

3.23 Lecture 2

The book will be on reserve in the library. The class members do not need to study in depth all of chapter 1 – 4.

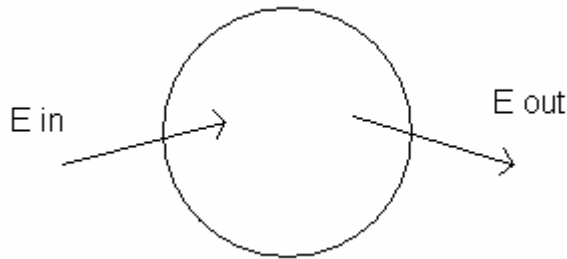
Equation of state

The equations of state that define a relationship between variables are not part of the framework of thermodynamics. The equation of state of an ideal gas is below. Other equations may contain electrical or magnetic constants.

$$pV = nRT$$

First law

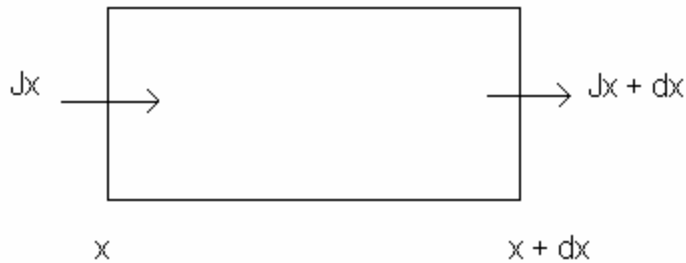
The first law involves the conservation of energy, and this can be a difficult concept. Track energy flows in and out.



The balance of fluxes in and out is labeled ΔE and is expressed as $E_{in} - E_{out}$. Taking a time derivative $\delta\Delta E_{sys} / dt = \delta\Delta E_{in} / dt - \delta\Delta E_{out} / dt$. The flux of energy in is $\delta E_{in} / dt$, and the flux of energy out is $\delta E_{out} / dt$. Below is a mass conservation relation.

$$\Delta(m/v) / dt = -div(J_m)$$

What does the divergence mean? It is the difference of flux at x and $x + dx$



The expression of mass conservation is the same idea as in the 1st law.

$$\delta(E/v) / dt = -div(J_E)$$

Energy of a system

What is ΔE_{sys} ? How can a system change its energy? It can change kinetic energy, gravitational energy, potential, or internal energy. The energy of a system is defined below.

$$\Delta E_{sys} = \Delta E_{KE} + \Delta E_{PE} + \Delta U$$

For stationary systems, the ΔE_{KE} is zero, and the potential and kinetic energy can be lumped together with the internal energy. The internal energy involves all energy that is internal to the system. For instance, the gas in the car and the charge in the battery contribute to the internal energy. Some energy gets stored in microscopic degrees of freedom. A physicist is concerned with how internal energy is stored. Kinetic energy and potential energy is stored in bonds at the microscopic level.

Variables describe the state of a system. A key concept is that the internal energy is defined by the state of the system. There can't be multiple values of energy associated with a given state.

Energy flows

Work, heat, and matter are associated with energy flows. The flow of energy by work and heat flow is not necessarily associated with matter. The flow of matter is a trivial energy flow. An example is joining systems, such as putting fuel in a car.

Work

Work is the transfer of energy by a “displacement” under a “force.” Below are different types of work.

Mechanical	Force times displacement
Electrical	Electric field times charge
Magnetic	Applied field times change in magnetization

The infinitesimal displacement vector is dr . Electric work involves displacing charge, dq , over a potential. Magnetic work results from the change in magnetization under an applied field. Quantities are per volume in electromagnetism. Work can also result from the flow of matter (μ_i, dN_i). The chemical potential is μ_i , and dN_i is the change in mole number.

In general, work results from the displacement of an extensive quantity. The force is labeled “ Y ”, and the response is “ dX ”. The units of the product of the pair of variables are

expressed as energy (J, cal, eV, \dots). The conjugate pair is a term of (X, Y) . For instance, F is conjugate to r .

Stress Strain Tensor

A material can be described with a stress strain vector

$$\begin{aligned}\varepsilon &= (\varepsilon_{11}, \varepsilon_{22}, \varepsilon_{33}, \varepsilon_{12}, \varepsilon_{13}, \varepsilon_{23}) \\ \sigma &= (\sigma_{11}, \sigma_{22}, \sigma_{33}, \sigma_{12}, \sigma_{13}, \sigma_{23})\end{aligned}$$

The normal stress terms are σ_{11}, σ_{22} , and σ_{33} , and the shear stress terms are σ_{12}, σ_{13} , and σ_{23} . The elastic deformation is given by the dot product of stress and strain.

$$V \sigma d\varepsilon$$

Where $d\varepsilon$ is the strain density multiplied by volume for correct units.

