

# Lecture 06/07 . (Energy).

Eng Chem 140

L 06 : 6.1 - 6.3

L 07 : 6.4

Recall :

## Overview of Part II [Energy] Material

Split into three related sections

### ✓ 5. Basic Physics of Energy (~4/5 lectures)

- Sources & consumption of energy
- Forms of energy, units etc
- Basic balance calculations

Here! →  
=

### 6. Basics of Energy Transfer (~6/7 lectures)

- Thermodynamics
- More sophisticated balance calculations etc.

### 7. Basics of Biological Energetics (~4 lectures)

- How do animals, cells etc store & use energy

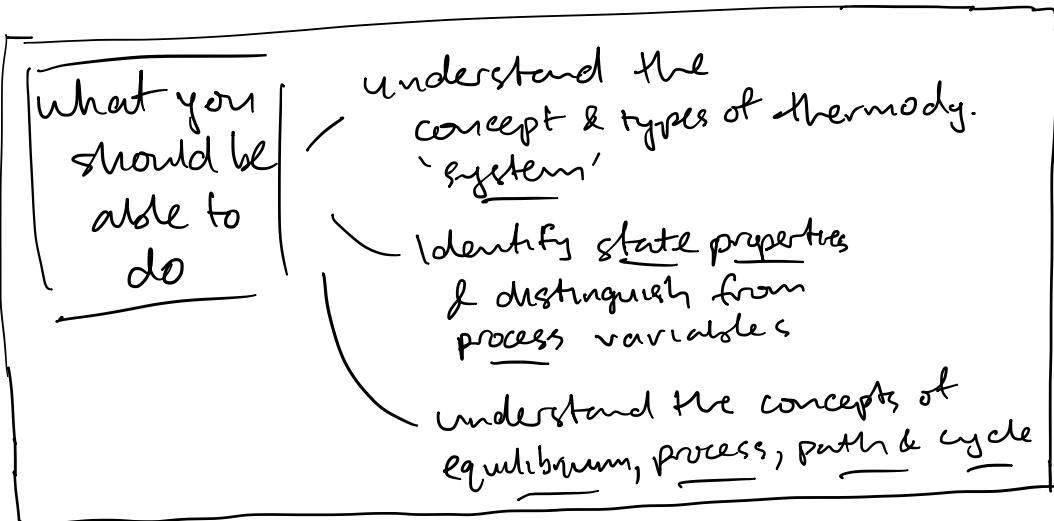
## Lecture 06

## Energy Transfer: Basics of Thermodynamics

TOPICS

= Systems  
Properties, state, equilibrium  
Processes, paths & cycles.

6.1 - 6.3



## Some 2017 Exam Qs

### Thermodynamics – 24 marks

29) Which are the following statements is FALSE, regarding properties of a thermodynamic system: **(1 mark)**

- A. Extensive properties can be converted to intensive properties by dividing by moles
- B. Intensive properties are independent of the quantity of matter
- C. Volume is an extensive property
- D. Heat is a property of the system
- E. Temperature is a property of the system

Answer: \_\_\_\_\_

30) One mole of an ideal gas, initially at  $T_1 = 25^\circ\text{C}$ ,  $P_1 = 101.3 \text{ kPa}$  and  $V_1 = 24.5 \times 10^{-3} \text{ m}^3$ , undergoes the following mechanically reversible processes in a closed system:

