

# Thermal Physics Notes

## 1 Chapter 1

### 1.1 Macroscopic and Microscopic worlds

We live in a macroscopic world but the atoms that dictate our behavior live in a microscopic world; these two worlds are completely different. Apparently, to describe a litre of water you would need close to  $10^{23}$  parameters in the microscopic world to account for the position of each atom. It is obvious that any attempt for such a goal is hopelessly impractical.

But again we shouldn't discourage ourselves, Because well frankly we don't care about the position of 10 billion'th atom in our macroscopic object (given that you are sane ofcourse). So we can use the macroscopic world to describe the microscopic world in a more practical way.

We will look into properties of microscopic world that are independent of their small size or time and make the theory of thermodynamics!

note that macroscopic measurement are super coarse and slow when compared to microscopic phenomena like when you are measuring length of bar then atoms at the edges have been vibrating at the frequency of  $10^{15}$ . so we need to study parameters of microscopic system that are time independent so that we can translate them into the macroscopic world. That's how the study of Thermodynamics begins.

### 1.2 Thermodynamic Parameters

### 1.3 Volume

Note that we will not consider any parameter that is spatially averaged out, for example if we consider a system of 9 atoms then there would be 9 normal modes associated to this system. Consider this nine atom arranged in a line. there would be different normal modes associated to this configuration hence different modes of different frequency but here we would just consider 9 of them. note that if wavelength is small enough then those guys will oscillate in smaller area with higher frequency hence in macroscopic worlds their effect would be averaged out.

but consider this, if the wavelength of these normal mode is larger than half of the length of these arrangement then this system would expand/ contract and it won't be spatially averaged out, hence this is our clue that length/volume should be considered as thermodynamic quantity since it can't be spatially averaged out.

other quantity we may consider is internal energy since it is time independent and it is not spatially averaged out.

Not that these modes in object have energy through which it vibrates. Hence transfer of this energy through these modes is called heat, alternatively transfer of heat through mechanical energy is called mechanical work

## 1.4 Internal energy

Note that now we have the concept of conservation of energy, and now it's obvious that such an energy should be conserved for microscopic particles in our system. But in earlier time people weren't aware of this they abstracted the concept of an thermodynamics concept of energy function that led to development of the concept of internal energy.

## 1.5 Idealisations

Note that here we will assume ideal nature of electrical properties, mechanical properties and etc for considering ideal macroscopic picture we will use parameters like volume and mole number of our chemical composition. These are extensive quantities (i.e. they add up nicely when we mix the system)

## 1.6 Equilibrium

Now note that every system has an influence on itself because of some local events in time. But we need a system that's time independent hence following definition is well justified

**Definition 1** *A system is said to be in equilibrium if it just depends upon Intrinsic parameters like  $U, V, N_1, N_2, \dots, N_n$  where  $N_i$  is the number of moles of the  $i^{\text{th}}$  chemical component.*

Note that these are ideal that that we will study Thermodynamics in some way these are the at the Heart of thermodynamics. This notion is captured by following postulate.

**Postulate 1** *There exist States (called equilibrium states) of a system that are completely determined by the intrinsic parameters of the system Like  $U, V, N_1, N_2, \dots, N_n$ .*

Note that Perfect Equilibrium is a really strong condition to ask for a system, note that structure of glass depends on the way it was cooled hence two glass pieces can never be in equilibrium hence note that we say a circular argument that

**A system is in equilibrium if it is well described by the law's of Thermodynamics**

hence we will only consider such systems in our study of thermodynamics. We call such States **Metastable Equilibrium**.

## 1.7 Walls and Constraints

For Describing a Thermodynamics System we need to specify Boundary condition of That system, in this case those are the walls That separates the system from its surroundings, We can describe such walls based on If it allows distribution of certain parameters or not. We call Them **non-restrictive and restrictive**

## 1.8 Measurability of Energy

Based on Our knowledge of mechanics and atomic structure of Microscopic realm. Its Natural to ask for a Energy function, But the question is Is this Energy function of any use to use? To answer This Question we will Use the concept of Adiabatic walls(for whic its Existence is taken for Granted). Hnece if such A wall exist then we can talk about energy of the system since there will be not energy loss due to heat tha would make our concept og enrgy bit ill-defined. Also Adiabatic wall gives us a way to control such systems since if been done mechanical work upon them Work done would be equal to change in internal energy since there is not other energy loss. Which is what we wan twe are intrested in Diffrence of internal energy of two sattes rather than Absolute internal energy.

