The conditions of equilibrium

Consider a system with energy U, entropy S,
Volume V and components $N_1, \ldots N_r$.
Let the fundamental equation of the system
be

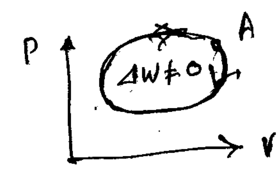
$$U = U(S, V, N_1, N_2 \ldots N_r)$$

$$dU = \underbrace{\left.\frac{\partial U}{\partial S}\right)_{V,\{N_i\}}}_{\substack{T \\ \text{(Temperature)}}} dS + \underbrace{\left.\frac{\partial U}{\partial V}\right)_{S,\{N_i\}}}_{\substack{-P \\ \text{(Pressure)}}} dV + \sum_{i=1}^{r} \underbrace{\left.\frac{\partial U}{\partial N_i}\right)_{S,V,N_{i'}\,(i'\neq i)}}_{\substack{\mu_i \\ \text{(chemical potential)}}} dN_i ,$$

$$dU = T\,dS - P\,dV + \sum_{i=1}^{r} \mu_i\, dN_i$$

To associate $\Delta W = -P\,dV$, the work has to be done
quasi-statistically. If sudden changes are made,
then pressure is not a well defined quantity.
It is a succession of equilibrium states ⇒
the time to attain equilibrium is much less than
the time in which dV occurs..

Note we do not use (dW) because W describes
this notation is used only when
the state of the system. Means that the
"amount of work" the system is defined by
Not possible. [give example of



$\Delta Q = T dS$ [heat flux] (quasi-static)

Equations of state

Consider ~~Fundamental~~ relations are

$T = T(S, V, \{N_i\})$ $\quad P = P(S, V, \{N_i\})$ $\quad \mu_j = \mu_j(S, V, \{N_i\})$

Here the intensive parameters are expressed in terms of extensive parameters.

A single equation of state is not equal to a fundamental relation. However all the equations of state is equivalent to knowledge of fundamental equation.

$$T(\lambda S, \lambda V, \lambda N_1 \ldots \lambda N_r) = T(S, V, \{N_i\})$$

$$\left.\frac{\partial S}{\partial U}\right)_{V,\{N_i\}} = \left.\frac{\partial(\lambda S)}{\partial(\lambda U)}\right)_{\lambda V, \{\lambda N_i\}} = T$$

$$\Big[U_s = \lambda U = U(\lambda S, \lambda V, \{\lambda N_i\})$$

$$\frac{\partial U_s}{\partial(\lambda S)} = \frac{\partial U}{\partial S} = T \Big]$$

P and μ are also intensive parameters.

We summarise for a quasi-static process

$$\Delta Q = T dS \; ; \quad \Delta W_{Mech} = -p\, dV \quad \Delta W_{chem} = \sum_{j=1}^{r} \mu_j \, dN_j$$

$$dU = \Delta Q + \Delta W_{Mech} + \Delta W_{chem}$$

$$= T dS - p dV + \sum_{j=1}^{r} \mu_j \, dN_j$$

For Single Component

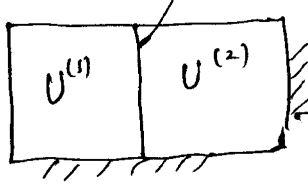
$$\boxed{dU = T dS - p dV + \mu dN}$$ I law of Thermodynamics.

Thermal equilibrium

Use of postulate II, III

rigid, no flow of particles

heat can flow.



Adiabatic. (closed system).