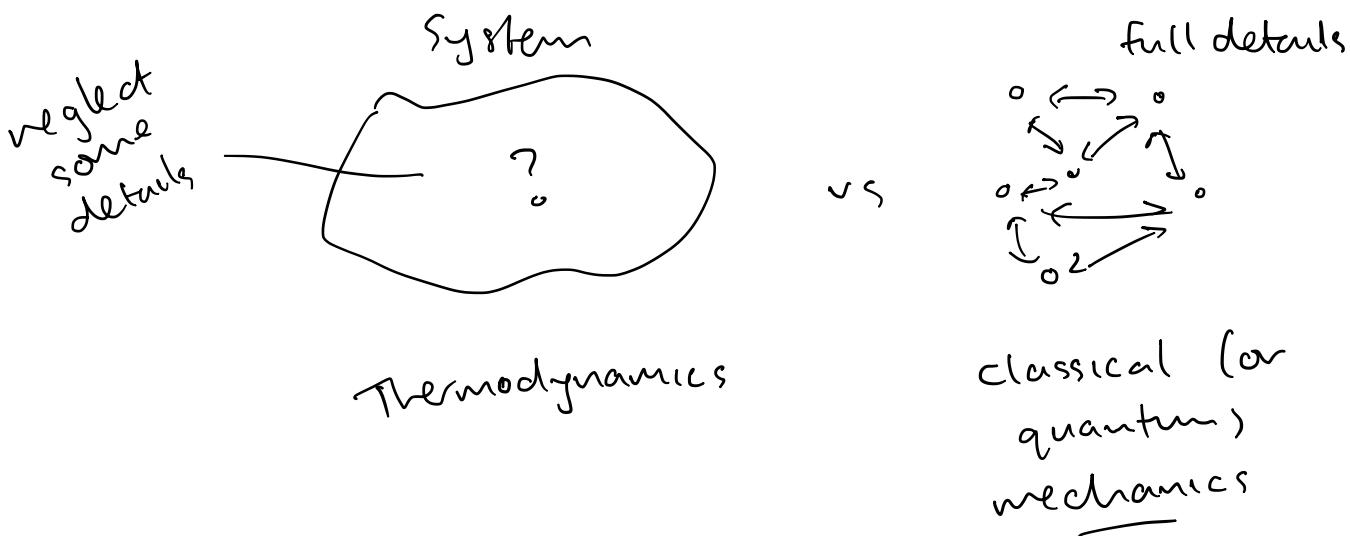
**Process I:** Adiabatic compression to  $T_2 = 473 \text{ K}$ ,  $P_2 = 505 \text{ kPa}$ , and  $V_2 = 7.65 \times 10^{-3} \text{ m}^3$ .  
**Process II:** Isobaric cooling to  $T_3 = 25^\circ\text{C}$ , and  $V_3 = 4.89 \times 10^{-3} \text{ m}^3$ .

- a. Draw these two processes on a pressure-volume graph, label the axes, identify each state, process and path. **(3 marks)**

## Overview of thermodynamics

Thermodynamics is a general science of (macroscopic) 'systems' & energy transfer between systems, & doesn't require detailed knowledge of the internal structure of the system, nor the specific process carried out.

- applies to 'all systems' regardless of details
- this is a strength & a weakness
  - ↳ often focus on what's possible, not what actually happens, nor the rate at which it happens
  - ↳ can often only provide bounds or best case/idealised answers (eg reversible case)
  - ↳ need additional constitutive assumptions for more detailed models/answers



As an extension of mechanics (to macroscopic, thermal, imperfect systems)

Thermodynamics:

→ allows us to extend mechanics to deal with macroscopically 'irreversible' (\*) / imperfect systems

↳ 'Irreversibility' is the price for partial, macroscopic description

↳ e.g. work 'lost' to 'heat' } will look at what this means

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(\*) at the most fundamental level, all key physical processes are thought to be reversible, hence 'pure mechanics' (classical, quantum etc)

BUT:

⇒ our partial descriptions & boundary conditions 'create' asymmetries / irreversibility.

⇒ we always work with partial descriptions ('coarse graining') & hence all 'real' processes we deal with are irreversible!

⇒ irreversible?

think: - imperfect/incomplete description  
- lump missing things as 'other stuff'

⇒ 'other stuff'?

- heat, temperature & entropy  
are 'macroscopic' / 'higher level',  
manifestations of 'lower level'  
mechanical processes

[Preview of the]

Laws (in brief - see later for proper def's)

Law 0 : Establishes concepts of thermal equilibrium & temperature

Law 1 : Energy is conserved

Law 2 : Entropy in an isolated system is non-decreasing

Upshot:

- energy can be transferred via both work & heat & is conserved

- There are limitations on how efficiently energy can be transferred between macroscopic systems, & this is related to entropy increase