## 1.9 Joules Experiment and Irreversibility

Suppose if we have two states **A** and **B** of a system, and we want to go from state **A** to **B** by doing some mechanical work on the system. If we do this in a reversible manner, then the work done will be equal to the change in internal energy of the system. hence concept of Internal energy will be well defined and we would be done, But the million dollar question is Is it always possible? The answer was given by Joule:

**Joule's Statement 1** *If we have two states **A** and **B** of a system, then it is always possible to go from state **A** to state **B** by doing some mechanical work on the system, but it may not be possible to go from state **B** to state **A** in the same manner. Suppose if we have two states with Adiabatic Boundary, and having same chemical composition **A** and **B**. Then, from the two processes  $\mathbf{A} \rightarrow \mathbf{B}$  or  $\mathbf{B} \rightarrow \mathbf{A}$ , one of them is always possible through doing just mechanical work, although both might not be simultaneously possible.*

Note that this statement is not a theorem but rather a postulate, since we have no way to prove it. But we will use it as a postulate in our study of thermodynamics.

## 1.10 Heat

**Defination 2** *Suppose if we have two states **A** and **B** of a system, then the heat transfered from state **A** to state **B** is defined as the difference of Internal energy Of two states and subtracting that with mechanical work done in that process.*

Through our previous discussion we know that Heat is a well-Defined Object hence We can talk about it.

As you might have notice Work and Heat can change depending on the process But the internal energy just depends Upon the diffrence of those two states, To write thsi rigorously we say that

$$dU = dQ + dW$$

where  $dQ$  is the inexact differential of heat and  $dW$  is the inexact differential of work. Note that these are not exact differentials since they depend on the path taken to go from one state to another.

Note that all this at constant mole number.

## 1.11 Goal

Our Goal in thermodynamics is to answer the following questions:

- Given a equilibrium state with a composite system with different internal constraints, if we remove some of the constraints then what will be the new equilibrium state that is thermodynamics summarized in a sentence this answer will be given by the concept of entropy

## 1.12 Entropy Postulate

Note that based on our past experience in physics we want a path that will be taken by system in certain scenarios hence it's natural for us to ask for an extremum principle to play a role here and our next postulate solidifies it

**Postulate 2** *There Exist a function of Extensive parameters( called Entropy  $S$ ) of our composite system, Defined only for Equilibrium states, such that in absence of any internal constraint the values of Extensive parameters change so that  $S$  is Maximized.*

Note that this postulate applies only to equilibrium states.

suppose if we have two equilibrium states A and B of a composite system, of Energy  $U^{(1)}$  and  $U^{(2)}$  respectively, And place diathermal wall between them and wish to learn how those internal energy would change (given conservation of energy of course), then if consider those two system with adiabatic wall measure their internal energy, then find the values of  $U$ 's for which  $S$  is maximized, That will be The required state. The Function  $S$  in terms of extensive parameters is called Fundamental relation, given Fundamental relation we know everything about the thermodynamics system.

**Postulate 3** *The Entropy of Composite System is additive over the entropy of subsystems. The entropy is differentiable, and monotonically increasing function of  $U$ .*

Hence we can say

1.

$$S = \sum_{\alpha} S^{(\alpha)}$$

2.

$$S^{\alpha} = S^{\alpha}(U^{(\alpha)}, V^{(\alpha)}, N_1^{(\alpha)}, N_2^{(\alpha)}, \dots, N_n^{(\alpha)})$$

Note that due to this additivity property we note that Entropy is an homogeneous function of extensive parameters. hence it's kinda linear function of extensive parameters.

**Postulate 4** *Entropy of system vanishes when*

$$\frac{\partial U}{\partial S_{V, N_1, N_2, \dots, N_r}} = 0$$

This statement is equivalent to Third law of thermodynamics we won't care about this in this course but just mentioned it cause, why not? Note that If Entropy is maximized that is equivalent to saying that energy for the System is minimized, this is true when Postulate 3 is true hence that explains our motivation for that postulate.