- S must be a maximum under the condition

$$U^{(1)} + U^{(2)} = \text{constant}$$

$$S = S^{(1)}(U^{(1)}, V^{(1)}, \ldots N_j^{(1)} \ldots) + S^{(2)}(U^{(2)}, V^{(2)}, \ldots N_j^{(2)} \ldots)$$

$V^{(1)}, N_j^{(1)}$; $V^{(2)}, N_j^{(2)}$ are fixed.

$$dS = \left.\frac{\partial S^{(1)}}{\partial U^{(1)}}\right)_{V^{(1)}, \{N_i^{(1)}\}} dU^{(1)} + \left.\frac{\partial S^{(2)}}{\partial U^{(2)}}\right)_{V^{(2)}, \{N_i^{(2)}\}} dU^{(2)} = 0$$

We also have $dU^{(1)} + dU^{(2)} = 0$.

$$dS = \left(\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}}\right) dU^{(1)} = 0$$

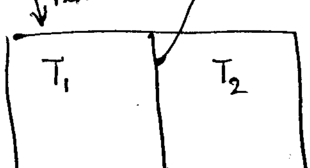
using $\left.\frac{\partial S^{(1)}}{\partial U^{(1)}}\right)_{(V^{(1)}, \{N_i^{(1)}\})} = \frac{1}{T^{(1)}}$.

$$\Rightarrow \quad T^{(1)} = T^{(2)}.$$

Stability needs $d^2 S < 0$ [later].

Adiabatic

Adiabatic wall



$T_1 > T_2$

Remove the wall

Entropy (Postulate II, III) increases.

$$\Delta S \simeq \left(\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}}\right) \Delta U^{(1)} \Rightarrow \Delta U^{(1)} < 0$$

Heat flows from (1) to (2) [Intutitively correct].

Mechanical equilibrium

Closed system

Separated by a wall which does not allow ~~more~~ particles to cross it. Heat can be exchanges. It can move inside (frictionless)

$$U^{(1)} + U^{(2)} = \text{Constant}; \quad V^{(1)} + V^{(2)} = \text{Const.}$$

$$dS = 0 = \left(\frac{\partial S^{(1)}}{\partial U^{(1)}} - \frac{\partial S^{(2)}}{\partial U^{(2)}}\right)_{V,N} dU^{(1)} + \left(\frac{\partial S^{(1)}}{\partial V^{(1)}} - \frac{\partial S^{(2)}}{\partial V^{(2)}}\right)_{U,N} dV^{(1)} = 0$$

$$\Rightarrow \quad = \left(\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}}\right) dU^{(1)} + \left(\frac{p^{(1)}}{T^{(1)}} - \frac{p^{(2)}}{T^{(2)}}\right) dV^{(1)} = 0$$

using $T \left.\frac{dS}{dV}\right)_U = \left.\frac{DQ}{dV}\right)_U = \left. p\frac{dV}{dV}\right)_U = p$

$$\Rightarrow \quad T^{(1)} = T^{(2)} \quad \text{and} \quad p^{(1)} = p^{(2)}.$$

Matter flow : Permeable to matter. (one component for simplicity.

$$dS = \left(\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}}\right) dU^{(1)} - \left(\frac{\mu^{(1)}}{T^{(1)}} - \frac{\mu^{(2)}}{T^{(2)}}\right) dN^{(1)}$$

$$\left[\, N^{(1)} + N^{(2)} = \text{Const.} \quad U^{(1)} + U^{(2)} = \text{Const} \right]$$

Use. $T\,dS = dU + p\,dV - \mu\, dN$.

One can think of Temperature as a potential for heat flux, pressure for volume change and the chemical potential for matter flux.

Example

[after discussing equations of state]

Consider the fundamental equation

$$u = \left(\frac{v_0^{1/2}\,\theta}{R^{3/2}}\right)\frac{s^{5/2}}{v^{1/2}} \qquad u = \frac{U}{N},\quad s = \frac{S}{N},\quad v = \frac{V}{N}$$

$$\frac{U}{N} = \left(\frac{v_0^{1/2}\,\theta}{R^{3/2}}\right)\frac{S^{5/2}}{V^{1/2}\,N^2}$$

$$U = \underbrace{\left(\frac{v_0^{1/2}\,\theta}{R^{3/2}}\right)}_{\Lambda}\frac{S^{5/2}}{V^{1/2}}\cdot\frac{1}{N} = U(S,V,N)$$

