5.60 Thermodynamics & Kinetics
Spring 2008

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 $$\Rightarrow \boxed{(dH)_{S,p_{ext}} < 0}$$

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 $$\boxed{(dS)_{H,p=p_{ext}} > 0}$$

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 <u>constant $T=T_{surr}$ and constant V</u>

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

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

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

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

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

We now come to the most <u>important and applicable</u> constraint:

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

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

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

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

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

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

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

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