

Mathematics Methods and Thermodynamics

Classical Thermodynamics

Dr. Andrew King

Chulalongkorn University



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MATHEMATICS

Based on the pre test there are a few pieces of math I'd like to cover briefly

1. When ever you square root there are 2 solutions
2. The differential of e^x is e^x
3. If any two columns or rows of a matrix are identical then the determinate is zero

If anyone wants to go over the specifics of their test and go through the maths please contact me afterwards

OVERVIEW

- ▶ Definition and Laws of Thermodynamics
- ▶ Thermodynamic functions and equations of state
- ▶ State vs Path Variables
- ▶ Exact vs Inexact Differentials
- ▶ Legendre Transform
- ▶ Maxwell Relations

THE LAWS OF THERMODYNAMICS

The 1st Law Energy Cannot be Created or Destroyed

The 2nd Law The Universe is Moving Towards its Most Probable State, which is that of Maximum Randomness

The 3rd Law There is an absolute zero Entropy: A perfectly ordered crystal at zero kelvin has zero entropy

THE LAWS OF THERMODYNAMICS

The 1st Law Energy Cannot be Created or Destroyed

The first law states that energy cannot be created or destroyed only transferred and transformed.

The total energy of any isolated system must therefore be constant.

ENERGY INTERCONVERSION

From \ To	Electrical	Gravitation	Chemical	Radiation	Thermal	Mechanical	Nuclear
Electrical		Electrolysis	Radio	Resistance	Motor		
Gravitation						Falling Weight	
Chemical	Cells			Chemiluminescence	Exothermal	Muscle	
Radiation	Photocell		Photosynthesis		Radiant Heating	Radiometer	Induced Reaction
Thermal	Thermocouple		Endothermal	Lightbulb		Expansion	
Mechanical	Generator	Lifted Weight	Pressure on Equilibrium	Triboluminescence	Friction compression		Bombardment
Nuclear	Electron emission			gamma emission	Fission, Fusion		

THE LAWS OF THERMODYNAMICS

The 2nd Law The Universe is Moving Towards its Most Probable State, which is that of Maximum Randomness

More specifically the entropy of a spontaneous process always increases

It can remain constant in situations such as a steady state

The second law provides a direction for natural process. For example heat will spontaneously transfer from hotter to colder.

THE LAWS OF THERMODYNAMICS

The 3rd Law There is an absolute zero Entropy: A perfectly ordered crystal has zero entropy as it approaches zero kelvin

This allows us to define absolute entropy values and to define the standard enthalpy of a reaction

At absolute zero kelvin all atoms are in the same identical state, the ground state. There is only one possible state and therefore entropy is zero

Some substances have degenerate ground states and so have non zero entropy even at zero kelvin. This is residual entropy. Water ice has a residual entropy of $3.4 \text{ J K}^{-1} \text{ mol}^{-1}$.

THE LAWS OF THERMODYNAMICS

The 1st Law You Cannot Win

The 2nd Law You Cannot Draw

The 3rd Law You Cannot not Play

THE LAWS OF THERMODYNAMICS

The 0th Law If two systems are in thermal equilibrium with a third system, then they are in thermal equilibrium with each other as well

This gives us a foundation in which "all heat is of the same kind" and allows us to create a labelling system for temperature

SYSTEMS

We define three types of system

- ▶ Open System
- ▶ Closed System
- ▶ Isolated System

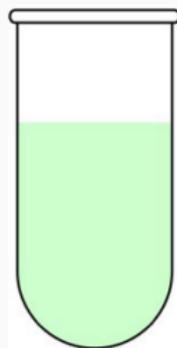
SYSTEMS

We define three types of system

- ▶ Open System
- ▶ Closed System
- ▶ Isolated System

An open system can exchange both matter and energy with the surroundings.

Gases will be lost to the surroundings and so reactions such as the decomposition of $\text{CaCO}_3(\text{s})$ will go to completion



Open

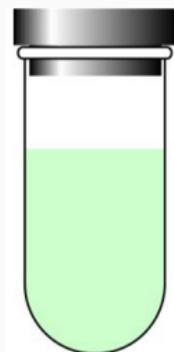
SYSTEMS

We define three types of system

- ▶ Open System
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A closed system can exchange energy but not matter with the surroundings.