$$P = -\left.\frac{\partial U}{\partial V}\right)_{S,N}$$

$$\ln U = -\ln N + \ln\Lambda + \frac{5}{2}\ln S - \frac{1}{2}\ln V$$

$$-\frac{1}{U}\left.\frac{\partial U}{\partial V}\right)_{S,N} = -\frac{1}{2}\frac{1}{V} \Rightarrow \boxed{P = \frac{U}{2V} = \frac{\Lambda N S^{5/2}}{2V^{3/2}}} \quad (1)$$

$$\frac{1}{U}\left.\frac{\partial U}{\partial S}\right)_{V,N} = \frac{5}{2}\frac{1}{S} = \frac{T}{U}\ ; \quad T = \frac{5}{2}\frac{U}{S}$$

$$\cancel{T = \frac{5}{2}\frac{N\Lambda S^{3/2}}{V^{1/2}}\cdot\frac{V}{N\Lambda}} \quad (2)$$

~~Eliminating~~

$$\boxed{T = \frac{5}{2}\frac{\Lambda S^{3/2}}{N V^{1/2}}} \quad (2)$$

$$\frac{(1)}{(2)^{5/3}} = \frac{P}{T^{5/3}} = \frac{\Lambda N S^{5/2}}{2V^{3/2}\left(\frac{5}{2}\frac{\Lambda}{V^{1/2}}S^{3/2}\right)^{5/3}}$$

$$= \frac{\Lambda N}{2V^{3/2}}\left(\frac{2}{5}\right)^{5/3} V^{5/6}$$

$$= N\frac{\Lambda}{2}\left(\frac{2}{5}\right)^{3/2} V^{\overbrace{5/6-3/2}^{-1/6}}$$

$$= N\frac{\Lambda}{2}\left(\frac{2}{5}\right)^{3/2}\frac{1}{V^{1/6}}$$

$$PV^{1/6} = N\frac{\Lambda\, 2^{1/2}}{5^{3/2}}T^{5/3}. \quad (2a)$$

(18) $\cancel{(16)}$

$$\frac{1}{U}\left.\frac{\partial U}{\partial N}\right)_{S,V} = \frac{\mu}{U} = -\frac{1}{N}$$

$$\mu = -\frac{U}{N} = -\frac{\Lambda S^{5/2}}{V^{1/2} N^2}$$ (3)

$$\frac{\mu}{T^{5/3}} = \frac{-\dfrac{\Lambda S^{5/2}}{V^{1/2}N^2}}{\left[\dfrac{5}{2}\dfrac{\Lambda S^{3/2}}{N V^{1/2}}\right]^{5/3}}$$

$$= \frac{-\dfrac{\Lambda S^{5/2}}{V^{1/2}N^2}}{\left(\dfrac{5}{2}\right)^{5/2}\left(\dfrac{\Lambda}{N}\right)^{5/3}\dfrac{S^{5/2}}{V^{5/6}}}$$

$$= -\left(\frac{2}{5}\right)^{5/2}\Lambda^{-2/3}\left(\frac{N^{5/3}}{N^2}\right)\frac{V^{5/6}}{V^{1/2}}$$

$$\frac{\mu}{T^{5/3}} = -\left(\frac{2}{5}\right)^{5/2}\frac{1}{\Lambda^{2/3}}\left(\frac{1}{N^{1/3}}\right)V^{1/3}$$

$$\mu = -\left(\frac{2}{5}\right)^{5/2}\frac{1}{\Lambda^{2/3}}\cancel{N^{1/3}}\left(\frac{V}{N}\right)^{1/3}T^{5/3}$$

From (2a) we have $PV^{1/6}$ Const for a fixed T.

Examples

(1) Fundamental relation for a perfect gas.

$$S = \frac{S_0 N}{N_0} + N R \ln\left[\left(\frac{U}{U_0}\right)^{3/2} \cdot \left(\frac{V}{V_0}\right) \left(\frac{N}{N_0}\right)^{-5/2}\right]$$

[will "derive" this later].

