Lecture 1 (21-9-2021)

Syllabus

Chapters 1-10 of the book Fundamentals of statistical and thermal Ph

by F. Reif.

Administration

(1) Weekly home work : (Study material + 3 probl each worth 5.)

(2) Midsemester (3) Final.

(4) 2 Quizes,

Mark distribution out of 100.

Weekly home work	20
Quizes	10
Mid semester	20
Final	50.

We will not discuss thermometry (which has a long history) but have reading assignments on these.

Lecture 1

If we consider a macroscopic body and study its properties like Volume, magnetic moment, pressure, temperature etc. it specifies the state of the body. If two different experiments prepare the system by ~~stabs~~ fixing a few variables one finds that all other properties of the two systems have identical properties. Such a result was obtained after painstaking work done over Centuries.

The development of the concepts of pressure and temperature was done in the sixteenth, seventeeth and the eighteenth Centuries. These concepts, as we know today, were in the final form after several twists turns and heated debates.

The Concept of heat is subtle and it was the work of Planck which formalized it, leading to the first law of thermodynamics. We will start with a brief discussion of these.

From an atomic point of view any macroscopic system is an agglomerate of $\sim 10^{23}$ electrons & nuclei. However one finds in day to day dealings

We will consider Simple systems

(1) Macroscopically homogeneous

(2) Isotropic

(3) Uncharged

(4) Chemically inert

(5) Neglect surface effects (sufficiently large)

(6) Ignore effects of gravity, magnetic and electric fields unless explicitly mentioned.

Relevant parameter

(7)

(1) Volume [extensive parameter]

(2) Number of k^{th} molecule (Chemical composition) [extensive parameter]

(3) Concept of internal energy

The total energy of the system including kinetic, & potential energy). Conservation of energy of a closed system (not interacting with the surroundings) is assumed.

(3) The internal energy is an extensive parameter

Thermodynamic equilibrium

Isolated systems evolve and finally reach a state when the properties of the system become fixed. Such states are equilibrium states.

We consider ~~this~~ the above statement as postulate I

At a later stage, we will get some more insight associated with this postulate.

Concept of constraints

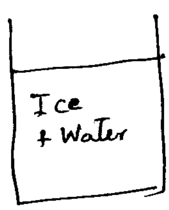
"Walls" separate a thermodynamic system from its surroundings. The walls can be moved and this will alter the parameters of the system.

Walls can restrict volume, Number of particles and energy. The restriction of energy needs special attention

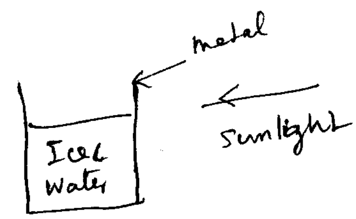
Energy. How does one measure it?

Example

(A)



(B)

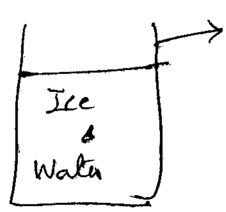


If it is stirred vigorously, ice will melt more rapidly & reach the state F. We are transferring energy to it mechanically (which is easily accountable).

← Sun light.

~~metal~~ glass/ Thermas flask.

(B)



(Exposed to Sun)

It will melt and reach the same state F

No mechanical energy was supplied.

So energy in the form of heat is been given to the system.

(C) One could have insulated the system by diffent substate & the "heat flow" will be at different rates

In the limit there is no heat flow

The wall is said to be adiabatic.

Measurement of energy

We have a measure of mechanical energy

$$\Delta W = \vec{F} \cdot \vec{\Delta D}.$$

Thus if one goes from a state A to B by an adiabatic process and a mechanical energy supplied to ΔW, then

$$E_B - E_A = \Delta W$$

E_A is the "standard" state.

So long as the "mole numbers" of the constituents are the same one can go from one state A to B by an adiabatic process. [Joule] (not necessarily from B → A; more about it later).

Example of Water + Ice $\xrightarrow{\downarrow \text{Work}}$ Water

$\Longleftarrow$
?