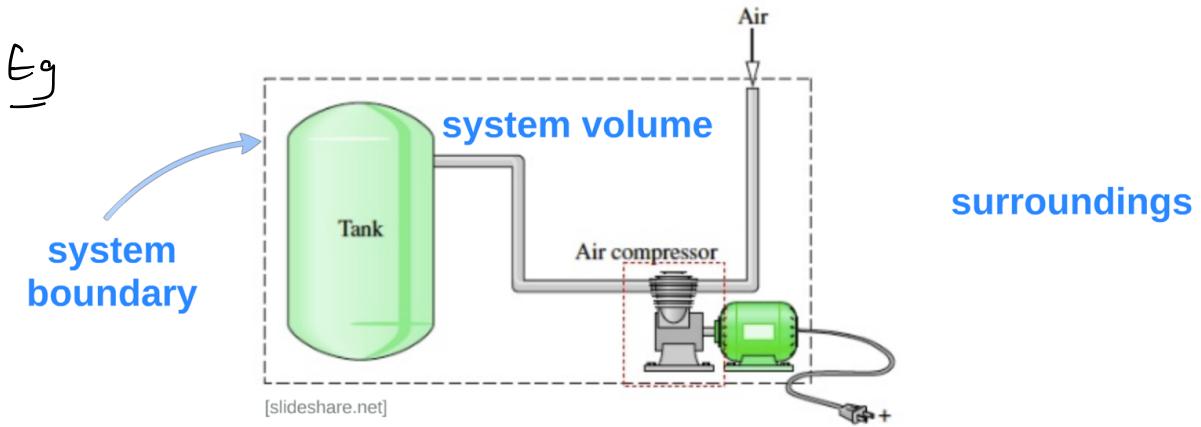
interplay  
between  
1<sup>st</sup> &  
2<sup>nd</sup>  
Law.

Note: we haven't properly defined  
'heat' etc yet  $\rightarrow$  next lecture!

## A thermodynamic system

'System': object / collection of objects or region that an analysis is performed on

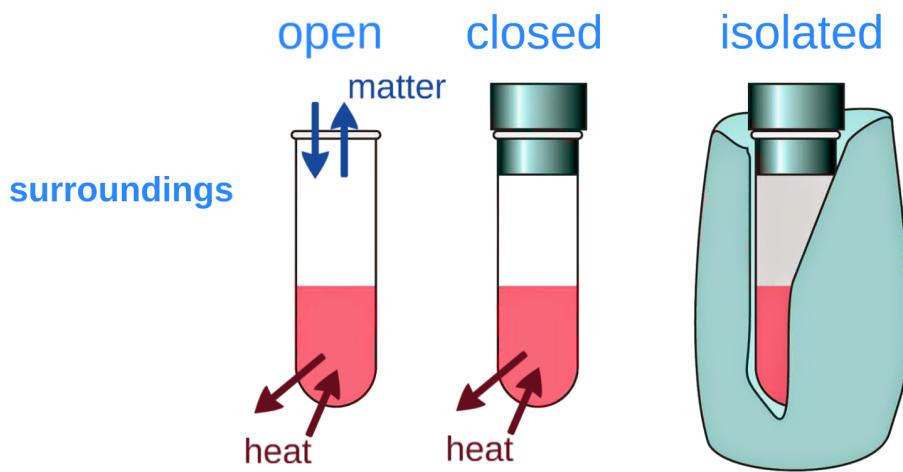
- Has
1. A boundary
  2. A volume
  3. A surroundings
- } hence a macroscopic region/object



Choosing a system defines what interactions are possible between the system & surroundings

- Open : Both matter & energy can cross boundary
- Closed : Energy can cross, matter cannot
- Isolated : Neither matter nor energy can cross

Eg.



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Key: what interactions (transfers) are possible:

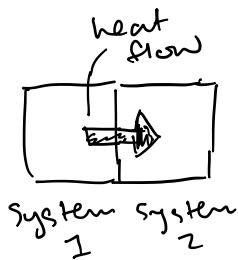
- mass
  - energy } ?
- 

Question: Classify (approx)

- River ← open
  - Interior of closed can of L&P ← closed
  - Interior of a closed freezer that is turned off ← isolated
  - Interior of a closed freezer that is turned on ← closed
  - A cat ← open
-

## Types of energetic interactions

- We assume the basic ideas from mechanics are given
  - eg mechanical work & mechanical energy
- We usually classify eg electrical current etc as 'mechanical' processes here
- A thermal interaction is a type of interaction that is ----  
'not (macroscopic) mechanical work' (or mass transfer)
  - ↳ 'something else' } (at macroscopic level)
- This arises because we know from experience we can place two closed systems in contact & have them exchange energy without either doing (macroscopic) mechanical work



⇒ this form of 'thermal energy transfer' or 'thermal work' will be called 'heat' & discussed in detail later

