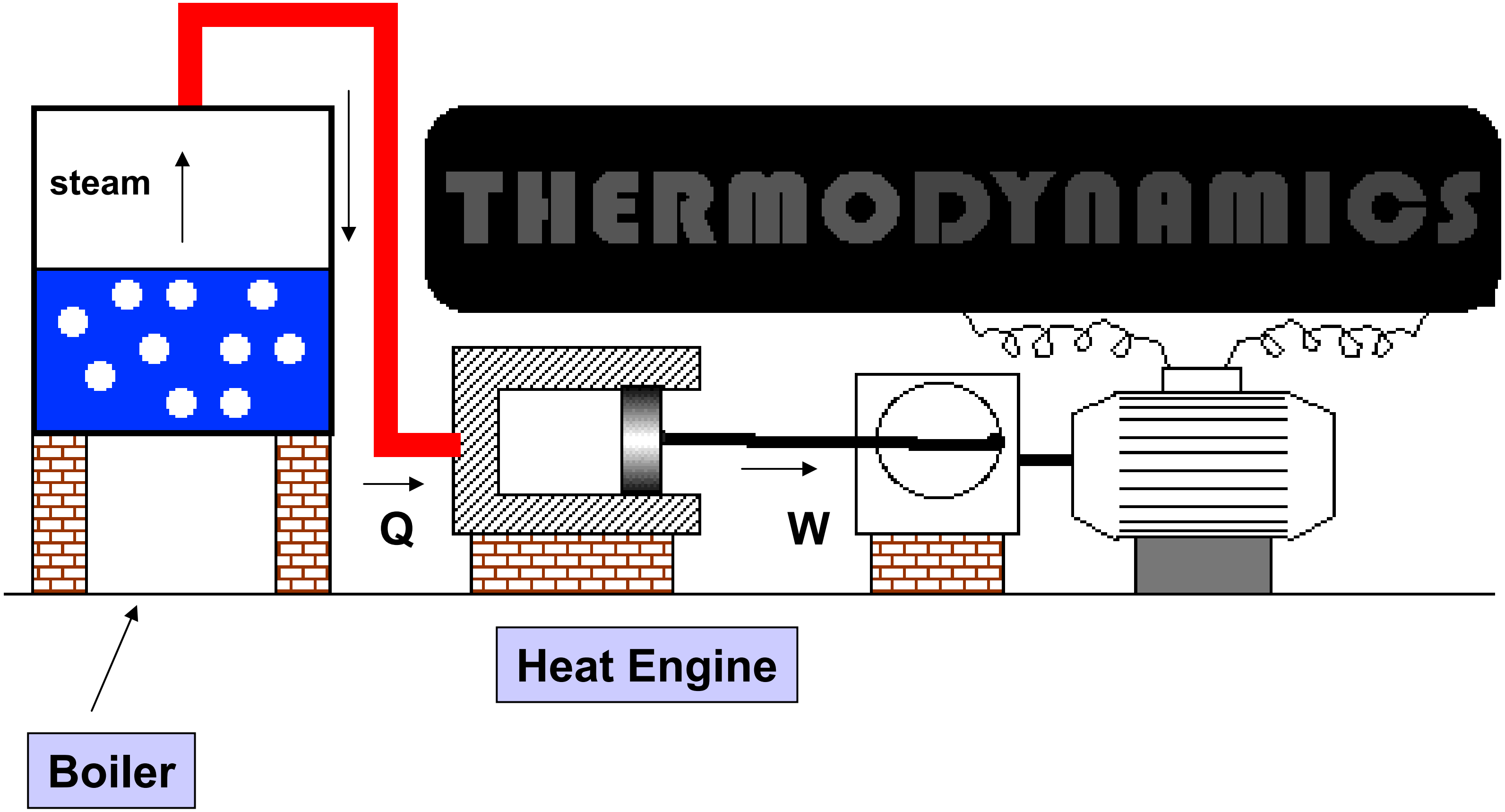
THERMODYNAMICS

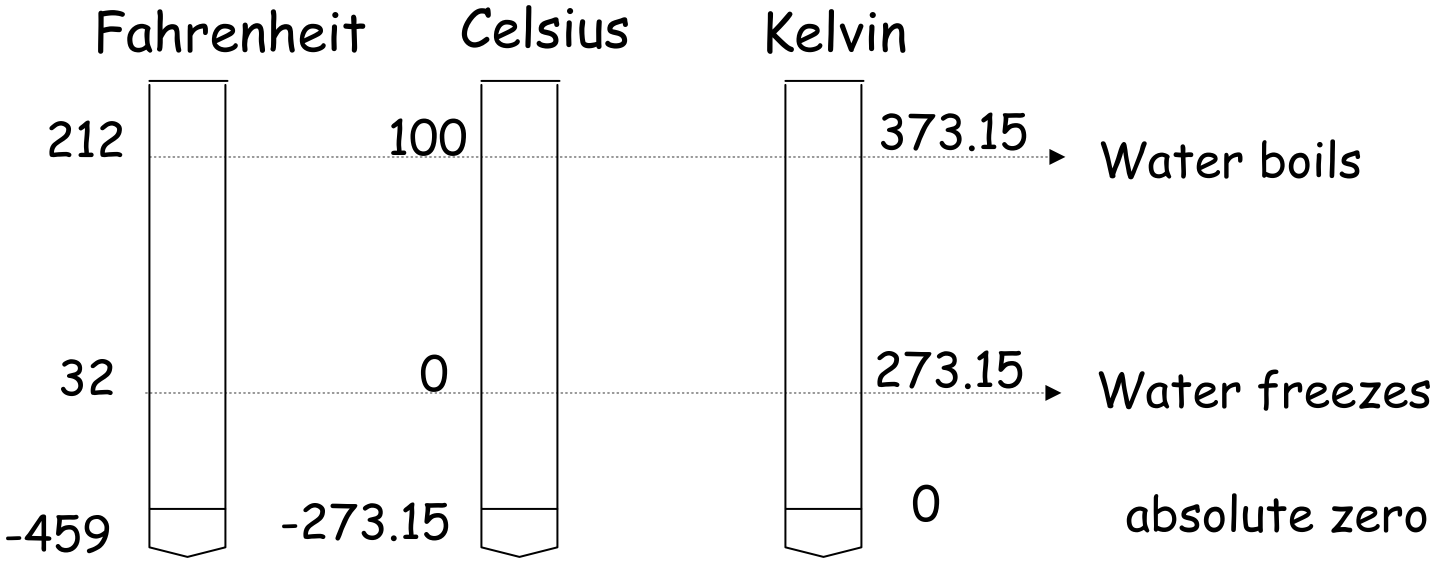


Lecture-1 [Basics]

Thermodynamics

- Section 1: Basics
  - Temperature Scale
  - Thermal Expansion
  - Internal Energy and Temperature
  - Specific Heat
  - Latent Heat

Temperature Scales



Fahrenheit	Celsius	Kelvin	
212	100	373.15	Water boils
32	0	273.15	Water freezes
-459	-273.15	0	absolute zero

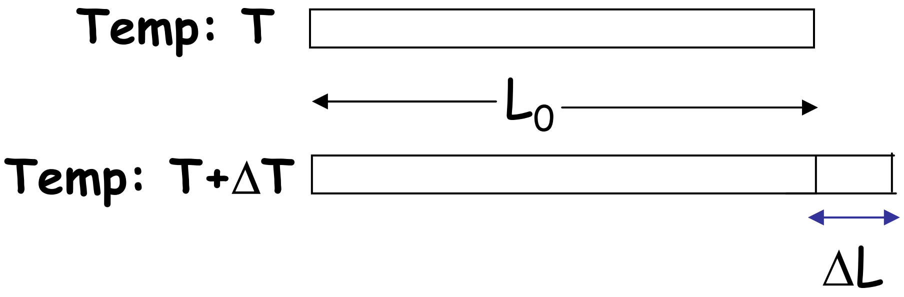
- Temperature scales:

$$T_K = T_C + 273.15$$

$$T_F = \frac{9}{5} T_C + 32$$

Thermal Expansion

- When **temperature rises**
  - molecules have more kinetic energy
    - they are moving faster, on the average
  - consequently, things tend to expand
- **amount of expansion** depends on…
  - change in temperature
  - original length
  - coefficient of thermal expansion
    - $\mathbf{L_0 + \Delta L = L_0 + \alpha\, L_0\, \Delta T}$
    - **ΔL (linear expansion)**
    - **ΔV (volume expansion)**



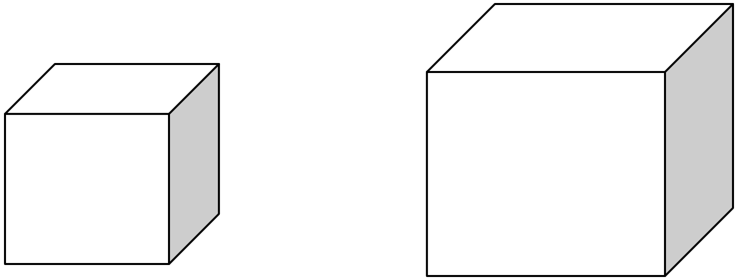
Concept Question

As you heat a block of aluminum from 0 C to 100 C its density

1. Increases
2. Decreases ← CORRECT
3. Stays the same

T = 0 C

T = 100 C



M, V_0

$\rho_0 = M / V_0$

M, V_{100}

$\rho_{100} = M / V_{100}$

$< \rho_0$

Concept Question

An aluminum plate has a circular hole cut in it. A copper ball (solid sphere) has exactly the same diameter as the hole when both are at room temperature, and hence can just barely be pushed through it. If both the plate and the ball are now heated up to a few hundred degrees Celsius, how will the ball and the hole fit (α (aluminum) > α (copper)) ?

1. The ball won’t fit through the hole any more
2. The ball will fit more easily through the hole ← CORRECT
3. Same as at room temperature

The aluminum plate and copper ball both have different coefficients of thermal expansion. Aluminum has a higher coefficient than copper which means the aluminum plate hole will expand to be larger than the copper ball's expansion and allow more space for the ball to pass through.