Heat (Quantitative)

$$E_B - E_A = \underbrace{\Delta W}_{\substack{\text{to the} \\ \text{system} \\ [-p\,dV]}} + \underbrace{\Delta Q}_{\substack{\text{Heat to} \\ \text{the system.}}}$$

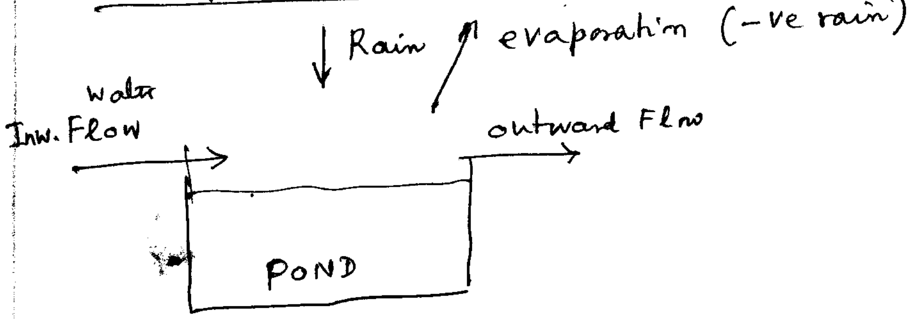
(First law of thermodymaics)

$$\text{DQ} = dU + p\,dV \quad (\text{at constant mole numbers}).$$

Concept of imperfect differential.

There is no Q or W having separate meaning.

A good example



Knowing the volume of water we can not decide how much came in the form of flow and how much in the form of rain.

Unless Flow meters can only tell about flow. He does not know there is a "rain meter" $\Rightarrow$ No such meter. how much came by rain

So he can cover the pond by a plastic sheet and so "rain flow" occurs. This gives him the flow meter. total water content just by measuring the inward & outward flow of water.

Now on knows the height of water in the pond (compared to the standard one) i.e. he knows the amount of water in the p ~~The ones used to find the flows difference between the~~

Suppose the amount of water came is F_1 and went out is F_2. Then the pond received $F_1 - F_2$ amount of water.

Lecture 1

~~and~~ The difference in height of the water level using a vertical stick gives $U_2 - U_1$ for the volume of water in the pond.

But if $U_2 - U_1 \neq F_2 - F_1$, the rest must be due to the rain.

Thus $U_2 - U_1 = \underbrace{F_2 - F_1}_{\text{Mechanical work}} + (\text{Amount due to rain})$

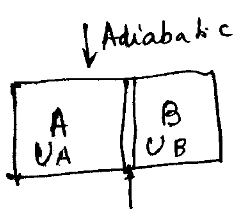
$\Downarrow$

Heat

Units (MKS system)

$1\ J = 4.186$ Cal.

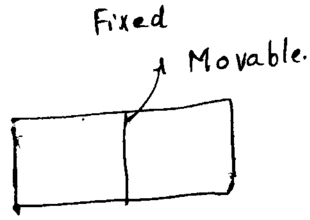
Main problem of equilibrium thermodynamics



A & B are same compound

energy U_A, U_B.

An equilibrium state



New equilibrium state.

Any removal of constraint ~~ea~~ (internal) of a closed system causes a system to move from one equilibrium state to another.

Main problem Given the initial state, find the final state.

Lecture 1

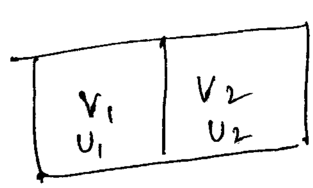
Postulate II

There exists a function called entropy S of the extensive parameters of any composite system defined for all equilibrium states having the property:

The entropy function reaches a maximum for the ~~values of the~~ different possible values of the extensive parameters, that the system possesses under the external constraint.

Thus if we allow volume to change in the previous example, it will reach a value such that the entropy (denoted by S) reaches a maximum value.

The external constraints are (a) total volume $V_1 + V_2 = \text{Constant}$ (b) total energy $(U_1 + U_2 = \text{Const})$



Once S is known function of extensive variables the problem is completely solved.

S (extensive Variables) = Fundemental relation.

Once a fundamental relation is ~~all~~ known, all its equilibrium properties are known, Lecture I

Postulate III The entropy is additive of composite sub systems.

