Fundamental Equations, Equilibrium, Free Energy, Maxwell Relations

- Fundamental Equations relate functions of state to each other using 1st and 2nd Laws

1st law with expansion work: $dU = \text{đ}q - p_{ext}dV$

need to express đq in terms of state variables because đq is path dependent

Use 2nd law: $\text{đ}q^{rev} = TdS$

For a reversible process $p_{ext} = p$ and $\text{đ}q = \text{đ}q^{rev} = TdS$

So…… ** $\boxed{dU = TdS - pdV}$ **

This fundamental equation only contains state variables

Even though this equation was derived for a reversible process, the equation is always correct and valid for a closed (no mass transfer) system, even in the presence of an irreversible process. This is because U, T, S, p, and V are all functions of state and independent of path.

AND The "best" or "natural" variables for U are S and V,

** $\boxed{U(S,V)}$ **

$$** \boxed{U(S,V)} **$$

From dU = TdS – pdV $\Rightarrow$ $** \boxed{\left(\frac{\partial U}{\partial S}\right)_V = T \quad ; \quad \left(\frac{\partial U}{\partial V}\right)_S = -p} **$

We can write similar equations for <u>enthalpy</u>

H = U + pV $\Rightarrow$ dH = dU + d(pV) = dU + pdV + Vdp

inserting dU = TdS – pdV

$$\Rightarrow \quad ** \boxed{dH = TdS + Vdp} **$$

The natural variables for H are then <u>S and p</u>

$$** \boxed{H(S,p)} **$$

From dH = TdS + Vdp $\Rightarrow$ $** \boxed{\left(\frac{\partial H}{\partial S}\right)_p = T \quad ; \quad \left(\frac{\partial H}{\partial Vp}\right)_S = V} **$

We can use these equations to find how S depends on T.

From dU = TdS – pdV $\Rightarrow$ $\boxed{\left(\frac{\partial S}{\partial T}\right)_V = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V = \frac{C_V}{T}}$

From dH = TdS + Vdp $\Rightarrow$ $\boxed{\left(\frac{\partial S}{\partial T}\right)_p = \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_p = \frac{C_p}{T}}$

Criteria for Spontaneous Change

The 2nd Law gave the Clausius inequality for spontaneous change

$$dS > đq/T_{surr.}$$

The 1st law gave us $dU = đq + đw$

Putting the two together, assuming only pV work, gives us the following general criterion for spontaneous change:

$$** \boxed{dU + p_{ext}dV - T_{surr}dS < 0} **$$

Equilibrium is when there is no possible change of state that would satisfy this inequality.

We can now use the general criterion above under specific conditions

- Consider first an isolated system ($q=w=0$, $\Delta V=0$, $\Delta U=0$)

Since $dU=0$ and $dV=0$, from the general criterion above, then

$$\boxed{(dS)_{U,V} > 0}$$

is the criterion for spontaneity for an isolated system

And equilibrium for an isolated system is then achieved when entropy is maximized. At maximum entropy, no spontaneous changes can occur.

- Consider now S and V constant

$$\Rightarrow \boxed{(dU)_{S,V} < 0}$$

is the criterion for spontaneity under constant V and S

At constant S and V, equilibrium is achieved when energy is minimized

- Consider now S constant and $p=p_{ext}$ constant

$$\Rightarrow \; dU + pdV < 0 \;\Rightarrow\; d\underbrace{(U + pV)}_{=H} < 0$$

So $$\Rightarrow \boxed{(dH)_{S,pext} < 0}$$

is the criterion for spontaneity under constant S and constant $p=p_{ext}$.

- Consider now H constant and $p=p_{ext}$ constant

$$dU + pdV - T_{surr}dS < 0$$

but $dU + pdV = dH$, which is 0 (H is constant)

So $\boxed{(dS)_{H,p=pext} > 0}$

is the criterion for spontaneity under constant H and constant $p=p_{ext}$.

Now let's begin considering cases that are experimentally more controllable.

- Consider now constant $T=T_{surr}$ and constant V

$$\Rightarrow\ dU - TdS < 0 \ \Rightarrow\ d(U - TS) < 0$$

Define $\boxed{A = U - TS}$, the $\boxed{\text{Helmholtz Free Energy}}$

$$\text{Then}\quad \boxed{(dA)_{V,T=Tsurr} < 0}$$

is the criterion for spontaneity under constant $T=T_{surr}$ and constant V.