Internal Energy and Temperature

- **All objects have "internal energy"** (measured in Joules)

  Examples: **kinetic energy of molecules (due to vibrational, rotational or electronic energy)**

  Thermal internal energy is the average kinetic energy of molecules in motion.
- Temperature is a measure of this average kinetic energy.
- The amount of thermal internal energy of an objects depends on
  - temperature
    - related to average kinetic energy per molecule
  - how many molecules
    - mass
  - "specific heat capacity"

Quest: Difference between Internal Energy and Heat?

Internal Energy

- Total translational kinetic energy of the gas due to the random thermal motion of its molecules.---Mono atomic gas where no rotaional or vibrational energy is present

$$U = \frac{3}{2} nRT$$

In general: Internal energy is the total energy associated with the internal states of atoms and molecules composing the system.

Heat

- *Heat* is the transfer of energy between a system and its environment because of a temperature difference between them
  - The symbol Q is used to represent the amount of energy transferred by heat between a system and its environment

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Units of Heat

- Calorie
  - An historical unit, before the connection between thermodynamics and mechanics was recognized
  - A *calorie* is the amount of energy necessary to raise the temperature of 1 g of water from 14.5° C to 15.5° C .
    - A Calorie (food calorie) is 1000 cal

How To Change the Temperature of a System (Solids or Liquids)?

- Add or subtract heat
  - Q = heat = energy that flows from warmer to cooler systems.

- **$Q = c\ m\ \Delta T$**
  - Q = amount of heat that must be supplied or subtracted to raise or lower the temperature of mass m by an amount ΔT.
    - Units of Q: Joules or calories
      - 1 cal = 4.186 J
      - 1 kcal = 1 Cal = 4186 J
  - c = specific heat capacity: Heat required to raise 1 kg by 1^{o}C.

- $\Delta T = Q/(cm)$ (just like $a = F/m$)

Numerical Values of **Specific Heat Capacity ‘c’ for different media**

Substance	c in J/(kg C)
Aluminum	**900**
Copper	**387**
Iron	**452**
Lead	**128**
Water (15 C)	**4186**
Ice (-15 C)	**2000**

$Q = c\ m\ \Delta T$

Q: Suppose you have equal masses of aluminum and copper at the same initial temperature. You add 1000 J of heat to each of them. Which one ends up at the higher final temperature

a) **aluminum**
b) **copper** ⟵ correct
c) **the same**

Quick Quiz 11.1

- iron, glass, water
- m = 1 kg
- T_i = 10 °C
- a) Q=100 J

  Lowest T_f -?
- b) ΔT = 20 °C

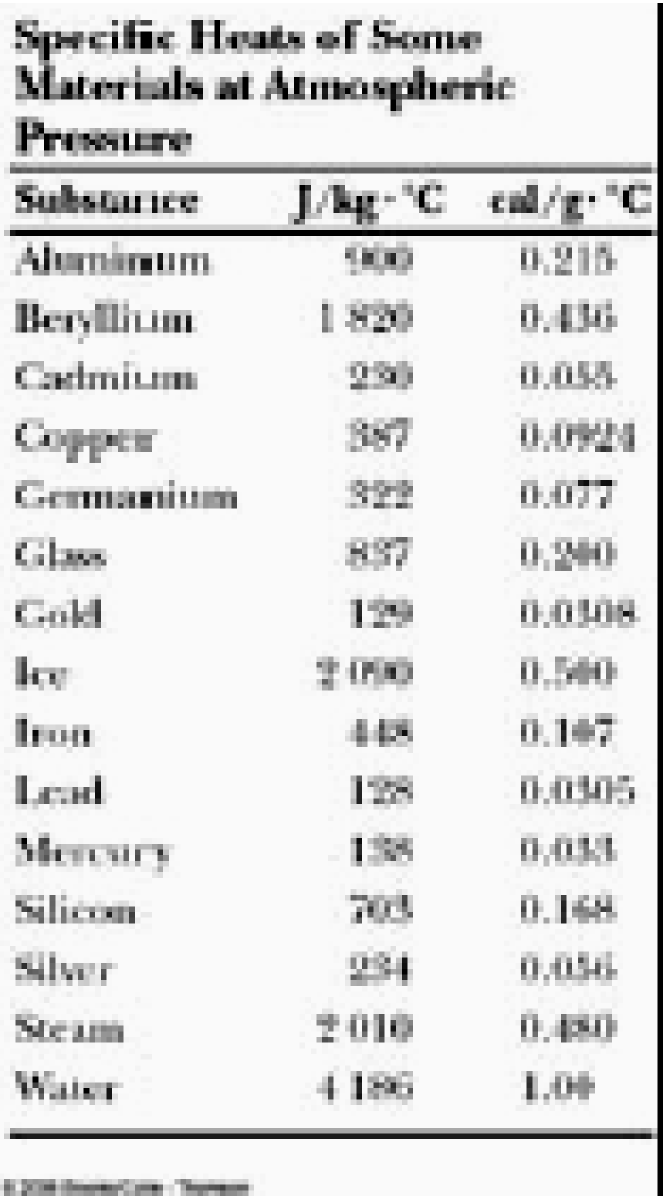
  Least Q -?