$S(U, V, N)$

$S(\lambda U, \lambda V, \lambda N) = \lambda S(U, V, N)$

(2) Start from the I law (page 14)

$$\Delta Q = T\,dS = dU + P\,dV$$

$$dS = \frac{1}{T}dU + \frac{P}{T}dV \Rightarrow dU = T\,dS - P\,dV$$

(N = fixed)

$$\frac{\partial^2 U(V,S)}{\partial V \partial S} = \frac{\partial^2 U(V,S)}{\partial S \partial V}$$

$$\frac{\partial}{\partial V}\left[\left(\frac{\partial U}{\partial S}\right)_V\right] = \left.\frac{\partial T}{\partial V}\right)_S$$

$$\left.\frac{\partial}{\partial S}(-P)\right|_V$$

$$\left.\frac{\partial T}{\partial V}\right|_S = -\left.\frac{\partial P}{\partial S}\right|_V$$

[One of several Maxwell's relation].

$$d(U + PV) = T\,dS + V\,dP$$

$U + PV = H$ Enthalphy

$$\left.\frac{\partial T}{\partial P}\right)_S = \left.\frac{\partial V}{\partial S}\right)_P$$ Maxwells relation

$$d(U - TS) = dU - T\,dS - S\,dT = -P\,dV - S\,dT$$

$U - TS$ = Free energy

$$\left.\frac{\partial P}{\partial T}\right)_V = \left.\frac{\partial S}{\partial V}\right)_T$$ Maxwell's relation

$$d(U - TS + PV) = -S\,dT + V\,dP$$

$U - TS + PV$ Gibb's free energy.

$$\left.\frac{\partial S}{\partial P}\right)_T = -\left.\frac{\partial V}{\partial T}\right)_P$$

Maxwell's relation.

$$\begin{matrix} S & P \\ V & T \end{matrix}$$

(3) Use of Maxwell's relations.

Co-efficient of thermal expansion

$$\alpha = \frac{1}{V} \left.\frac{\partial V}{\partial T}\right)_P$$

Co-efficient of compressibility

$$K_T = -\frac{1}{V} \left.\frac{\partial V}{\partial P}\right)_T$$

Specific heat at constant pressure (per mole)

$$C_p = T \left.\frac{\partial S}{\partial T}\right)_P \qquad S \text{ is for one mole.}$$

$$= \left.\frac{\Delta Q}{\partial T}\right)_P.$$

Similary specific heat at constant volume

$$C_V = \left.\frac{\Delta Q}{\partial T}\right)_V = T \left.\frac{\partial S}{\partial T}\right)_V$$

Relation between the sp. heats, α & K_T

[F. Reif Section 5.7]

$$\Delta Q = T\,dS = T\left[\left.\frac{\partial S}{\partial T}\right)_P dT + \left.\frac{\partial S}{\partial P}\right)_T dP\right]$$

[with $S(T,P)$]

$$= C_p\,dT + T\left.\frac{\partial S}{\partial P}\right)_T dP$$

with $S(T,V)$

$$\Delta Q = C_p\,dT + T\left.\frac{\partial S}{\partial P}\right)_T \left[\left.\frac{\partial P}{\partial T}\right)_V dT + \left.\frac{\partial P}{\partial V}\right)_T dV\right]$$

$$C_V = \left.\frac{\Delta Q}{dT}\right)_V = C_p + T\left.\frac{\partial S}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V$$

$$\left.\frac{\partial p}{\partial T}\right)_V = \frac{-\left.\frac{\partial V}{\partial T}\right)_P}{\left.\frac{\partial V}{\partial p}\right)_T} = \frac{-\alpha V}{-K_T V} = \frac{\alpha}{K_T}$$

$$C_v = C_p + T \left.\frac{\partial S}{\partial p}\right)_T \frac{\alpha}{K_T} = C_p - T \left.\frac{\partial V}{\partial T}\right)_p \frac{\alpha}{K_T}$$

$$= C_p - \frac{T \alpha^2 V}{K_T}$$

$$C_p = C_v + \frac{T \alpha^2}{K_T} V$$