Remember - at a microscopic level, heat is a form of mechanical work e.g.  $\text{O} \begin{smallmatrix} \leftarrow \\ \rightarrow \\ \dots \end{smallmatrix} \text{O} \rightarrow \text{O} \begin{smallmatrix} \leftarrow \\ \rightarrow \\ \dots \end{smallmatrix} \text{O}$  → pass on vibrations

- but we neglect some detail, so call it 'thermal' work or thermal energy transfer

## Properties, Equilibrium & State

- A thermodynamic property is any measurable characteristic of a system 'at equilibrium' eg volume, pressure, temperature--

- Properties can be
  - intensive } independent of size (mass, vol, etc) of system
  - extensive } depend on size (mass, vol, etc) of system

examples } extensive : volume, mass, energy, amount (moles), entropy, heat capacity  
} intensive : temperature, density, pressure, concentration, specific heat capacity

can convert extensive  $\rightarrow$  intensive

by dividing by size eg moles, vol etc

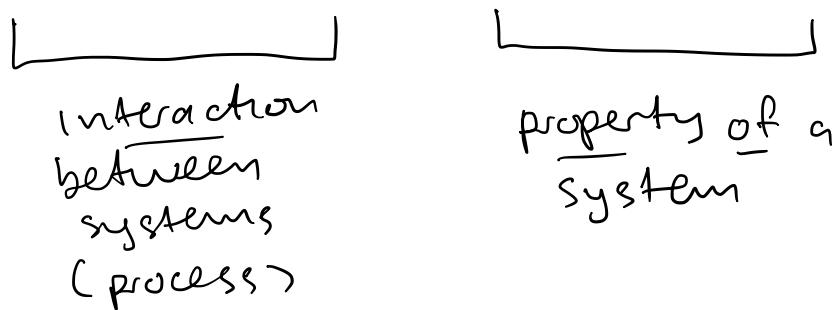
(or by taking ratio of two extensive quantities)

$\Rightarrow$

- Note :

Heat & Work are interactions between systems & are not properties of systems

Think: bank transfer vs bank balance



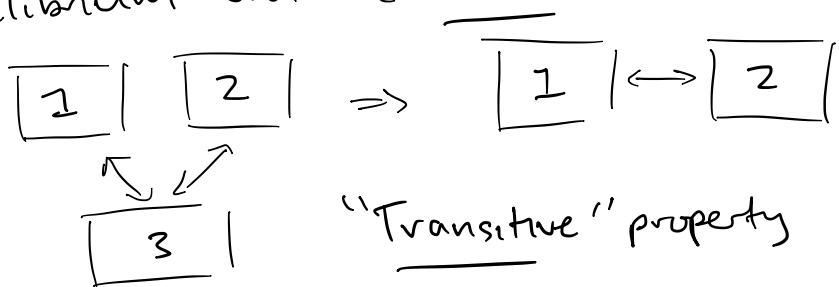
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# Equilibrium?

- equilibrium: 'nothing is happening'
  - neither the system nor environment are changing in time
  - 'no interactions'/processes are occurring
- Thermal equilibrium
  - In thermal equilibrium when they are placed in thermal contact & no heat flows between them

## Zeroth law:

- Two systems in thermal equilibrium with a third are in thermal equilibrium with each other



- establishes 'empirical temperature' as the key property we can use to characterise thermal equilibrium

## Upshot:

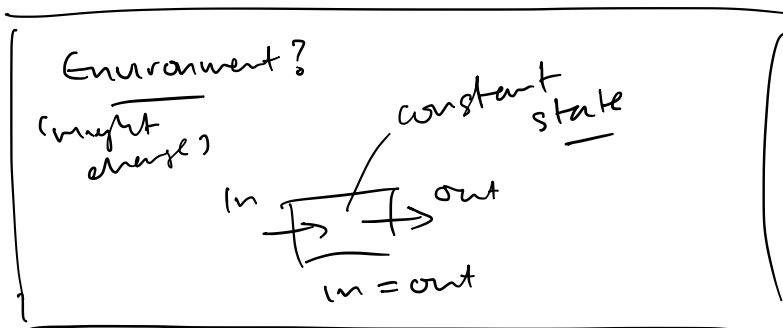
We can safely compare systems thermally using real numbers  $T$  since

$$T_1 = T_3 \text{ & } T_2 = T_3 \Rightarrow T_1 = T_2$$

(If didn't satisfy zeroth law then couldn't use a real number since these are always transitive)