Gasses are not lost to the surroundings and so reactions such as the decomposition of $\text{CaCO}_3(\text{s})$ go to an equilibrium



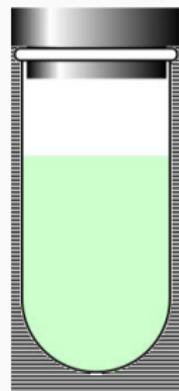
Closed

SYSTEMS

We define three types of system

- ▶ Open System
- ▶ Closed System
- ▶ Isolated System

An isolated system cannot exchange energy or matter with the surroundings. In practise this can be difficult to truly achieve.

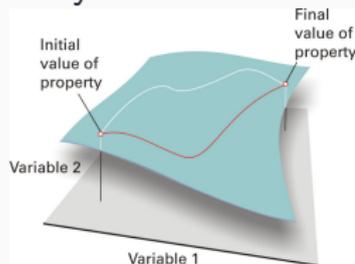


Isolated

FUNCTIONS OF STATE

The system is specified in terms of **functions state**

A function of state is a property that depends only upon the state of system and is independent of how it got there



Altitude is an example of a function of state, since no matter the route taken the value is the same

FUNCTIONS OF STATE

There are five functions of state elementary to thermodynamics

- ▶ Pressure (P)
- ▶ Volume (V)
- ▶ Temperature (T)
- ▶ Energy (U)
- ▶ Entropy (S)

All of thermodynamics can be derived from these function but often we use other functions for convenience

Any function that is made up of only functions of state is also a function of state

FUNCTIONS OF STATE

By convention:

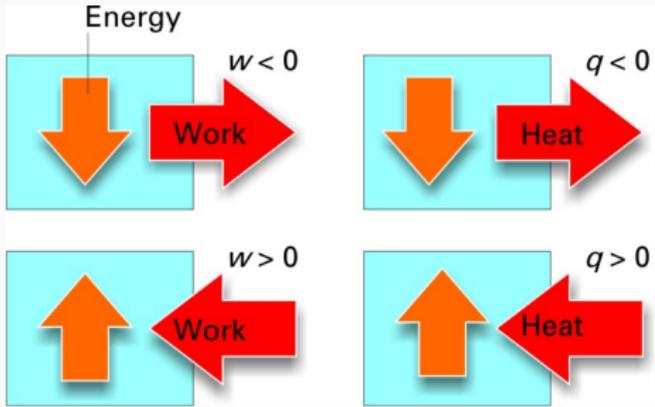
Anything leaving the system is given a negative sign

Anything entering the system has a positive sign

Overall change in a state function, as in change between initial and final state is given with Δ e.g.

$$\Delta P = P_{\text{final}} - P_{\text{initial}}$$

FUNCTIONS OF STATE



Anything leaving the system is given a negative sign
 Anything entering the system has a positive sign

EQUATIONS OF STATE

Only a small number of state functions can be varied independently, they are typically linked by what is known as an **equation of state**

You already know an equation of state for the Ideal Gas

$$PV = nRT$$

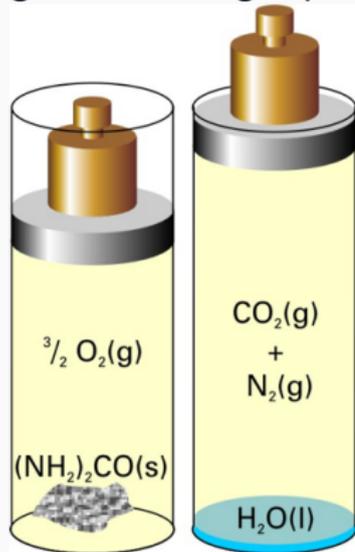
The ideal gas law states that only combinations of P , V and T that fit into this formula can exist

From the ideal gas equation we can see that the internal energy (U) is independent of the pressure and volume, at constant T .

$$\left(\frac{dU}{dP}\right)_T = 0$$

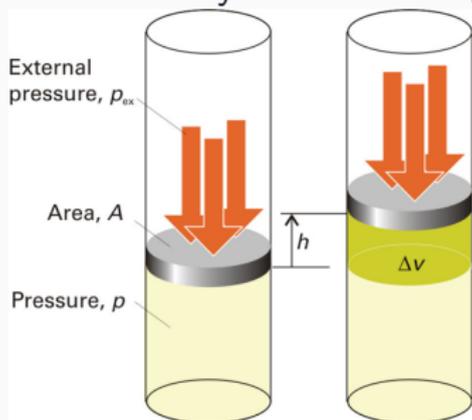
WORK

Work is the effect of a force causing movement in a fixed direction.
This can be visualised with as a reaction causing an expansion in gas and lifting a piston