$$Q = c \cdot m \cdot \Delta T$$

837

448

4186



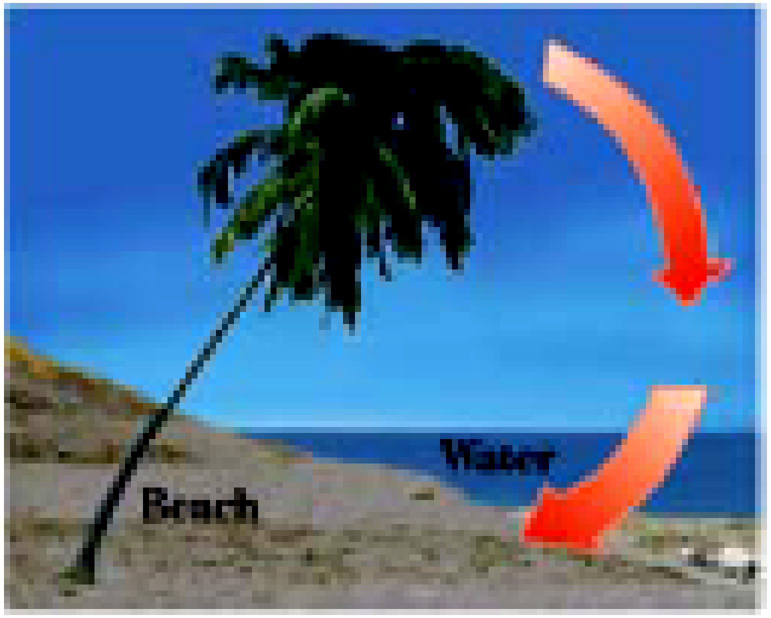
Specific Heats of Some Materials at Atmospheric Pressure

Substance	J/kg·°C	cal/g·°C
Aluminum	900	0.215
Beryllium	1 820	0.436
Cadmium	230	0.055
Copper	387	0.0924
Germanium	322	0.077
Glass	837	0.200
Gold	129	0.0308
Ice	2 090	0.500
Iron	448	0.107
Lead	128	0.0305
Mercury	138	0.033
Silicon	703	0.168
Silver	234	0.056
Steam	2 010	0.480
Water	4 186	1.00

(a) Water (b) Iron

A Consequence of Different Specific Heats

- Water has a high specific heat compared to land
- On a hot day, the air above the land warms faster
- The warmer air flows upward and cooler air moves toward the beach resulting in a breeze



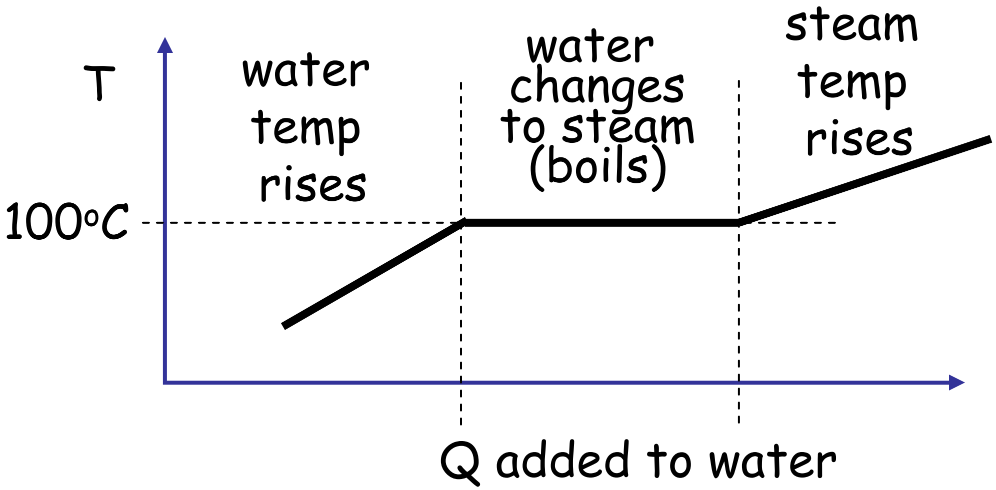
Latent Heat

- During a phase change, the amount of heat is given as

$$Q = \pm m \cdot L$$

- L is the *latent heat* of the substance
    - Latent means hidden
    - L depends on the substance and the nature of the phase change
- Positive sign if you are adding energy to the system and a negative sign if energy is being removed from the system

Latent Heat



Q = m L with L = Latent Heat L [J/kg]:

Q is the amount of heat needed to add or remove from a substance with mass m to change the state of that substance.