Hydrostatic Pressure

$$\begin{aligned}\sigma_{11} &= \sigma_{22} = \sigma_{33} = -P \\ \sigma_{12} &= \sigma_{13} = \sigma_{23} = 0\end{aligned}$$

The convention is a negative sign when the pressure pushes on things. The amount of work is given in the expression below.

$$\begin{aligned}dW &= -PVd(\varepsilon_{11} + \varepsilon_{22} + \varepsilon_{33}) \\ dW &= -PdV\end{aligned}$$

The amount of work done under hydrostatic pressure is equal to $-PdV$.

Deforming a volume is a form of doing work on a material. When pushing, dw is positive, and energy is flowing into the system. It is possible to either absorb energy or give energy to surroundings. The total work is found by integrating the above expression.

There needs to be information known about the material. The functions $p(V)$ and $\sigma(\varepsilon)$ are needed.

Isothermal compressibility and compliance

$$\beta_T = -1/V (\delta V / \delta P)_T$$

The quantity is normalized to be intensive, and the negative sign is there to ensure that β_T is positive.

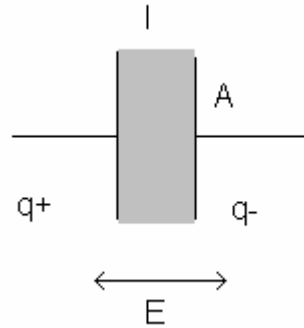
In non-hydrostatic situations, there is an elastic constant called compliance.

$$C_{jkl} = d\varepsilon_{ij} / d\sigma_{kl}$$

The above equations can be thought of as equations of state. They can be functions of the material itself. For instance, the elastic constants can change with temperature.

Dielectric Work

Apply an electric field to a dielectric (not a conductor)



$$dW = \varepsilon dq$$

$$dW = \varepsilon_0 V E dE + V E dP$$

As a potential is applied, an electric field is set up. Work results from moving charge from one side to another.

The permittivity is ε_0 . When applying a potential across the dielectric, there are two ways to transfer energy. Energy is stored in the dielectric, and there is no material constant

$$\varepsilon_0 V E dE$$

There is also energy through polarization. This is a material dependent quantity. There is energy in the material.

$$V E dP$$

In electromagnetism, the field quantity is in terms of volume.

$$P = V P$$

Magnetic Work

The applied field is H and the induction is B . The induced magnetization is M and is stored in the material

$$B = \mu_0 H + \mu_0 M$$

$$dW = nVdB$$

$$dW = \mu_0 n d(VM)$$

The quantity M' is an extensive quantity.

Exact differential

An exact differential is denoted by the symbol d . An exact differential does not depend on path. For instance, it would not matter how P is related to V .

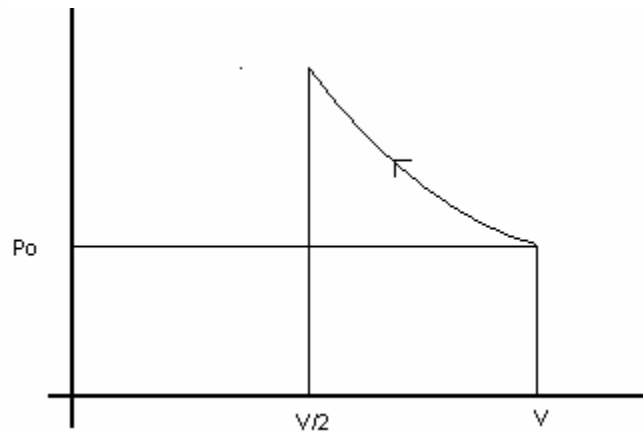
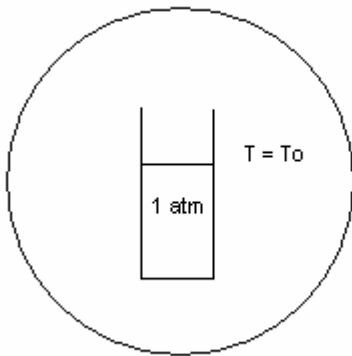
$$\text{Int}[-PdV, 1, 2]$$

$$\text{Int}[\mu_0 n d(VM), 1, 2]$$

Inexact differential

An inexact differential is associated with a path dependent integral. This integral is undefined without path specification.