## 2 Chapter 2

Note that we know that from fundamental relation we can write

$$U = U(S, V, N_1, \dots, N_r)$$

now computing the differential of following gives us following equation

$$dU = \left( \frac{\partial U}{\partial S} \right)_{V, N_1, \dots, N_r} dS + \left( \frac{\partial U}{\partial V} \right)_{S, N_1, \dots, N_r} dV + \sum_{j=1}^r \left( \frac{\partial U}{\partial N_j} \right)_{S, V, N_1, \dots, N_r} dN_j$$

Now note that since following equation had property of linearity over field of real number it is natural to expect that the following derivative are invariant under such scalar transformation.

hence these properties would be called Intensive properties, and does not depend on quantity of the substance ( i.e  $F(\lambda x, \lambda y, \lambda z) = F(x, y, z) \forall \lambda \in R$  )

Hence it would be fruitful to name these derivatives, So here it goes

$$\begin{aligned} \left( \frac{\partial U}{\partial S} \right) &:= T \\ - \left( \frac{\partial U}{\partial V} \right) &:= P \\ \left( \frac{\partial U}{\partial N_j} \right) &:= \mu_j \end{aligned}$$

Hence our equal looks like

$$dU = TdS - PdV + \sum_{j=1}^r \mu_j dN_j$$

Here P is called Pressure, T is called temperature and  $\mu_j$  is called chemical potential of j'th component.

note that these notion coincide with our usual definition of these terms which we will prove later. we define  $-PdV = \bar{d}W$  to be quasi-static work. hence we can write our equations as  $TdS = dU - \bar{d}W$  Given That  $dN_j = 0, \forall j$

Hence from this we can conclude that  $\bar{d}Q = TdS$

### 2.1 Equation of state

Now if we have following three equations

$$T = T(U, X_1, \dots, X_t)$$

$$P = P(U, X_1, \dots, X_t)$$

$$\mu_j = \mu_j(U, X_1, \dots, X_t)$$

then we can retrieve Fundamental Equation from this Hence this is Equavalent to saying fundamental equation. Note that here we have adopted the following notation  $(V, N_1, \dots, N_r) = (X_1, \dots, X_t)$

suppose that  $u := \frac{1}{N}U(S, V, N)$  then  $u = u(s, v)$  , where  $s = \frac{1}{N}S$  and  $v = \frac{1}{N}V$  then we can say that

$du = \frac{\partial u}{\partial v}dv + \frac{\partial u}{\partial s}ds$  from basic calculus

$$\frac{\partial u}{\partial s} = \frac{\partial U}{\partial S} = T$$

$$\frac{\partial u}{\partial v} = -P$$

hence following equation makes sense  $du = Tds - Pdv$ .

Note that we had  $U = U(S, V, N_1, N_2, \dots, N_r)$  but since  $\frac{\partial U}{\partial S} > 0$  we can invert the formula and write the following  $S = S(X_0, X_1, \dots, X_t)$  where  $X_0 = U$  for convienience.

$$dS = \sum_{j=0}^t \left( \frac{\partial S}{\partial X_j} \right) dX_j$$

where  $\left( \frac{\partial S}{\partial X_j} \right) = F_j$  and  $F_j = \frac{P_j}{T}$  where  $P_j = \left( \frac{\partial U}{\partial X_j} \right)$

## 2.2 Thermal Equilibrium

Suppose we had a composite system With two simple system That is fixed ( doesn't allow volume change), and impermeable (doesn't allow exchange of gases) then only remaining thing is U, we will do the following analysis in Entropy representation (Considering U as a independant variable)

We know for two system  $U^{(1)} + U^{(2)} = \text{constant}$  from conservation of energy. note that  $S = S^{(1)} + S^{(2)}$  hence

$$dS = \left( \frac{\partial S^{(1)}}{\partial U^{(1)}} \right) dU^{(1)} + \left( \frac{\partial S^{(2)}}{\partial U^{(2)}} \right) dU^{(2)}$$

hence  $dS = \left( \frac{1}{T^{(1)}} - \frac{1}{T^{(2)}} \right) dU^{(1)}$  using  $dS = 0$  gives the equation  $\frac{1}{T^{(1)}} + \frac{1}{T^{(2)}}$  (we are using inverse formula to highlight the fact that currently we are in Entropy representation Hence S is a function of U , which gives us the inverse formulas for temperature) which is a relation between  $U^{(1)}, U^{(2)}$  which combined with relation given by conservation of energy. Gives us a precise value of both energy for which S is maximized.