Liquid <-> Solid (fusion energy)   Liquid <-> Gas (vaporization energy)

Solid <-> Gas (sublimation energy)

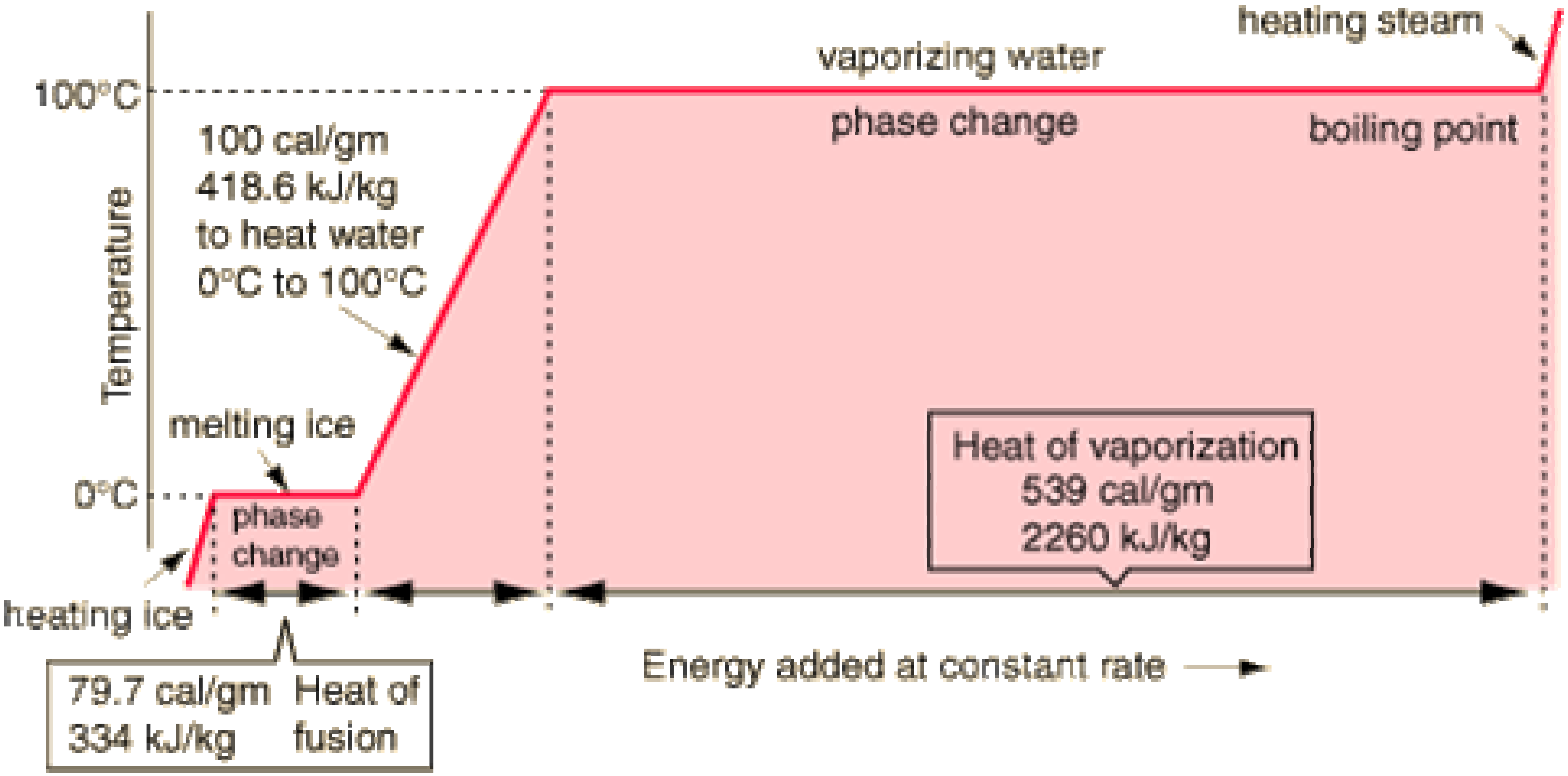
Substance	L_f (J/kg)	L_v (J/kg)
water	33.5×10^4	22.6×10^5

Phase changes

1. **Transitions between solid, liquid, and gaseous phases typically involve large amounts of energy compared to the** specific heat.

2. If heat were added at a constant rate to a mass of **ice** to take it through its **phase changes to liquid water** and then to **steam,**
3. The energies required to accomplish the phase changes (called the latent heat of fusion and latent heat of vaporization) would lead to plateaus in the temperature vs time graph.

The graph below presumes that the pressure is one standard atmosphere.



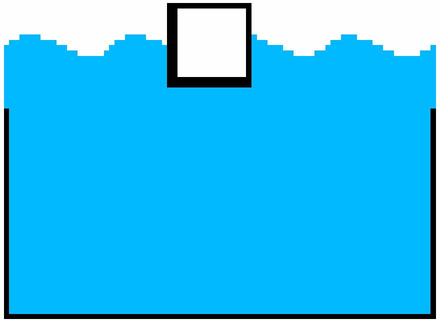
Example:

- m_{ice} = 100 g
- T_{ice} = 0°C
- m_{water} = 1.0 kg
- T_{ice} = 80°C

water $_{final}$ = ?

c_w = 1486 J/kg°C

L_f = 3.33x10^5 J/kg



$$Q_m = L_f m$$

$$Q_h = cm\Delta T$$

Heat lost by water = heat gain by ice

$$-c_w m_w (T_f - T_i)_{water} = m_{ice} L_f + c_w m_{ice} (T_f - T_i)_{ice}$$

Ans: 52.54 ^{0}C

Problem Solving Strategies

- Apply Conservation of Energy
  - Transfers in energy are given as $Q=mc\Delta T$ for processes with no phase changes
  - Use $Q = m\,L_f$ or $Q = m\,L_v$ if there is a phase change
  - In $Q_{cold} = -\,Q_{hot}$ be careful of sign
  - ΔT is $T_f - T_i$
- Use consistent units

Cooling a Cup of Coffee

Quest: You have a 200 gram cup of coffee at 100 C, too hot to drink. Various cooling strategies demonstrate specific heat, phase changes, and the approach to thermal equilibrium.