Example – compress ideal gas



Compress the volume by $1/2$.

$$dW = - \text{Integrate}[-PdV]$$

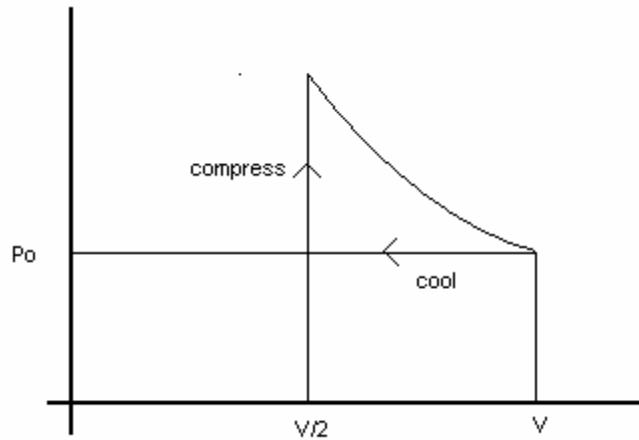
$$P = nRT / V$$

$$dW = - nRT \text{Inegratet}[dV / V, V, V/2]$$

$$dW = -nRT[\ln V / 2 - \ln V]$$

$$dW = RT \ln 2$$

At 298 K, this is equal to 1,717 J. Imagine an alternate path.



$$\begin{aligned}
 W &= -P_o(V/2 - V) + 0 \\
 W &= P_o V / 2 \\
 W &= RT / 2
 \end{aligned}$$

At 298 K, this is equal to 1,239 J.

The integral is path dependent. It is necessary to specify what happens to T as the system traverses a path.

What makes a differential exact?

A differential is exact when it is the differential of some function. The expression of force times displacement is an exact differential if the force is a differential of a function.

$$F = \text{grad}[\varphi(\mathbf{r})]$$

The vector F is a gradient. Below are expressions of the force in 2-D.

$$\begin{aligned}
 F_x &= \delta\varphi/\delta x \\
 F_y &= \delta\varphi/\delta y
 \end{aligned}$$

Get the function when integrating the differential

$$\begin{aligned}
 \text{Integrate}[\delta x] &= \text{Integrate}[\delta\varphi] \\
 &= \text{Integrate}[(\delta\varphi/\delta x)dx + (\delta\varphi/\delta y)dy] \\
 &= \varphi(x, y)
 \end{aligned}$$

Integrate the work flow to get the function back.

Imagine moving an object through a landscape of different height. The height of the room is given as a function, $h(x, y)$, and a contour plot is below.



Imagine an infinitesimally slow process where acceleration is not a concern. Internal energy is conserved. Energy is absorbed as the object moves downhill; work is done on the object. As the object goes uphill, internal energy is released to the environment. Calculate the work done on the system as it moves through the landscape. The gradient is needed.

$$\begin{aligned}
 \text{Pot } E &= mgh(x, y) \\
 \Delta U_{\text{sys}} &= W \\
 &= \text{Int}[F \, dr, 1, 2]
 \end{aligned}$$

The force is the gradient in the potential energy field.

$$F = - \text{grad}[E_{\text{field}}]$$

Integrate the gradient of the field

$$\begin{aligned}
 F &= -\text{Integrate}[\text{grad}[E_{\text{field}}] \, dr, 1, 2] \\
 \Delta U &= -[E_2 - E_1] \\
 \Delta U &= -mg(h_2 - h_1)
 \end{aligned}$$

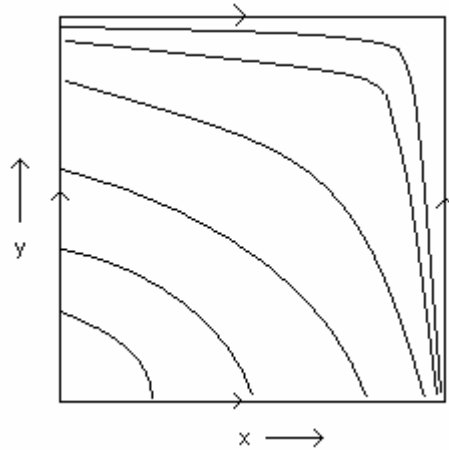
Always check the sign after finding the answer. Positive work comes from going downhill. There is a benefit from the field, and the internal energy has increased.

A conservative force is involved. The result of integrating in a loop is zero. Energy is conserved as the object goes through the loop. The value of the function is the same at the start and at the end.

How does the differential become inexact?

A mechanical example can show how a differential becomes inexact.

Missing forces can cause a differential to become inexact. Imagine a 2-D landscape



There are no work terms as the object travels up along the far left of the landscape and to the right along the top. Missing a force term makes the differential inexact.