EXPANSION WORK

Consider an ideal gas contained in a cylinder with a piston defining the boundary between the gas and the surrounding



The gas expands in the container against the area A which is acted upon by an external force F_e , this expansion causes the piston to rise by distance h

EXPANSION WORK

The work done is given by:

$$\begin{aligned}dw &= \text{distance} \times \text{opposing force} \\ &= F_e \Delta h \\ &= P_{ex} (Ah) \\ &= P_{ex} \Delta V\end{aligned}$$

By convention work done on surrounding is negative such that

$$dw = -P_{ex} \Delta V$$

If there is no external pressure no work is done

EXPANSION WORK

As an example consider an expansion of $\Delta V = 5.0 \times 10^{-3} \text{ m}^3$
against atmospheric pressure $P_{\text{ex}} = 101 \text{ kPa}$

$$dw = -P_{\text{ex}}\Delta V$$

$$dw = 1.01 \times 10^5 \text{ Pa} \times 5.0 \times 10^{-4} \text{ m}^3$$

$$dw = -51 \text{ Pa m}^3 = -51 \text{ J}$$

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EXPANSION WORK

- ▶ When there is no external pressure there is no work
- ▶ The higher the external pressure the more work done for the same change in volume

However external pressure cannot be greater than internal pressure

- ▶ Therefore maximum work occurs when $P_{ex} = P$ and the system is in mechanical equilibrium at every stage

EXPANSION WORK

To calculate the amount of work applied w when in equilibrium at every stage we think of the process as occurring in many small steps against a constant external pressure

The smaller we make these steps the more accurately we can calculate the work

What can we do to take the very smallest steps? An integral takes infinity small steps and so is well suited for this task

The maximum work done is therefore given by

$$w = - \int_{V_i}^{V_f} P dV$$

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EXPANSION WORK

$$w = - \int_{V_i}^{V_f} P dV$$

Since we know how pressure and volume are related

$$P = \frac{nRT}{V}$$

We use this to calculate the integral

$$w = - \int_{V_i}^{V_f} \frac{nRT}{V} dV$$

$$w = - nRT \ln \left(\frac{V_f}{V_i} \right)$$

EXPANSION WORK

Consider this example

A piston confines 0.1 mol of Ar(g) in a volume of 1 L at 25 °C.

Two experiments are performed, in the first the piston is allowed to expand through 1 L against a constant 1 atm, in the second experiment it is allowed to expand reversibly and isothermally in equilibrium

Experiment 1

We use

$$\begin{aligned}dw &= - P_{\text{ex}}\Delta V = && - (1 \text{ L} \times 1 \text{ atm}) \\ &= - (1 \text{ L} \times 101 \text{ J L}^{-1}) \\ &= - 101 \text{ J}\end{aligned}$$

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Experiment 2

We use

$$\begin{aligned}w &= -nRT \ln \left(\frac{V_f}{V_i} \right) \\&= - \left(0.1 \text{ mol} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K} \times \ln \left(\frac{2}{1} \right) \right) \\&= -172 \text{ J}\end{aligned}$$

HEAT

Heating (dq) is the transfer of energy as a result of **temperature difference**

If there is no phase change then heating depends upon the specific heat capacity

$$dq = CdT$$

C is the heat capacity

$$dq = nC_m dT$$

C_s is the molar heat capacity

$$dq = mC_s dT$$

C_s is the specific heat capacity

HEAT

For heating at a phase boundary e.g. melting or boiling at constant pressure then

$$dq = dm\Delta H_{fus}$$

dm is the mass of material converted ΔH_{fus} is the latent heat of fusion or vaporisation

HEAT

For a 100 g of water how much is the temperature raised by 1 kJ of energy

$$dq = nC_m\Delta T$$

$$C_{p,m} = 75 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$100 \text{ g H}_2\text{O} = 5.55 \text{ mol}$$

$$\begin{aligned}\Delta T &= \frac{q}{nC_m} = \frac{1000 \text{ J}}{5.55 \text{ mol} \times 75 \text{ J K}^{-1} \text{ mol}^{-1}} \\ &= 2.4 \text{ K}\end{aligned}$$

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INTERNAL ENERGY

In most processes both heat and work occur at the same time
In general for a closed system the change in internal energy is given by

$$\Delta U = w + q$$

U , Internal energy measure the energy stored inside the system, (as kinetic and potential). It is hard to measure absolute U , but changes can be measured

STATE FUNCTIONS

Are heat and work state functions?

