

3.23 Lecture 3

The work, δW , and heat flow, δQ , are inexact differentials, but the sum is an exact differential. The internal energy, U , defines the properties of the system, and the differential is below

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

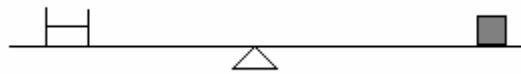
The work is in terms of the force times displacement

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

It is desirable to put this expression in terms of properties of the system. Entropy enters when writing in terms of variables of the system.

Why is it a hard problem showing the equivalence of work and heat

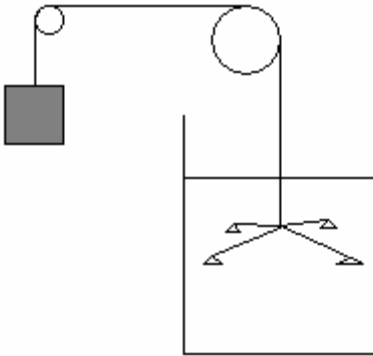
There was a belief that heat was based on particles. This is the caloric theory, and there was criticism from Scheele and Rumford. Scheele was associated with ideas about heat radiating from fire. Rumford did many experiments that brought into doubt the belief that heat is particle based. Imagine a balance with a mass and heated water. Watch the balance as water cools down. The scale should move; it doesn't, and an explanation is that the particles are really light.



Rumford performed experiments involving rubbing two things together. There was no loss of weight or volume. There was an experiment with cannon boring. The cannon was placed in a large vessel of water as horses drilled a hole in a cylinder of metal. The water boiled, and there was a measure of how hot the water gets. The experiment was called "Heat is a form of motion: An experiment in boring cannon. The units were candles. Work was shown to generate heat.

Quantitative experiments were performed by Julius Mayer and Joule. These were experiments involving electrical current in water. There were paddle wheel experiments that related the potential energy to how much water heated.

Mayer did as much work as Joule, but Joule won the fight about who did what first. Kelvin ("Degree Kelvin") was on Joule's side.



Heat Capacity

$$C = (1 / m) \delta Q / \delta T \text{ [J/(mol K)]}$$

The division by mass normalizes this quantity. The term $\delta Q / \delta T$ is not a partial derivative. The term Q is not a function, and δQ is path dependent. A path must be specified for there to be meaning. The variables must be specified to describe what happens to the independent variable.

$$\begin{aligned} (\delta Q)_P \\ (\delta Q)_V \end{aligned}$$

$$C_P = (1 / m) (\delta Q / \delta T)_P$$

$$C_V = (1 / m) (\delta Q / \delta T)_V$$

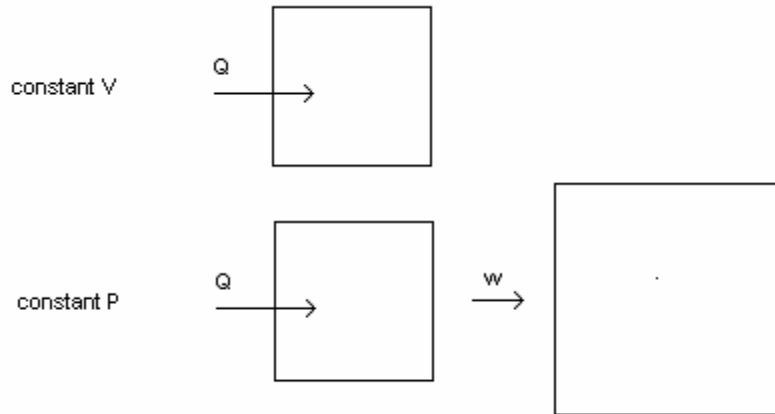
The path does not need to follow a path with a constant variable. The heat capacity along two independent paths can be used to calculate along any path.

Is C_P or C_V greater?

When energy is added to a system the temperature rises.

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

At constant V, the system cannot expand or contract, so no work is performed. At constant P, the work done is negative.



As a result, the change in internal energy is greater in the case of constant P. At constant P, less remains as internal energy. This heat capacity is greater

$$C_P > C_V$$

Typical values for heat capacity

It is useful to remember heat capacity values.

Air	30 J / (mol K)	
Fe	24 J / (mol K)	
H ₂ O	75 J / (mol K)	(1 kcal / kg)

There are simple rules for calculations of heat capacity of gases

Monoatomic	$C_V = 3 / 2 R$
	$C_P = 5 / 2 R$

Diatomic	$C_V = 5 / 2 R$
	$C_P = 7 / 2 R$

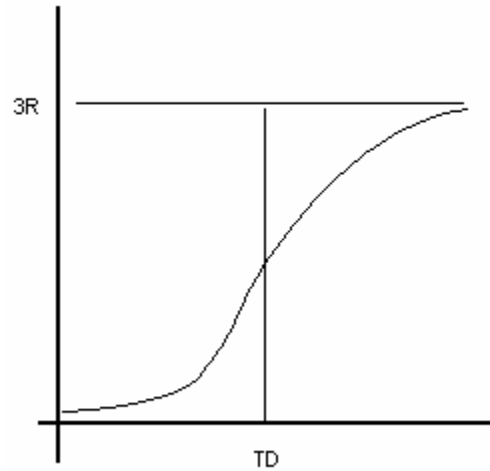
The heat capacity is $\frac{1}{2} R$ times the number of degrees of freedom. There are three velocity degrees of freedom. There are six degrees of freedom minus one constrained by a bond in a diatomic gas. The bond in a diatomic molecule is stiff and doesn't absorb energy, so the bond in a diatomic molecule is not counted. Below are typical values

$$R = 8.314$$

$$(5/2)R = 20.79 \text{ J / (mol K)}$$

$$(7/2)R = 29 \text{ J / (mol K)}$$

In a solid there are three positional degrees of freedom and three velocity degrees of freedom that can absorb energy. When moving an atom in a gas, there isn't a change in energy. In a solid moving an atom takes energy. Below is a plot of the heat capacity of a solid.