Note that as you can see this co-incides with our usual intuition of temperature, which says that it should always go from higher temperature to lower temperature.

## 2.3 Units of temperature

Note that while defining Entropy we didn't specify its dimension, infact it can have arbitrary dimension, since suppose if we add 1 with some arbitrary unit to Original function S then its

Unit will change, but we will still get a function that satisfies the extremum principle. hence we take the most simplest route we **DEFINE** the entropy to be dimension-less , hence temperature gets the dimension of energy. although they both are not the same thing kelvin and joule are just as different as joule and whatever the hell unit of Torque is.

## 2.4 Mechanical Equilibrium

Note that now if we allow Change in volume along with energy then we would have following 2 equations  $U^{(1)} + U^{(2)} = \text{constant}$  and  $V^{(1)} + V^{(2)} = \text{constant}$

Hence

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

Hence following equation simplifies when we add following condition  $dS = 0$  to

$$T^{(1)} = T^{(2)}$$

$$P^{(1)} = P^{(2)}$$

this gives us 4 equations to solve in  $U^{(1)}, U^{(2)}, V^{(1)}, V^{(2)}$  which we all are capable enough to do.

i Think we all are smart enough to guess what will happen if we now vary  $\mu'_j$ s hence it would be more fruitful to just do problems from callen rather than typing all that bullshit (at this point i dont have Github Copilot so writing this file is a pain in ass) hope you understand

## 3 Chapter 3

### 3.1 Euler Equation

From linearity of  $U$  we know that  $U(\lambda S, \lambda X_1, \dots, \lambda X_t) = \lambda U(S, X_1, \dots, X_t)$  now differentiating both sides by  $\lambda X_j$  we get  $\frac{\partial U(\dots, \lambda X_j, \dots)}{\partial S} \frac{(\lambda S)}{\lambda} + \frac{\partial U(\dots, X_j, \dots)}{\partial \lambda X_k} \frac{\partial \lambda X_k}{\partial \lambda} + \dots = U(S, X_1, \dots, X_t)$  now taking  $\lambda = 1$  we get that  $\frac{\partial U}{\partial S} S + \sum_{j=1}^t \frac{\partial U}{\partial X_j} X_j = U$  hence

$$U = TS - PV + \sum_{j=1}^r \mu_j N_j$$

in entropy representation

$$S = \frac{U}{T} + \frac{P}{T} V - \sum_{j=1}^r \frac{\mu_j}{T} X_j$$

### 3.2 Gibbs-Duhem Relationships

Note that all of our extensive parameters are independent of each other. but the intensive parameters that we get are not! there is an implicit relation between them !! this relation IS GIVEN BY Gibbs-duhem relation.

Now note that  $P_k(X_0, \dots, X_{r+2}) = P_k(\frac{X_0}{X_{r+2}}, \dots, \frac{X_{r+1}}{X_{r+2}}, 1)$  hence We have written the entire term in terms of 1 less parameter.

Now Hence we have

$$dU = TdS + SdT + \sum_{j=1}^r dP_j X_j + \sum_{j=1}^r P_j dX_j$$

we know that

$$dU = TdS + \sum_{j=1}^r dP_j X_j$$

subtracting both equations we get

$$SdT + \sum_{j=1}^r P_j dX_j = 0$$

in a single particle composition

$$SdT - VdP + Nd\mu = 0$$

Dividing both sides by  $N$  we get

$$d\mu = -sdT + vdP$$

This gives us a relation between our intensive parameters. hence they are not independent, the explicit form of following relation depends on The equation of fundamental relation we



have, Hence integrating this gives us desired equation of state.  
Hence we can say that in a thermodynamics of  $r$  components we have  $r+1$  degrees of freedom.  
the entropy representation of Gibbs-Duhem equation looks like

$$Ud\left(\frac{1}{T}\right) + d\left(\frac{P}{T}\right) - \sum_{k=1}^r N_k d\left(\frac{\mu_k}{T}\right) = 0$$

### 3.3 Summary till now

we have discussed That the fundamental relation is equivalent of specifying all the equation of states, and the Gibbs-Duhem relation provides a connection between the intensive parameters.

Note that

$$X_j(A, B, \dots, N) = X_j(\tilde{A}, \tilde{B}, \dots, 1)$$

where  $\tilde{A} = \frac{A}{N}$ ,  $\tilde{B} = \frac{B}{N}$ ,  $\dots$ , and  $X_j$  is any intensive parameter.