$S(E)$ is continuous and $\frac{\partial S}{\partial E}$ exists and > 0

Let (α) denote subsystems

$$S = \sum_\alpha S^{(\alpha)} \quad ; \quad S^\alpha(U^{(\alpha)}, V^{(\alpha)}, N_1^{(\alpha)} \cdots N_r^{(\alpha)})$$

$$S(\lambda U, \lambda V, \lambda N_1 \cdots \lambda N_r) = \lambda S(U, V, N_1 \cdots N_r)$$

$$\left.\frac{\partial S}{\partial U}\right)_{V, N_1 \cdots N_r} > 0.$$

Monotonicity implies S is single valued function of energy.

$\Rightarrow$ U is single valued, continuous diff. function of $S, V, \ldots N_r$.

$$U = U(S, V, N_1 \cdots N_r).$$

Let $u = \frac{U}{N}$, $v = \frac{V}{N}$ (one component system)

$$N s(u, v) = \cancel{S(N, V, \ldots)} \; S(U, V, N)$$

$$s(u, v) = S(u, v, 1)$$

Postulate IV $\left.\frac{\partial U}{\partial S}\right)_{V, N_1 \cdots N_r} = 0$ for any system.

[Needs quantum mechanics to understand this postulate] we will study this at the end.

Some mathematics

Partial derivations.

$$\psi(x, y, z) \quad : \quad \frac{\partial \psi}{\partial x}, \ \frac{\partial \psi}{\partial y}, \ \frac{\partial \psi}{\partial z}$$

$$\frac{\partial}{\partial x}\left(\frac{\partial \psi}{\partial x}\right) = \frac{\partial^2 \psi}{\partial x^2} \qquad \frac{\partial}{\partial y}\left(\frac{\partial \psi}{\partial x}\right) = \frac{\partial^2 \psi}{\partial y \, \partial x} \quad \text{etc.}$$

ψ assumed to be "well behaved" if we have

$$\frac{\partial^2 \psi}{\partial y \, \partial x} = \frac{\partial^2 \psi}{\partial x \, \partial y}.$$

$$d\psi = \left.\frac{\partial \psi}{\partial x}\right)_{y,z} dx + \left.\frac{\partial \psi}{\partial y}\right)_{x,z} dy + \left.\frac{\partial \psi}{\partial z}\right)_{x,y} dz$$

Let x, y, z depend only on one variable u.

$$d\psi = \underbrace{\left[\left.\frac{\partial \psi}{\partial x}\right)_{y,z} \frac{dx}{du} + \left.\frac{\partial \psi}{\partial y}\right)_{x,z} \frac{dy}{du} + \left.\frac{\partial \psi}{\partial z}\right)_{x,y} \frac{dz}{du} \right]}\, du$$

$$\frac{d\psi}{dz} = \quad ''$$

If $\quad x = x(u, v) \qquad y = y(u, v) \qquad z = z(u, v)$

$$d\psi = \left[\left(\frac{\partial \psi}{\partial x}\right)_{y,z} \left(\frac{\partial x}{\partial u}\right)_v + \left(\frac{\partial \psi}{\partial y}\right)_{x,z} \left(\frac{\partial y}{\partial u}\right)_v + \left(\frac{\partial \psi}{\partial z}\right)_{x,y} \left(\frac{\partial z}{\partial u}\right)_v \right] du$$

$$+ \left[\left(\frac{\partial \psi}{\partial x}\right)_{u,v} \left(\frac{\partial x}{\partial v}\right)_u + \left(\frac{\partial \psi}{\partial y}\right)_{x,z} \left(\frac{\partial y}{\partial v}\right)_u + \left(\frac{\partial \psi}{\partial z}\right)_{x,y} \left(\frac{\partial z}{\partial v}\right)_u \right] d$$

$$= \left.\frac{\partial \psi}{\partial u}\right)_v du + \left.\frac{\partial \psi}{\partial v}\right)_u dv.$$

If $\quad u = x$

$$\left.\frac{\partial \psi}{\partial x}\right)_v = \left[\left.\frac{\partial \psi}{\partial x}\right)_{y,z} \overset{\nearrow 1}{\left.\frac{\partial x}{\partial x}\right)_v} + \left.\frac{\partial \psi}{\partial y}\right)_{x,z} \left.\frac{\partial y}{\partial x}\right)_v + \left(\frac{\partial \psi}{\partial z}\right)_{x,y} \left(\frac{\partial z}{\partial x}\right)_v \right]$$