An inexact differential is δW . If the differential is of a function, but there is a missing part, (in the case above, y) then the function is not regained upon differentiation. The energy exchange is missing flow.

Consider the differential below

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

This is an exact differential. Integrate around the loop and the same energy is returned.

Heat Flow

It is hard to measure heat flow. People working with heat flow didn't know it was energy flow, not mass flow. Experimentally verifying this is not trivial. Joule and Kelvin were involved, and Joule designed the paddle experiment.

Work and Heat

Work and heat are descriptions of flow of energy. Heat and work are ways to exchange energy. Look at the water balance of a lake. There are different flows, but the water that is the lake is considered water and not named by what it was before entering the lake. For instance, there is no distinction between stream water and rain water.

First Law

The first law is written below

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

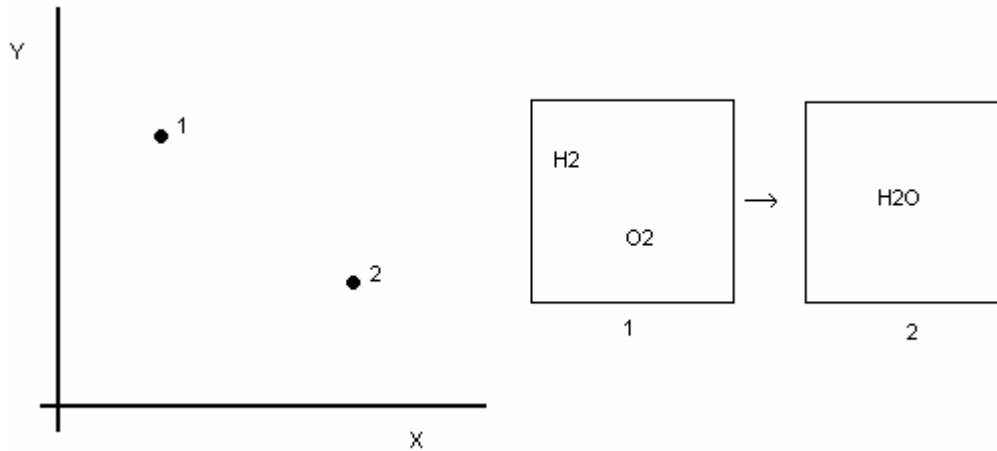
$$dU = \delta W + \text{Sum}[Y_i, dX_i]$$

Types of processes

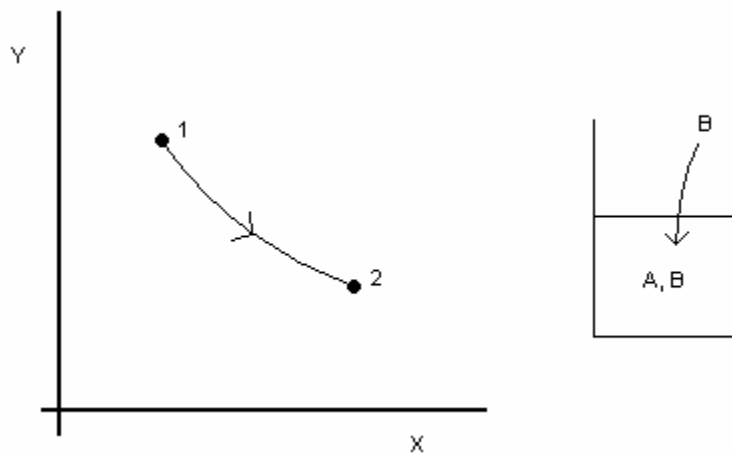
Consider three types of processes

- 1) Discontinuous
- 2) Continuous, quasi-static, irreversible
- 3) Continuous, quasi-static, reversible

1) In a discontinuous process, a state function cannot be defined. The process is discontinuous in thermodynamic quantities. Consider an explosion.



2) A continuous process is slow enough that variables are defined. Consider mixing B into a solution of A and B. The solution is homogeneous after every drop is added. The system is not in equilibrium with what is driving the change. When adding salt to water, the salt is only at equilibrium with the solution when the solution is at the solubility limit. The system in this case is not in equilibrium with the environment along the path.



3) In the third type of process, the system is in equilibrium with the environment along the path from 1 to 2.

There are subtleties in the classification scheme. As problems are worked, it is apparent that a division is distinguishable only with drawn boundaries. The type of process is dependent on where the process is drawn. For the system, there is no difference between state 2 and 3. The same set of points are traversed. There is a difference in the environment. In the second process type, there is more energy dissipated to the environment.