## Steady state

- system properties (measurable characteristics) are not changing, but the environment may be
- interactions may be occurring as long as system properties unchanging



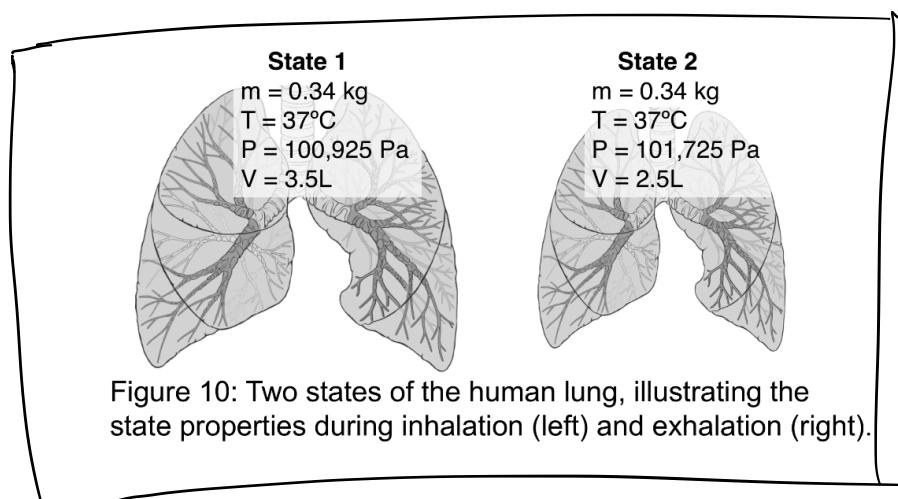
## State?

- List of properties that are sufficient to describe the system (for our purposes)

e.g. a  $(P, V)$  system is described by pressure & volume

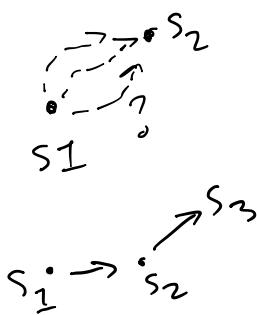
- independent of path, history etc

Example!



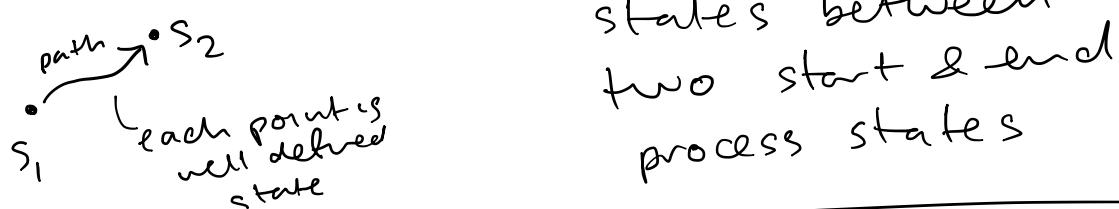
# Process, paths & cycles

- o Process :- a change (or series of changes) from one equilibrium state to another

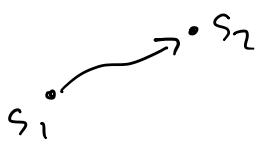


- we don't necessarily specify the path between, but do give the start & end at least

- o Process path: a continuous sequence of equilibrium states between two start & end process states

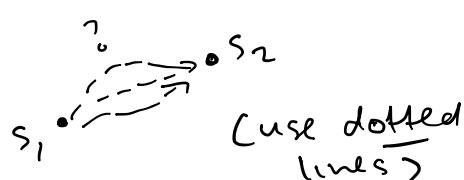


- o Quasi-equilibrium process:



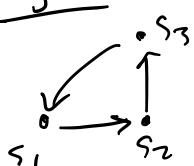
system follows a well-defined path (sequence of equilibrium states) during process

- o Non-equilibrium process:



system doesn't have a well-defined path (continuous sequence of equilibrium states) during process