Implicit functions

If ψ = Constant. then x, y, z cannot vary independently.

$$\psi(x, y, z) = \text{Const.}$$

$$\left.\frac{\partial \psi}{\partial x}\right)_{y,z} dx + \left.\frac{\partial \psi}{\partial y}\right)_{x,z} dy + \left.\frac{\partial \psi}{\partial z}\right)_{x,y} dz = 0, \Rightarrow (A)$$

Let $dz = 0$ $\longrightarrow$ need ψ and z to be Constant.

$$\left.\frac{\partial \psi}{\partial x}\right)_{y,z} + \left.\frac{\partial \psi}{\partial y}\right)_{x,z} \left.\frac{\partial y}{\partial x}\right)_{\psi,z} = 0 \quad \rightarrow \quad (B)$$

$$\left.\frac{\partial y}{\partial x}\right)_{\psi,z} = - \frac{\left.\frac{\partial \psi}{\partial x}\right)_{y,z}}{\left.\frac{\partial \psi}{\partial y}\right)_{x,z}} . \quad (B1)$$

Similarly

$$\left.\frac{\partial z}{\partial x}\right)_{\psi,y} = - \frac{\left(\frac{\partial \psi}{\partial x}\right)_{y,z}}{\left(\frac{\partial \psi}{\partial z}\right)_{x,y}} \quad (B2)$$

$$\left.\frac{\partial z}{\partial y}\right)_{\psi,x} = - \frac{\left.\frac{\partial \psi}{\partial y}\right)_{x,z}}{\left.\frac{\partial \psi}{\partial z}\right)_{x,y}} . \quad (B3)$$

From (A) we write

$$\left.\frac{\partial \psi}{\partial x}\right)_{y,z} \left.\frac{dx}{dy}\right)_{\psi,z} + \left.\frac{\partial \psi}{\partial y}\right)_{x,z} = 0$$

$$\cancel{\frac{\partial \psi}{\partial y}} \left.\frac{\partial x}{\partial y}\right)_{\psi,z} = - \frac{\left.\frac{\partial \psi}{\partial y}\right)_{x,z}}{\left.\frac{\partial \psi}{\partial x}\right)_{y,z}} = \frac{1}{\left.\frac{\partial y}{\partial x}\right)_{\psi,z}} .$$

(B1) × (B2) × (B3) ⇒

$$\left(\frac{\partial x}{\partial y}\right)_{\psi, z} \left(\frac{\partial y}{\partial z}\right)_{\psi, x} \left(\frac{\partial z}{\partial x}\right)_{\psi, y} = -1.$$

If x, y, z depend only on one variable u

$$d\psi = \left[\left.\frac{\partial \psi}{\partial x}\right)_{y,z} \frac{dx}{du} + \left.\frac{\partial \psi}{\partial y}\right)_{x,z} \frac{dy}{du} + \left.\frac{\partial \psi}{\partial z}\right)_{y,z} \frac{dz}{du}\right] du.$$

If ψ is a constant

$$0 = \left.\frac{\partial \psi}{\partial x}\right)_{y,z} \frac{dx}{du} + \left.\frac{\partial \psi}{\partial y}\right)_{x,z} \frac{dy}{du} + \left.\frac{\partial \psi}{\partial z}\right)_{y,z} \frac{dz}{du}$$

If $\frac{dz}{du} = 0$

$$\left.\frac{\partial \psi}{\partial x}\right)_{y,z} \left.\frac{\partial x}{\partial u}\right)_{\psi,z} + \left.\frac{\partial \psi}{\partial y}\right)_{x,z} \left.\frac{\partial y}{\partial u}\right)_{\psi,z} = 0$$

or

$$\frac{\left.\frac{\partial y}{\partial u}\right)_{\psi,z}}{\left.\frac{\partial x}{\partial u}\right)_{\psi,z}} = -\frac{\left.\frac{\partial \psi}{\partial x}\right)_{y,z}}{\left.\frac{\partial \psi}{\partial y}\right)_{x,z}} = \left.\frac{\partial y}{\partial x}\right)_{\psi,z}$$

from B3.

We will need this in deriving several useful relations amongst various physical quantities.