Work - No

Think of a system with a gas that we want to expand to 100 cm^3 at a constant Temp. It might expand against an external P thus doing work. However we could also expand it into a vacuum requiring no work

Heat - No

If we want to raise the temp of system by 10°C we could supply the energy required with an electric heater (q would be +ve) or we could stir it vigorously, thus supplying energy as work (q would be 0

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STATE FUNCTIONS

What about internal energy?

Internal Energy - Yes

Consider an isothermal expansion of a gas. As expansion is isothermal (i.e. temp is same at beginning as end). Then mean speed of molecules is same at beginning as end (kinetic energy is unchanged). As in a perfect gas there are no interactions there cannot be a change in potential energy either.

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HEAT OF A REACTION

We can use the heat of the reaction to judge the energy involved in a reaction

If the volume is kept constant then there is no work, $dV = 0$,
 $w = 0$

Then $\Delta U = q$, where q is the heat changes that occur from the rearrangement of bonds and intermolecular forces

However heating is related to temperature by the heat capacity

At constant volume

$$C = \frac{q}{\Delta T}$$

$$\Delta U = q$$

$$C_v = \frac{\Delta U}{\Delta T}$$

ENTHALPY OF A REACTION

In general when a reaction happens and it is open to the surrounding then a change in volume can also happen
As a result not all energy supplied as heat will equate to the change in internal energy some will be lost as work
We use a new term to describe this situation where some of the heat is leaked back to the environment as work. This term is called Enthalpy

ENTHALPY

Enthalpy is defined as:

$$H = U + pV$$

p is the pressure of the system

V is the volume

Since H is defined only with state functions it too is a state function

ENTHALPY

Now consider the change in enthalpy at constant pressure

$$H_2 = U_2 + p_2 V_2$$

$$H_1 = U_1 + p_1 V_1$$

$$\Delta H = \Delta U + (p_2 V_2 - p_1 V_1)$$

At constant pressure

$$\Delta H = \Delta U + P(V_2 - V_1)$$

$$\Delta H = \Delta U + P\Delta V$$

(0.1)

ENTHALPY

$$\Delta H = \Delta U + P\Delta V$$

We can simplify this further, assuming all work is expansion work

$$\Delta U = q - w$$

$$w = -P\Delta V$$

$$\Delta H = q - p\Delta V + P\Delta V$$

$$\Delta H = q$$

(0.2)

ENTHALPY

For solids and liquids the changes in volume and pressure is negligible and $\Delta H = \Delta U$

In an ideal gas however $\Delta PV = \Delta nRT$, which is important especially as T increases

The difference between U and H increases as T increases

ENTROPY

So far we have dealt primarily with the first law. Keeping track of changes in the system and ensuring that the energy is balanced

To tell if a reaction is spontaneous we consider the second law, which deals with entropy

Entropy can be considered as the dispersal of energy and matter

ENTROPY

We define entropy mathematically as this

$$\Delta S = \frac{\delta q_{rev}}{T}$$

δq_{rev} We consider reversible heating as it gives smooth careful transfer of energy and does not generate heat spots that might later disperse spontaneously

Why heat and not work? Entropy considers random motion it follows that to measure changes in entropy we use changes in heat T is the temperature of the surroundings, this takes into account the random motion already present. The more random the surroundings already are the smaller the change in entropy caused by heating

ENTROPY

$$\Delta S = \frac{\delta q_{rev}}{T}$$

This equation holds if we keep T constant, but what happens if we change T ?

This is best done again with infinitesimally small changes...

integration

$$\delta q = C dT$$

$$dS = \frac{C}{T} dT$$

$$\Delta S = \int_{T_1}^{T_2} C \frac{1}{T} dT = C \ln \left(\frac{T_2}{T_1} \right)$$

ENTROPY

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ENTROPY

What about when changing just the volume?

