**Phase and equilibrium**

Below definition states that the entropy of an isolated system with will tend to increase at constant U and V.

dSU,V $\geq $0

At equilibrium, the entropy of the system maximizes-------dSU,V =0

State of the system

S

At equilibrium, dSU,V=0

This can also be demonstrated by the plot above. At fixed T and U, entropy of the system will reach a maximum at which the first derivative is 0 and d2SU,V $\leq $0.

At the same time, the following equalities are provided at equilibrium:

dU=0, dA=0, dG=0 but unlike entropy, internal energy, they tend to attain their minimum at eu

Considering isolated systems having ***multiple phases*** (phase 1 and 2), the equilibrium criteria can be derived by the following equations. Let’s atart with the derivative form

dS=$\frac{dU}{T}+$ $\frac{PdV}{T}- \frac{μdN}{T}$

Since the system is totally isolated, total internal energy, total volume and the total number of moles of for system are all constant (but phases can exchange material and energy):

U=U1+U2 = contant

V=V1+V2  = contant

N=N1+N2  = contant

Their derivatives will give:

0= dU1+dU2 0=dV1+dV2  0=dN1+dN2

Writing the relation for entropy for an isolated system comprising two different phases at the equilibrium:

dS=$\frac{dU\_{1}}{T\_{1}}+\frac{dU\_{2}}{T\_{2}}+$ $\frac{P\_{1}dV\_{1}}{T\_{1}}+\frac{P\_{2}dV\_{2}}{T\_{2}}-$ $\frac{μ\_{1}dN\_{1}}{T\_{1}}-\frac{μ\_{2}dN\_{2}}{T\_{2}}$ =0

Since dU1= – dU2, dV1= – dV2, dN1 = – dN2

$dS= \left(\frac{1}{T\_{1}}-\frac{1}{T\_{2}}\right) dU\_{1}$ +$\left(\frac{P\_{1}}{T\_{1}}-\frac{P\_{2}}{T\_{2}}\right) dV\_{1}$ $–dN\_{1}$ $\left(\frac{μ\_{1}}{T\_{1}}-\frac{μ\_{2}}{T\_{2}}\right)=0$

which makes

$T\_{1}=T\_{2}$ ……… thermal equilibrium

$P\_{1}=P\_{2}$……………….mechanical equilibrium

$μ\_{1}=μ\_{2}$……………chemical equilibrium

**Degrees of Freedom Analysis for the systems with multiple phases**

It is essential to answer this question; how many properties are needed to define the state of a system at equilibrium. Then we have to refer to the following equation:

F = C +2 – P

C represents the number of components, P respresents the number of phases and F is the degrees of freedom. For a system having 2 components and 2 phases at equilibrium, F will be equal to 2. This means that two properties will be enough to define the state of the system such as T and P.

**References:**

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