(1) Add cold water:

How much will the coffee be cooled by adding 50 gm of water at 0 C?

(2) Add Ice:

How much will the coffee be cooled by adding 50 gm of Ice at 0 C?

(3) Force Evaporation:

Suppose you start with 300 gm of coffee at 100 C and force 50 grams of it to vaporize, leaving the final mass at 250 gm?

Reference:

http://hyperphysics.phy-astr.gsu.edu/hbase/hframe.html

Answer:

(1) Add cold water:

(2) Add Ice

(3) Force Evaporation

Solution:

Cooling a Cup of Coffee

You have a 200 gram cup of coffee at 100 C, too hot to drink. How much will you cool it by adding 50 gm of water at 0 C?

Heat lost by coffee = Heat gained by water

$$-Q_{coffee} = Q_{water}$$

$$-cm_c\Delta T_{coffee} = cm_w\Delta T_{water}$$

$$\left(1\frac{\text{cal}}{\text{gm °C}}\right)(200\text{ gm})(100 - T_f)$$

$$= \left(1\frac{\text{cal}}{\text{gm °C}}\right)(50\text{ gm})(T_f - 0)$$

$$20{,}000 - 200\,T_f = 50\,T_f$$

$$\frac{20{,}000}{250} = T_f = 80°\text{C}$$

Cooling a Cup of Coffee

You have a 200 gram cup of coffee at 100 C, too hot to drink. How much will you cool it by adding 50 gm of ice at 0 C?

Heat lost by coffee = Heat gained by ice

$$-Q_{coffee} = Q_{ice}$$

$$-cm_c\Delta T_{coffee} = m_iL_f + cm_i\,\Delta T_{ice}$$

$$\left(1\frac{cal}{gm\ ^\circ C}\right)(200\ gm)(100 - T_f)$$

$$= (50\ gm)(80\ cal/gm) + \left(1\frac{cal}{gm\ ^\circ C}\right)(50\ gm)(T_f - 0)$$

$$20,000 - 200\ T_f = 4,000 + 50\ T_f$$

$$\frac{20,000 - 4,000}{250} = T_f = 64^\circ C$$

Cooling a Cup of Coffee

You have a 300 gram cup of coffee at 100 C, too hot to drink. How much will you cool it by forcing 50 gm to evaporate, leaving 250 gm?

Heat lost by coffee = Heat of vaporization

$$-Q_{coffee} = Q_{vaporization}$$

$$-cm_c \Delta T_{coffee} = m_i L_v$$

$$\left(1 \frac{cal}{gm\ {}^\circ C}\right)(250\ gm)(100 - T_f) = (540\ cal/gm)(50\ gm)$$