At constant T internal energy does not change with volume

$$\left(\frac{dU}{dV}\right)_T = 0$$

$$\Delta U = 0 = w + q$$

$$q_{rev} = -w_{rev}$$

ENTROPY

Recall that work done as the volume changes is as follows

$$-w_{rev} = nRT \ln \left(\frac{V_2}{V_1} \right)$$

Therefore

$$\Delta S = \frac{q_{rev}}{T} = nR \ln \left(\frac{V_2}{V_1} \right)$$

There is a similar law for pressure

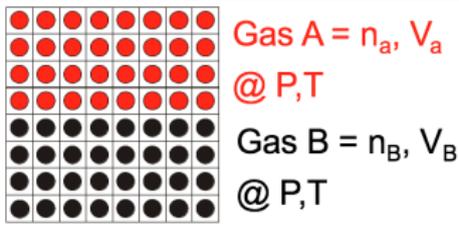
$$\Delta S = \frac{q_{rev}}{T} = nR \ln \left(\frac{P_2}{P_1} \right)$$

ENTROPY

When changing temperature and pressure at the same time, the entropy change is simply the sum of the two

$$\Delta S = \Delta S_{step\ 1} + \Delta S_{step\ 2}$$

We can use this when calculating the entropy change of mixing two gasses



ENTROPY

$$\Delta S_A = n_A R \ln \left(\frac{V_A + V_B}{V_A} \right) = n_A R \ln \left(\frac{n_A + n_B}{n_A} \right)$$

$$\Delta S_B = n_B R \ln \left(\frac{V_A + V_B}{V_B} \right) = n_B R \ln \left(\frac{n_A + n_B}{n_B} \right)$$

$$\Delta S_{mix} = \Delta S_A + \Delta S_B$$

We can simplify this by using mole fractions $\chi_A = \frac{n_A}{n_A + n_B}$

$$\Delta S_{mix} = -n_A R \ln \left(\frac{n_A}{n_A + n_B} \right) - n_B R \ln \left(\frac{n_B}{n_A + n_B} \right)$$

$$\Delta S_{mix} = -n_A R \ln (\chi_A) - n_B R \ln (\chi_A)$$

$$\Delta S_{mix} = -R (n_A \ln (\chi_A) + n_B \ln (\chi_A))$$

ENTROPY

Entropy changes at the phase transition can also be calculated if you consider what is happening

1. At the transition temperature there is no change in T as all energy goes into bond breaking
2. At the transition the transfer of heat is reversible (external pressure is fixed)
3. Since it is at constant pressure then

$$\Delta H = q_p$$

As a result we can say that entropy of a phase transition is

$$\Delta S = \frac{\Delta H}{T}$$

INEXACT DIFFERENTIATION

You may have noticed that some differences used the symbol d while others used δ

The first are exact differences and the latter are inexact differentials

INEXACT DIFFERENTIATION

An inexact differential is a difference that depends upon the path that was taken

An example would be the path length between points A and B on a random walk

INEXACT DIFFERENTIATION

An exact differential is a difference between state functions

An example would be distance between points A and B on random walk

INEXACT DIFFERENTIATION

In thermodynamics we should use δ when ever we take differences of path variables such as heat and work.

For inexact differentials there are typically no antiderivatives (integral)

INEXACT DIFFERENTIATION

You can convert an inexact differential to an exact one with an appropriate integrating factor for example the T in the entropy equation

SUMMARY

1. The laws of thermodynamics govern the chemistry in the world around us
 - 1st Law Energy cannot be created or destroyed
 - 2nd Law Spontaneous reactions are accompanied with a net increase in entropy
 - 3rd Law There is an absolute zero entropy
2. There are three types of systems open, closed and isolated the treatment of these systems helps us derive the laws of the world around us
3. Functions of state are properties that depend only on the final and initial states and not the path taken between states
4. Equations of state relate the state functions and only contain state functions

SUMMARY

5. Any function that contains only state functions is also a state function
6. Work is a path variable and is directed movement
7. Heat is also a path variable and is random movement
8. Enthalpy can reveal the internal energy changes of a reaction while entropy reveals the spontaneity
9. Differences between path variables are inexact and are given the δ sign