Diamond is so stiff that the degrees of freedom cannot be excited at low temperatures. (T_D high)

With stiffer bonding and the freezing of degrees of freedom, the heat capacity is linear. Heat capacity numbers should be in heads of material scientists.

An equation used to relate macroscopic to microscopic is below

$$R = N_A k_B$$

What is true per mole is true per atom. Most electrons do not participate in heat capacity. The electron heat capacity is usually small.

What variables are needed to describe a system?

It's important to distinguish between variables and parameters.

- 1) Work terms

All the extensive parameters are needed. Below is a table of $Y dX$ terms

Y	$Y dX$
Volume	$-p dV$
Length, l	$F dl$
$V \epsilon$	$V \sigma \epsilon$

A	
N_i	

- 2) Conjugate forces
- 3) Temperature
- 4) Conjugate to temperature (S)

Parameters

Anything used to fully describe the internal energy can be a parameter. Parameters do not vary but are used to describe the system. In a closed system, the number of moles is a parameter. The shape can be a parameter, as well as the number of dislocations, which may result from cold-working or annealing. Dislocation density is a parameter because it describes U . The parameter does not need to be a number. The phase of a material, such as liquid, gas, or fcc, could be a parameter. Free energy curves are different for each parameter.

How define a system, how it interacts with environment

A simple system is described by two variables (specify path) Only pdV work is performed. In this simple system, there are two heat capacities, C_P and C_V . When magnetism is added, there must be more path specification.

$$\begin{matrix} C_{P,u} & C_{V,u} \\ C_{P,M} & C_{V,M} \end{matrix}$$

Prove that $(\delta U / \delta P)_T = 0$ and $C_P - C_V = R$

The ideal gas is a prototypical system and is defined by $pV = nRT$ and $(\delta U / \delta V)_T = 0$. There is no volume derivative in internal energy. Prove that $(\delta U / \delta P)_T = 0$ and $C_P - C_V = R$. Remember that this is true only for an ideal gas and that an equation is good if the basis of how it is derived is remembered.

Below is a multivariable differential.

$$dU = (\delta U / \delta T)_V dT + (\delta U / \delta V)_V dV$$

The term $(\delta U / \delta V)_T$ is defined as zero in the definition. For a simple system, the following relationship is true

$$(dU)_V = (\delta Q)_V - pdV$$

The dU term is zero and the term $(\delta Q)_V$ is equal to $nC_V dT$, where n is the number of moles. Therefore,

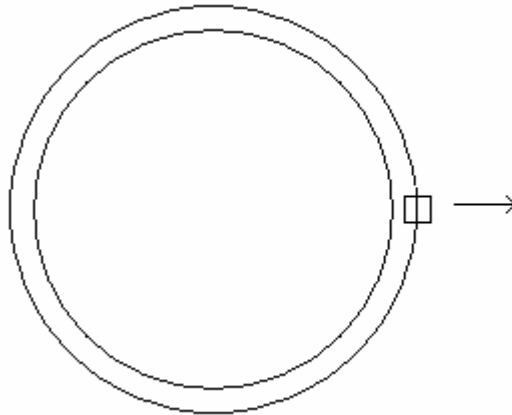
$$(\delta U / \delta T)_V = nC_V$$

$$dU = nC_VdT$$

Under what conditions is this valid? The condition was not used that we are only looking at energy under constant volume. Internal energy is only a function of T. We just found a differential, and the relation is universally true.

Tire

Consider a tire at 40 psi before and after the air is let out. There are two expansions occurring.



Since fewer moles fill the same space after the air is let out, there is an expansion of the air remaining in the tire. The pressure in the tire of gas goes down. There is an expansion in the valve. The air into the valve leaves at a lower pressure.

Look at some element of gas in the tire. Find out what happens to the temperature as the gas is released. What is the temperature as a function of P ? What is the constraint on the system? The tire could be treated as the system at constant volume and the energy balance would be written.

Treat the volume element as the system. There is no heat flow between the elements. Solve under this approximation.

Use the relation of $T(P)$ and $Q=0$. Below is the First Law.

$$dU_{gas} = \delta Q + \delta W$$

Turn the δW into state variables.

$$dU_{gas} = \delta Q - pdV$$

$$dU_{gas} = nC_VdT$$

Eliminate a variable with an equation of state

$$nC_V dT = -pdV$$

$$pV = nRT$$

$$V = nRT/P$$

$$dV = (nRT/P^2)dP + (nR/P)dT$$

$$C_V dT = (RT/P)dP - R dT$$

Solve this equation by a separation of variables.

$$(C_V + R) dT/T = R dP/P$$

$$(T_2/T_1)^{C_P/R} = P_2/P_1$$

$$C_V + R = C_P$$