For constant V and constant $T=T_{surr}$, equilibrium is achieved when the Helmholtz free energy is minimized.

We now come to the most important and applicable constraint:

- Consider now constant $T=T_{surr}$ and constant $p=p_{ext}$.

$$(dU + pdV - TdS) < 0 \quad \Rightarrow \quad d(U + pV - TS) < 0$$

Define $\boxed{G = U + pV - TS}$, the $\boxed{\text{Gibbs Free Energy}}$

(can also be written as $G = A + pV$ and $G = H - TS$)

$$\text{Then}\quad \boxed{(dG)_{p=pext,T=Tsurr} < 0}$$

is the criterion for spontaneity under constant $T=T_{surr}$ and constant $p=p_{ext}$.

At constant $p=p_{ext}$ and constant $T=T_{surr}$, equilibrium is achieved when the Gibbs free energy is minimized.

Consider the process:

$$A(p,T) = B(p,T) \qquad \text{(keeping p and T constant)}$$

Under constant $p=p_{ext}$ and $T=T_{surr}$,

$\Delta G < 0$ $A \rightarrow B$ is spontaneous
$\Delta G = 0$ A and B are in equilibrium
$\Delta G > 0$ then $B \rightarrow A$ is spontaneous

Maxwell Relations

- With the free energies

Helmholtz free energy $A = U - TS$
Gibbs free energy $G = H - TS$

we've introduced all our state functions. For closed systems,

$$\boxed{\begin{aligned} &U(S,V) \Rightarrow dU = TdS - pdV \\ &H(S,p) \Rightarrow dH = TdS + Vdp \\ &A(T,V) \Rightarrow dA = -SdT - pdV \\ &G(T,p) \Rightarrow dG = -SdT + Vdp \end{aligned}}$$

Fundamental equations

From $$dA = \left(\frac{\partial A}{\partial T}\right)_V dT + \left(\frac{\partial A}{\partial V}\right)_T dV$$

and $$dG = \left(\frac{\partial G}{\partial T}\right)_p dT + \left(\frac{\partial G}{\partial p}\right)_T dp$$

$$\boxed{\begin{matrix} \left(\frac{\partial A}{\partial T}\right)_V = -S & \left(\frac{\partial A}{\partial V}\right)_T = -p \\ \left(\frac{\partial G}{\partial T}\right)_p = -S & \left(\frac{\partial G}{\partial p}\right)_T = V \end{matrix}}$$

The <u>Maxwell relations</u>: $\frac{\partial^2 A}{\partial V\,\partial T} = \frac{\partial^2 A}{\partial T\,\partial V}$ and $\frac{\partial^2 G}{\partial p\,\partial T} = \frac{\partial^2 G}{\partial T\,\partial p}$

now allow us to find how S depends on V and p.

$$\Rightarrow \quad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \qquad \left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$$

These can be obtained from an equation of state.

We can now also relate U and H to p-V-T data.

$$\left.\begin{aligned}\left(\frac{\partial U}{\partial V}\right)_T &= T\left(\frac{\partial S}{\partial V}\right)_T - p = T\left(\frac{\partial p}{\partial T}\right)_V - p\\ \left(\frac{\partial H}{\partial p}\right)_T &= T\left(\frac{\partial S}{\partial p}\right)_T + V = V - T\left(\frac{\partial V}{\partial T}\right)_p\end{aligned}\right\} \rightarrow \text{U and H from equations of state!}$$

- For an ideal gas $pV = nRT$

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{nR}{V} = \frac{p}{T} \quad \Rightarrow \quad \left(\frac{\partial U}{\partial V}\right)_T = 0$$

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{nR}{p} = \frac{V}{T} \quad \Rightarrow \quad \left(\frac{\partial H}{\partial p}\right)_T = 0$$

This <u>proves</u> that for an ideal gas U(T) and H(T), functions of T only. We had <u>assumed</u> this was true from Joule and Joule-Thomson expansion experiments. Now we know it is rigorously true.