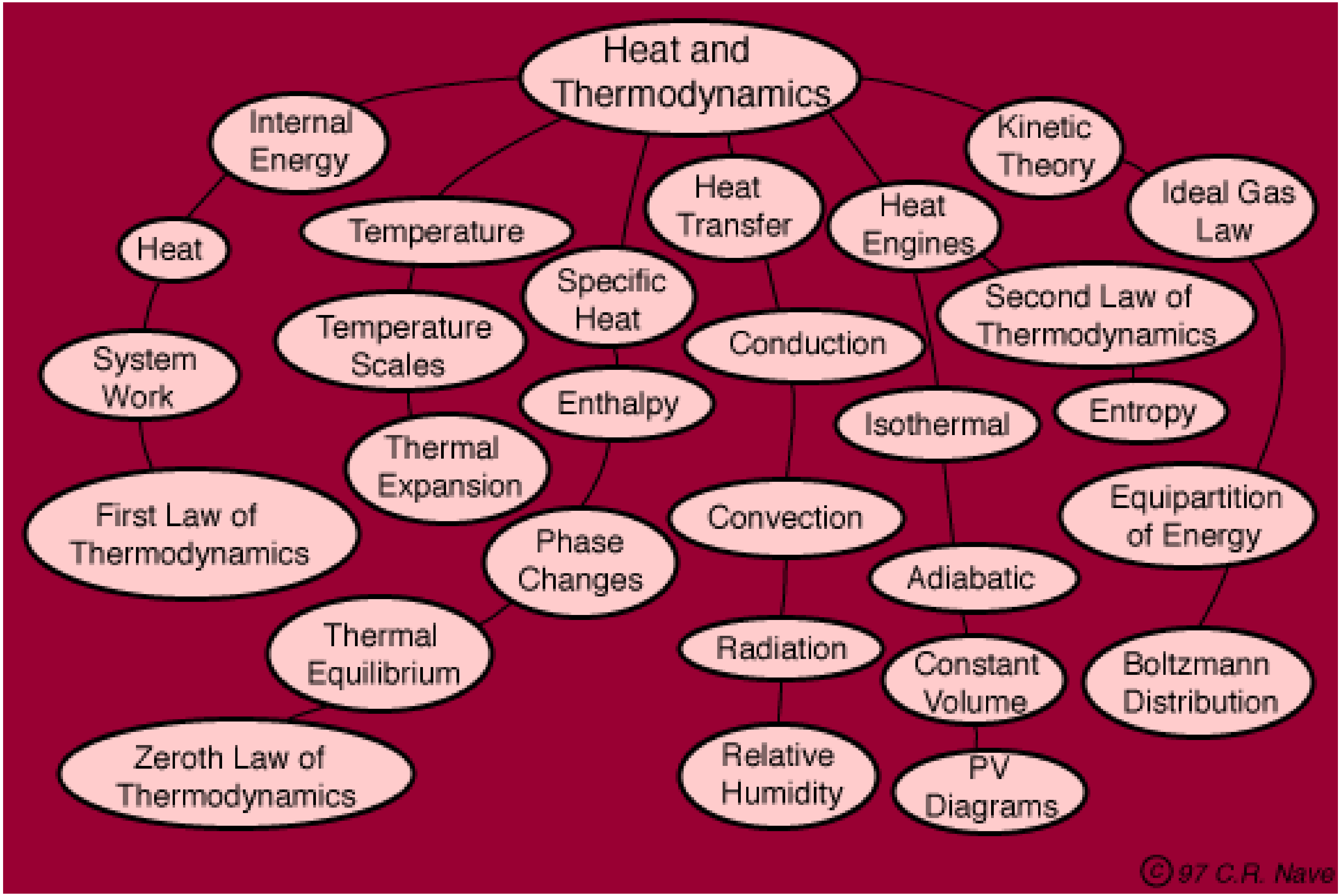
$$25{,}000 - 250\ T_f = 27{,}000$$

But this can't be right because it gives a negative temperature (-8 C) and the specific heat equation $Q = cm\Delta T$ is valid only so long as a phase change is not encountered, so we can't pass 0 C with this equation. If 25000 calories are extracted, we have cooled the coffee to 0 C but still have 2000 cal to remove. This will freeze some of the coffee:

$$\frac{2000\ cal}{80\ cal/gm} = 25\ gm\ frozen\ at\ 0^\circ C$$

Reference:

http://hyperphysics.phy-astr.gsu.edu/hbase/hframe.html



Thermal science is macroscopic or microscopic?

- Macroscopic quantities like P, V & T characterizes thermal properties of gas. So we can say that the science of ‘Thermal Physics’ is understood in a macroscopic level.
- It can also be understood in a microscopic level. Example: Temperature of a gas is a measure of the average kinetic energy of the gas molecules.
- P, V & T ➲commonly called ‘thermodynamic variables of the system’.

The relationship between energy and temperature (for monatomic ideal gas)

$$\text{ave KE/molecule} = \frac{1}{2} m \left\langle v^2 \right\rangle = \frac{3}{2} k_B T$$

- Internal Energy U

  = number of molecules x ave KE/molecule

  = N (3/2) k_BT

  = (3/2) n RT = (3/2) P V (ideal gas)

The Ideal Gas Law
(review)

- $P\ V = N\ k_B\ T$
  - N = number of molecules
    - N = number of moles (n) x N_A molecules/mole
  - k_B = Boltzmann's constant = 1.38×10^{-23} J/K