Hence in single chemical mixture we write just that  $T(s, v)$  instead of  $T(S, V, N)$ .

in energy representation we can write differential of  $U$  in single chemical mixture as

$$du = T(s, v)ds - P(s, v)dv$$

.  
integrating this gives us the fundamental equation needed, although we can also use these  $P, T$  to find other intensive parameters using Gibbs-Duhem relation. then using euler equations to get fundamental relation.

Though as we will see this method is really 'moronic' and only psychopaths use that, all the good people use first method.

suppose we have  $U = U(S, V, N)$  then we also have  $T = T(S, V, N)$  hence in fundamental relation we can eliminate  $S$  and write

$$U = U(T, V, N)$$

. but that wont be equivalent to fundamental relation. since  $T$  here is a differential equation hence it would have arbitrary functions as its solution hence no single path we can take.

### 3.4 Ideal gas

Suppose we have two equation

$$PV = NRT$$

and

$$U = cNRT$$

,then we can write that

$$T = \frac{U}{cN} = \frac{u}{c}$$

and

$$\frac{P}{T} = \frac{R}{v}$$

. hence we can write equation in entropy representation as  $ds = \frac{1}{T}du + \frac{P}{T}dv$  Hence

$$ds = \frac{c}{u}du + \frac{R}{v}dv$$

integrating the following equation gives us

$$S = \frac{cR}{u} \ln u + \frac{R}{v} \ln v + c$$

multiplying both sides by  $N$  gives us

$$S = \frac{cR}{u} N \ln u + \frac{R}{v} N \ln v + C$$

hence this is the fundamental equation for the ideal gas. But note that this is true only for single component mixtures, if we had  $r$  components in our mixture then fundamental equation is written in parametric form of  $T$  as follows.

$$S = \sum_j N_j s_{j0} + \left( \sum_j N_j c_j \right) R \ln \frac{T}{T_0} + \sum_{j=1} N_j R \ln \frac{V}{N_j v_0}$$

$$U = \left( \sum_j N_j c_j \right) RT$$

where all the terms have their usual meaning.

**Theorem 1** *The entropy of a mixture is given by the sum of the entropies of its components measured separately at the same volume and temperature, each weighted by their respective mole fractions.*

- also note that this is measured when all gases are occupying the same volume as the mixture.

we define a term called entropy of mixing, this is given by

$$-R \sum_j N_j \ln y_j$$

where  $y_j = \frac{N_j}{N}$  is the mole fraction of  $j$ 'th component.

### 3.5 Van Der Waals Fluids

Here equation of state is given as

$$\frac{RT}{v-b} = P + \frac{a}{v^2}$$

here we only have one equation hence we will find that equation. We will use entropy representation here although we can do equivalent calculus in energy representation. Hence

the equation that we have is  $\frac{P}{T} = \frac{R}{v} - \frac{a}{v^2T}$ .

let  $T = f(u, v)$  then we can do some algebra (read callen for it) and show that

$$\frac{\partial}{\partial \frac{1}{v}} \left( \frac{1}{T} \right) = \frac{\partial}{\partial \frac{u}{a}} \left( \frac{1}{T} \right)$$

Hence we conclude that  $\frac{1}{T}$  should be a simple sum of those two parameters of partials. Hence we leave rest of calculations to the reader.

### 3.6 Rubber Bands

Here we consider Rubber band then we can write following 2 equations of state

$$U = cL_0T$$

and

$$\mathcal{F} = bT \frac{(L - L_0)}{(L_1 - L_0)}$$

Note that we have chosen the temperature dependence in a specific way to reflect the physical behavior of rubber bands. and so that our 2nd derivative test is maintained. Here we consider length instead of volume and tension  $-\mathcal{F}$  as pressure.

hence

$$dS = \frac{1}{T}dU + \frac{\mathcal{F}}{T}dL$$

. integrating the following gives us the desired fundamental relation.

### 3.7 Some other 2nd derivative

We define three terms first is *isothermal compressibility* given by

$$\kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T$$

next is co-efficient of thermal expansion

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

next is molar heat capacity at constant pressure

$$C_P = T \left( \frac{\partial s}{\partial T} \right)_P$$

All the other 2nd derivatives possible can be obtained from these Derivatives.