

## Revision of Thermodynamics

This section will mainly be a recap of last year's Energy and Matter course

We will start with the Functions of State:

### Functions of State

Functions of state are macroscopic observables that do not change when equilibrium is reached. They are:

$$P, T, V, S, U$$

In thermodynamic equilibrium, these do not depend on time.

A "thermodynamical transformation" is a change taking an initial equilibrium state to a final equilibrium state.

A "quasistatic transformation" is a transformation in which the system passes through equilibrium states at all time. This is impossible to achieve in practice.

A "reversible transformation" is such that it is possible to bring the system back to its initial state with no change in the surroundings. This is only possible with quasistatic transformations and can be plotted on a  $P, V$  diagram as a path.

As explained previously, functions of state have exact differential forms since in a cyclic transformation ( $\oint$ ) there should be no change in their values. This is only true for exact differentials.

Functions of state can be put into two classes:  
extensive or intensive, depending on how the variable  
scales with volume. i.e. for a function of state  $X$ ,  
if volume  $V \rightarrow \lambda V$ :

if  $X \rightarrow \lambda X$  it is extensive  
 $X \rightarrow X$  it is intensive

Extensive:  $V, U, N, S$

Intensive:  $P, T$

An equation of state is an equation relating functions of state. An example of this is the ideal gas law:

$$PV = Nk_B T$$

We will use lots of line integrals when dealing with functions of state.

### Laws of Thermodynamics

0<sup>th</sup> Law:

If system A is in thermal equilibrium with both B and C,  
then systems B and C are in thermal equilibrium with each other.

This law establishes temperature for a system in equilibrium.

1<sup>st</sup> Law:

In a quasistatic transformation, the work  $dW$  and the  
heat  $dQ$  are an exact differential:

$$dW + dQ = dU$$

This law establishes conservation of energy for thermodynamical systems

2<sup>nd</sup> Law:

No process is possible whose sole result is the transfer of heat from a colder body to a hotter body.

This helps us define a function of state  $S$  called entropy:

$$\underline{ds = \frac{\delta Q_R}{T}} \quad \underline{ds \geq \frac{\delta Q}{T}}$$

3<sup>rd</sup> Law:

Entropy at absolute 0 is taken to be 0. It is constant at this temperature.

### The Fundamental Relation of TD

For a reversible heat transfer:

$$\delta Q_R = T ds \quad \delta W_R = -pdv$$

But we know  $dU = \delta Q_R + \delta W_R$  so:

$$dU = \delta Q_R + \delta W_R = Tds - pdv$$

This is the fundamental relation.

Note that  $Tds$  and  $pdv$  are independent of reversibility so the fundamental relation is true for all processes.

$dU = Tds - pdv$  so we can say  $U = U(S, V)$  which implies:

$$dU = \left(\frac{\partial U}{\partial S}\right)_V ds + \left(\frac{\partial U}{\partial V}\right)_S dV$$

$$\text{so} \quad \underline{T = \left(\frac{\partial U}{\partial S}\right)_V} \quad \underline{p = -\left(\frac{\partial U}{\partial V}\right)_S}$$

We can also combine the first and second laws like this:

$$\delta W + \delta Q = dU$$

$$ds \geq \frac{\delta Q}{T}$$

$$\Rightarrow Tds \geq \delta Q = dU - \delta W$$

In an isolated system,  $dU = 0$   $\delta W = 0$

so we find  $Tds \geq 0 \Rightarrow ds \geq 0$  An important result.

Example:

Show that  $dS$  is an exact differential

$$dS = \frac{dU}{T} + \frac{P dV}{T} \quad \text{from fundamental relation, choose } U = U(T, V)$$

$$\text{so: } dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$$

$$\Rightarrow dS = \frac{1}{T} \left\{ \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT \right\} + \frac{P}{T} dV$$

$$= \frac{1}{T} \left(\frac{\partial U}{\partial V}\right)_T dV + \frac{P}{T} dV + \frac{1}{T} \left(\frac{\partial U}{\partial T}\right)_V dT$$

$$dS = \left[ \frac{1}{T} \left(\frac{\partial U}{\partial V}\right)_T + \frac{P}{T} \right] dV + \frac{1}{T} \left(\frac{\partial U}{\partial T}\right)_V dT$$

$$\Rightarrow dS = f_V dV + f_T dT$$

$$\text{so to be exact: } \frac{\partial f_V}{\partial T} = \frac{\partial f_T}{\partial V}$$

$$\frac{\partial}{\partial T} \left[ \frac{1}{T} \left(\frac{\partial U}{\partial V}\right)_T + \frac{P}{T} \right] = \frac{1}{T} \frac{\partial^2 U}{\partial V \partial T} - \frac{1}{T^2} \frac{\partial U}{\partial V} - \frac{P}{T^2} + \frac{1}{T} \frac{\partial P}{\partial T}$$

$$\frac{\partial}{\partial V} \left[ \frac{1}{T} \left(\frac{\partial U}{\partial T}\right)_V \right] = \frac{1}{T} \frac{\partial^2 U}{\partial V \partial T} + \underbrace{\frac{\partial U}{\partial T} \cdot \frac{\partial}{\partial V} \left( \frac{1}{T} \right)}_{=0}$$

so to be exact:

$$\frac{1}{T} \frac{\partial^2 U}{\partial V \partial T} - \frac{1}{T^2} \frac{\partial U}{\partial V} - \frac{P}{T^2} + \frac{1}{T} \frac{\partial P}{\partial T} = \frac{1}{T} \frac{\partial^2 U}{\partial V \partial T}$$

$$\Rightarrow -\frac{1}{T^2} \frac{\partial U}{\partial V} - \frac{P}{T^2} + \frac{1}{T} \frac{\partial P}{\partial T} = 0$$

$$\underline{\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P} \quad \text{to be exact differential}$$

This is confirmed experimentally for an ideal gas and turns out to be true. Therefore  $dS$  is an exact differential.



## Equation of State of an Ideal Gas

The equation of state for an ideal gas is:

$$\text{or } \boxed{PV = nRT} \quad \text{where } N = nN_A$$

## Thermodynamic Potentials

Starting from the fundamental relation:

$$\boxed{dU = Tds - pdv} \quad (1)$$

consider  $pdv$ :  $d(pv) = pdv + vdp$

$$\Rightarrow pdv = d(pv) - vdp \quad \text{subbing this into}$$

$$dU = Tds - d(pv) + vdp$$

$$dU + d(pv) = Tds + vdp \quad \text{we define a new variable } dH$$

$$dH = Tds + vdp$$

$$(2) \quad \boxed{dH = Tds + vdp} \quad \text{where } H \text{ is enthalpy, another Thermodynamic Potential, alongside } U \text{ internal energy.}$$

heat capacity at con. pressure is:

$$C_p = \left. \frac{\partial H}{\partial T} \right|_p$$

We can do the same two more times:

$$(3) \quad \boxed{dF = -SdT - pdv} \quad \text{where } F \text{ is free energy or Helmholtz function}$$

$$(4) \quad \boxed{dG = -SdT + vdp} \quad \text{where } G \text{ is the Gibbs function.}$$

We have thus found all 4 Thermodynamic Potentials.