, P, F, ...$ properties and quantities that
do not depend on the size of the system

**EXTENSIVE PROPERTIES**

$E, Q, S, V, ...$ depend on the size!

EXAMPLE: 1 kg of WATER @ 100° contains

$E^{\circ} \text{JOULES} \Rightarrow$

3 kg of WATER @ 100° contains

$3 \times E^{\circ} \text{JOULES} !$

⇒ Energy is Extensive, Volume too (obvious)
Heat too (⇒ Therefore $S$)

IN THERMODYNAMICS INTENSIVE & EXTENSIVE ARE ASSOCIATED

\[- PolV \quad T \quad dS \quad \delta \quad \text{soon} \]

\[ \downarrow \quad \Downarrow \quad \downarrow \quad \uparrow \]

Q is extensive \implies S is extensive

\textbf{BOLTZMANN IDEA} \hspace{1cm} \# \text{of states}

1) at constant energy, the system can be in \( S(E) \)
   \text{number of states} \hspace{1cm} (\text{DEFINITION})

2) all states \underline{are equiprobable} \hspace{1cm} (\text{ASSUMPTION})
   (why a state should be more probable?)

3) \( 2+2 \implies P_e(x) = \frac{1}{S(E)} \) \hspace{1cm} \begin{equation} \sum_e P_e(x) = 1 \end{equation}

\textbf{BOLTZMANN SAYS}

\text{Entropy measures the prob. distribution}
\begin{equation} S(E) = \int P_e(x) = \int [-2(E)] \end{equation}

\text{But } S \text{ is extensive} \implies \text{take system of energy } E \text{ & cut in two}
\begin{equation} E_1, E_2 \end{equation}

\begin{equation}
\begin{bmatrix}
E_1 \\
E_2
\end{bmatrix}
\begin{bmatrix}
1 \\
2
\end{bmatrix}
\end{equation}

\begin{equation}
S(E) = \int [-2(E)]
\begin{equation}
S_1(E_1) = \frac{1}{f(2(E_1))} \quad S_2 = \frac{1}{f(2(E_2))}
\end{equation}

\text{but if } 1 \text{ has } S(E_1) \text{ states} & 2 \text{ has } S(E_2) \text{ states, then } 1+2 \text{ for a total of } S(E_1) \times S(E_2) \text{ possible configurations}

\text{TIO} \hspace{1cm} \begin{equation} (\text{for every one of one, pick one of the other}) \end{equation}
\[ S(E) \propto \log R(E) \Rightarrow S(E) = R_0 \log R(E) \]

DEFACTS. (FRENKEL)

\[ N_I = N_A \exp \left( -\frac{Q_I}{kT} \right) \]

\[ \Rightarrow N_A \text{ sites} \]
\[ N_I \text{ possible defects} \Rightarrow \]

choose \( N_I \) on a set of \( N_A \) places

\[ R = \# \text{choose } N_I \text{ identical defects on a set of } N_A \text{ identical places} \]

\[ \binom{N_A}{N_I} = \frac{N_A!}{N_I!(N_A-N_I)!} \]

\[ && \Rightarrow (N_A-N_I) \text{ identical good places} \]

\[ \Rightarrow \text{function has this property?} \]
\[ f(a*b) = f(a) + f(b) \? \]

\[ \Rightarrow \text{log} \]

\[ \text{to get Joules after multiplying for } T \]
and remember Sterling \( \log n! \approx n \log n - n \)

and \( x = \frac{N_x}{N_x^*} \)

\[ S = -kT \left[ x \log x + (1-x) \log (1-x) \right] \]

No defect: how many choices? \( I \Rightarrow R = 1 \Rightarrow S = 0 \)

All defects: how many choices? \( I \Rightarrow R = 1 \Rightarrow S = 0 \)

\[ y = - \left[ x \log x + (1-x) \log (1-x) \right] \]

\[ y \sim \frac{1}{x^2} \]

To form Frenkel (from double vacancy)

I TOLD THIS ! ! ! \[ N_x = N_x^* e^{-\frac{\Phi}{2kT}} \]

\[ \frac{\Phi}{2kT} = -\log x \]

IS THIS TRUE ?? \[ Q = -2kT \log x \]

MUST PROVE !

T12
\[ G = E - TS + PV \]
\[ \Delta G = \Delta E - T \Delta S + P \Delta V \]
\[ \Delta G = \Delta E - T \Delta S - \frac{1}{2} \]

\[ N_A \chi \Rightarrow \Delta G = N_A \chi \left[ \frac{xQ}{2} - T \Delta S(x) \right] \]
\[ \Rightarrow N_A \chi \left[ \frac{xQ}{2} + kT \left[ x \log x + (1-x) \log(1-x) \right] \right] \]
\[ \Rightarrow \min \Delta G \Rightarrow \min \Delta G \text{ over all possible configurations} \]

\[ \Rightarrow \frac{\partial \Delta G}{\partial x} = 0 \]
\[ \Rightarrow 0 = \frac{\partial}{\partial x} \left[ \frac{xQ}{2} + kT \left[ x \log x + kT (1-x) \log(1-x) \right] \right] \]
\[ 0 = \frac{Q}{2} + kT \log x - kT \log(1-x) \]
\[ \Rightarrow x = \frac{Q}{2} \]

\[ N_b = N_A e^{-\frac{Q}{2kT}} \]

Equilibrium Concentration