- o Cycle



- Process that returns to initial state

- can be equilibrium or non-equilibrium process

Example: beating heart

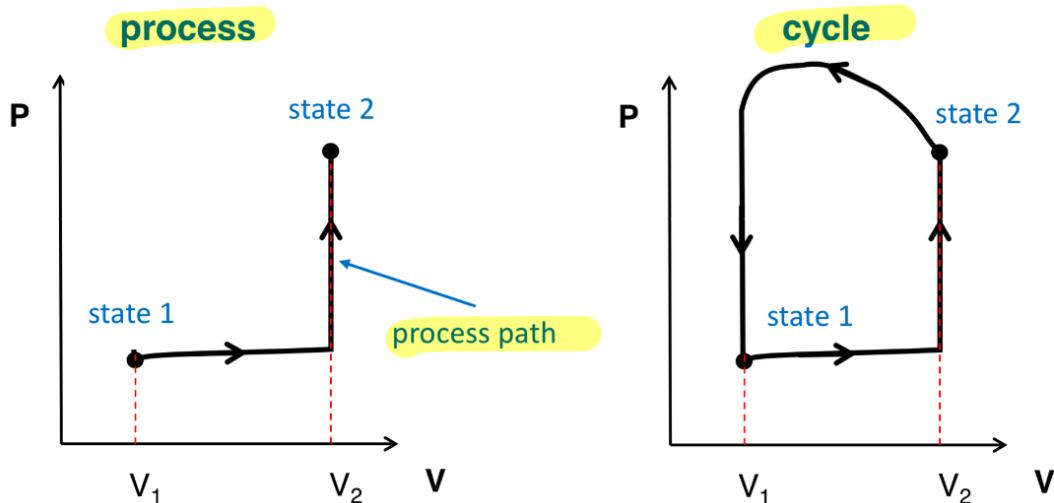


Figure 11: Process (left) and complete cycle (right) of the beating heart (i.e. the cardiac cycle). Sometimes referred to as a 'PV loop'.

Some 2017 Exam Qs

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**Answer:** \_\_\_\_\_

30) One mole of an ideal gas, initially at  $T_1 = 25^\circ\text{C}$ ,  $P_1 = 101.3 \text{ kPa}$  and  $V_1 = 24.5 \times 10^{-3} \text{ m}^3$ , undergoes the following mechanically reversible processes in a closed system:

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## Lecture 07

## Energy Transfer; Basics of Thermodynamics

Topics

Heat & thermal energy  
Internal energy  
Heat capacity  
Latent heat & phase transitions  
Types of heat transfer

6.4

what you  
should be  
able to  
do

- understand the concepts of heat, thermal energy & internal energy
- do basic calculations involving heat capacity & latent heat

## 2017 Exam

31) Briefly define Internal Energy, U

Total energy stored in system,  
incl. translational, rotational (1 mark)  
vibrational & chemical energy of molecules

## Course book

Given the specific heat capacity of water is  $4.186 \text{ J.g}^{-1}\text.{}^{\circ}\text{C}^{-1}$ , how much heat is required to raise the temperature of 200 g of water from 20 to  $50^{\circ}\text{C}$ ?

A 5.10 g sample of iron is heated from  $36.0^{\circ}\text{C}$  to  $75.0^{\circ}\text{C}$ . The amount of energy required is 89.5 J. What is the specific heat capacity of iron?

## Work & Energy

We can usefully think of energy as the capacity to do work or transfer heat

Recall : - heat is like 'thermal work' defined as 'not mechanical work'

- introduce because we look at macroscopic, imperfect systems

→ 'other stuff'  
(microscopic mechanical work)

## Internal energy

'Total' energy stored inside system

⇒ includes the molecules'

- translational, rotational & vibrational
- chemical energy in bonds
- long range interactions between molecules
- etc

note!

↓  
} thermal  
} (microscopic  
kinetic)

⇒ only defined up to a reference value / state  
so don't actually need to track  
all, just those that will change.

# Internal energy for ideal gas (easy case)

- o Ideal gas :- molecules don't interact
  - internal energy is sum of (microscopic) kinetic energy of molecules
  - this is (approximately) just the thermal energy (microscopic kinetic energy)
  - thermal energy of an ideal gas is proportional to temperature

only  
for  
ideal  
gas

## Energy of ideal gas

$$\text{E}_{\text{molecule}} = \frac{3}{2} k_B T \quad \left. \begin{array}{l} \text{micro} \\ \text{kinetic energy} \\ \text{can derive from} \\ \text{from micro:} \end{array} \right\}$$

(prop.  $\rightarrow$  to temp.)

Boltzmann's constant

Total internal:

$$U = E_{\text{molecule}} \times \text{molecules}$$

$$= \frac{3}{2} k_B N T = \frac{3}{2} n R T \quad \left. \begin{array}{l} k_B: \text{Boltzmann's} \\ \text{constant} \\ R: \text{ideal gas} \\ \text{constant} \end{array} \right\}$$

$\times \text{Temp.}$

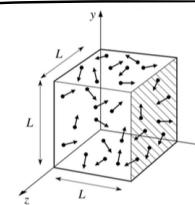


Figure 12: Ideal gas within a volume,  $L^3$ . An ideal gas considers collisions between point-like particles to be elastic and there are no other interactions amongst the particles.

$N$ : number of molecules  
 $n$ : number of moles

So:

key:  
(prop.  $\rightarrow$  to temp.)  $\rightarrow U = \frac{3}{2} n R T$  }  $\left. \begin{array}{l} \text{internal energy for an} \\ \text{ideal gas} \\ (= \text{thermal energy here}) \end{array} \right\}$  only dep. on T & amount

- o Most common eqn used in ideal gas problems:

Ideal gas law (constitutive eqn).

can derive from microscopic/statistical mechanics

empirical/constitutive eqn

so:

$$\left. \begin{array}{l} PV = N k_B T \\ PV = n R T \end{array} \right\}$$

two equiv. forms.

$$k_B = \frac{n}{N} R$$

$\hookrightarrow$  links micro & macro

(for fixed mass,  
two of  $P, V, T$   
define state  
 $\rightarrow$  other is  
det. by these  
via law)

## Heat Capacity

- Measures amount of heat (energy) required to change a given substance's temperature by a given amount

Symbol: Capital C

Units :  $\left\{ \begin{array}{l} J \cdot K^{-1} \\ J \cdot {}^\circ C^{-1} \end{array} \right. \xleftarrow{\text{SI}} \begin{array}{l} (\text{energy per } \Delta \text{Temp}) \\ (\text{energy per } \Delta \text{Temp}) \end{array}$

→ extensive quantity: more mass, more capacity

- Can also measure per unit mass

Call 'specific' heat capacity

Symbol: lower-case c

Units :  $\left\{ \begin{array}{l} J \cdot K^{-1} \cdot g^{-1} \\ J \cdot {}^\circ C^{-1} \cdot g^{-1} \end{array} \right. \xleftarrow{\text{SI}} \begin{array}{l} (\text{energy per } \Delta \text{temp per mass}) \\ (\text{energy per } \Delta \text{temp per mass}) \end{array}$

- Need to specify whether at constant pressure, volume etc

$C_p$  constant pressure

$C_v$  constant volume

## Heat Capacity

Key equations:

$$\left. \begin{array}{l} Q = C_p \Delta T \\ Q = c_p m \Delta T \end{array} \right\}$$

constant pressure  
←  $C$  is extensive.  
←  $c$  per unit mass (specific)

⇒ can tell by units!

Examples:

Given the specific heat capacity of water is  $4.186 \text{ J.g}^{-1}\text.{}^{\circ}\text{C}^{-1}$ , how much heat is required to raise the temperature of 200 g of water from  $20^{\circ}\text{C}$  to  $50^{\circ}\text{C}$ ?

$$\begin{aligned} Q = c_p m \Delta T &= 4.186 \frac{\text{J}}{\text{g.}^{\circ}\text{C}} \times 200 \cancel{\text{g}} \times (50 - 20)^{\circ}\text{C} \\ &= 25116 \text{ J} \approx 25 \cancel{\text{kJ}} \end{aligned}$$

A 5.10 g sample of iron is heated from  $36.0^{\circ}\text{C}$  to  $75.0^{\circ}\text{C}$ . The amount of energy required is 89.5 J. What is the specific heat capacity of iron?

$$\begin{aligned} Q = c_p m \Delta T \Rightarrow c_p &= \frac{Q}{m \cdot \Delta T} \\ &= \frac{89.5}{5.10 \times (75 - 36)} \frac{\text{J}}{\text{g.}^{\circ}\text{C}} \\ &\approx 0.45 \frac{\text{J.g}^{-1}\text.{}^{\circ}\text{C}^{-1}}{} \end{aligned}$$

A 350.0 g sample of metal is heated to  $100.0^{\circ}\text{C}$ , then dropped into 400.0 g of water at  $21.4^{\circ}\text{C}$ . The temperature of the water rises to  $28.0^{\circ}\text{C}$ . Assuming there is no heat lost to the surroundings, what is the heat capacity of the metal?

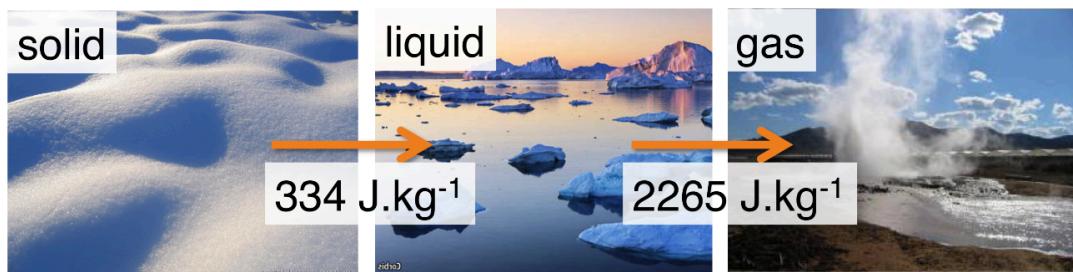
$$\begin{aligned} Q_{\text{water}} &= c_p m \Delta T = 4.186 \times 400 \times (28 - 21.4) \\ &\approx 11,051 \text{ J} \end{aligned}$$

Assume metal cools to equil. with water

$$\begin{aligned} Q_{\text{metal}} &= Q_{\text{water}} \\ &= c_{p,\text{metal}} \times 350 \times (100 - 28) \\ \Rightarrow c_{p,\text{metal}} &= \frac{11,051}{350 \times (100 - 28)} \approx 0.44 \frac{\text{J}}{\text{g.}^{\circ}\text{C}} \\ \Rightarrow c_{p,\text{metal}} &= \underline{m \times c_{p,\text{metal}} = 350 \times 0.44 = 154 \frac{\text{J}}{\text{g.}^{\circ}\text{C}}} \end{aligned}$$

## Latent heat & phase transitions

=> Amount of heat (energy) required to completely carry out a change in phase (e.g solid, liquid, gas) for a given substance



Eg latent heat of fusion: melting  
latent heat of vaporisation: boiling

Can measure extensively or intensively

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Examples:

Table 4: Examples of specific latent heat of fusion and specific latent heat of vaporisation.

Substance	Specific Latent Heat of Fusion ( $\text{kJ} \cdot \text{kg}^{-1}$ )	Melting Point ( $^{\circ}\text{C}$ )	Specific Latent Heat of Vaporisation ( $\text{kJ} \cdot \text{kg}^{-1}$ )	Boiling Point ( $^{\circ}\text{C}$ )
Water	334	0	2264.76	100
Alcohol, ethyl	108	-114	855	78.3
Oxygen	13.9	-219	213	-183
Hydrogen	48	-259	455	-253
Carbon dioxide	184	-78	574	-57
Lead	23	327.5	871	1750

What is the energy (heat) required to convert 250 g of ice to liquid water?

# Latent heat & phase transitions

## examples

Table 4: Examples of specific latent heat of fusion and specific latent heat of vaporisation.

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What is the energy (heat) required to convert 250 g of ice to liquid water? (melting)  
/fusion

$$0.25 \text{ kg} \times 334 \frac{\text{kJ}}{\text{kg}} = 83.5 \text{ kJ}$$

(vapourisation)

What is the energy required to evaporate 28 g of sweat? Given the specific heat capacity of water is 4.18 J.g<sup>-1</sup>.°C<sup>-1</sup>, what is the effective cooling effect of this evaporation for a 70 kg person?

$$0.028 \text{ kg} \times 2264.76 \frac{\text{kJ}}{\text{kg}} \approx 63 \text{ kJ}$$

$$Q = c_p m \Delta T$$

$$\Delta T = \frac{Q}{c_p \cdot m} = \frac{63 \times 10^3 \text{ J}}{4.18 \frac{\text{J}}{\text{g}^\circ\text{C}} \times 70 \times 10^3 \text{ g}}$$
$$\approx 0.22^\circ\text{C}$$

# Heat transfer

- 1 - Conduction
- 2 - Convection
- 3 - Radiation

Key types

High temp  $\rightarrow$  Low Temp.

Example  
 $\rightarrow$  next lecture

Humans must lose  $\sim 90 \text{ J/s}$  (**90 W**) of heat as a result of basal metabolism