- $P\ V = n\ R\ T$
  - R = ideal gas constant = $N_A k_B$ = 8.31 J/mol/K

Zeroth Law of Thermodynamics

0. Law: Thermal equilibrium

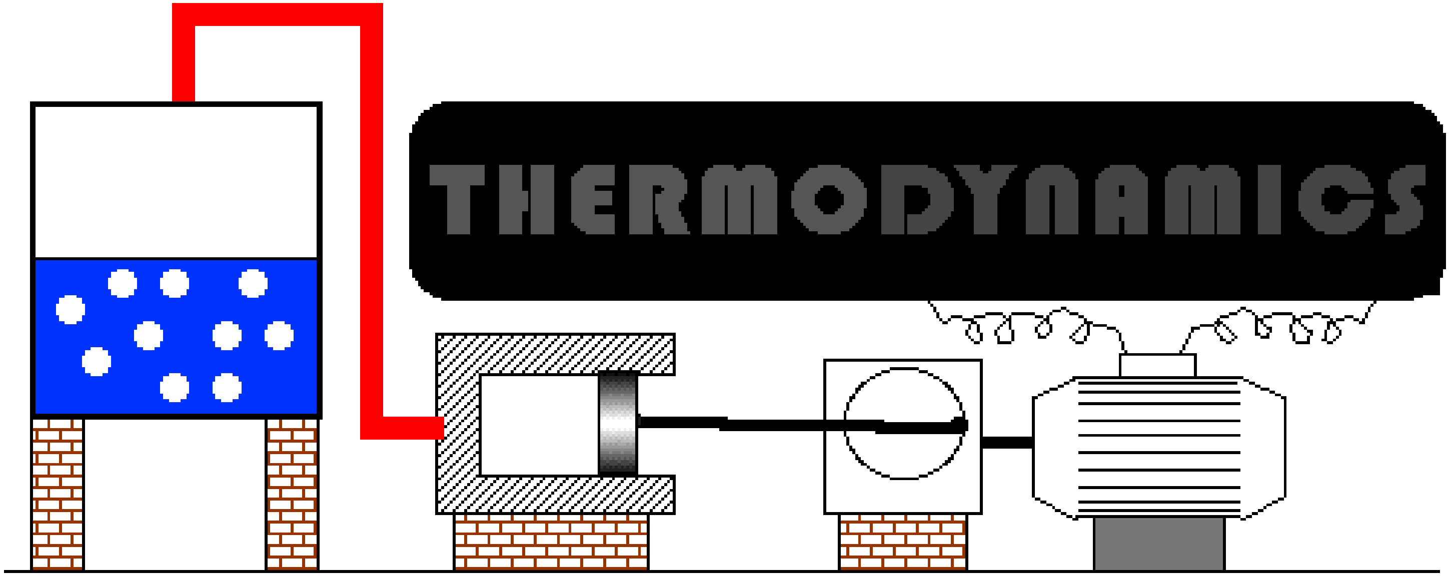
(Mechanics: $\Sigma \underline{F} = 0$, $\underline{a}=0$)

Indicator of **thermal equilibrium: $\Delta T=0$**

(like $\underline{a}=0$)

If two systems are individually in equilibrium with a third system,

they are in thermal equilibrium with each other.



THERMODYNAMICS

Lecture-2

The first law of Thermodynamics

- The first law of Thermodynamics is a generalization of the **law of conservation of energy** and includes possible changes in internal energy.
- When a system undergoes an infinitesemial change in state, where a small amount of heat, dQ, is transferred and a small amount of work, dW, is done, the internal energy also changes by a small amount, dU. Thus for infinitesimal process we can express the first law as

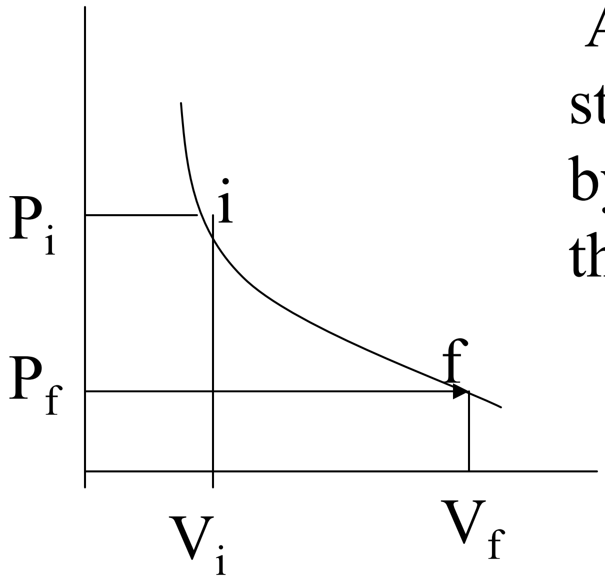
$$\begin{aligned} dU &= dQ - dW \\ &= dQ - PdV \\ dQ &= dU + PdV \end{aligned}$$

The work done

- The work done in the expansion from the initial state is the **area under the curve in a PV diagram.**
- The work done by the system depends on the process by which the system goes from the initial to the final state.
- In other words, the work done depends on the initial, final and **intermediate states** of the system.

PV Diagrams

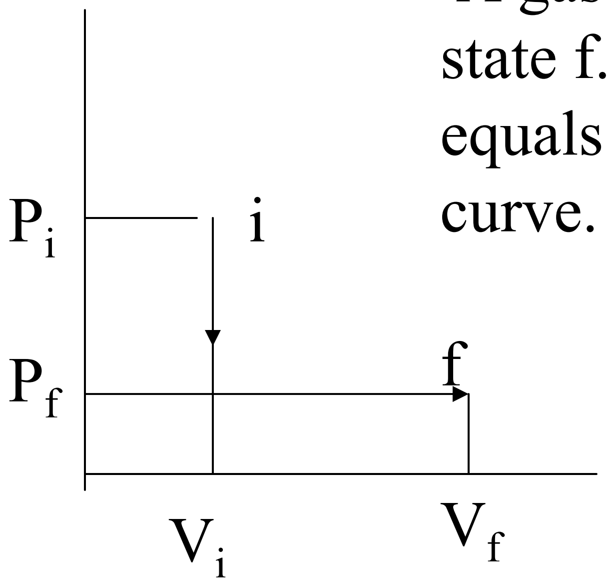
- PV Diagram-1



A gas expands (slowly) from state i to state f. The work done by the gas equals the area under the PV curve.

PV Diagrams

- PV Diagram-2



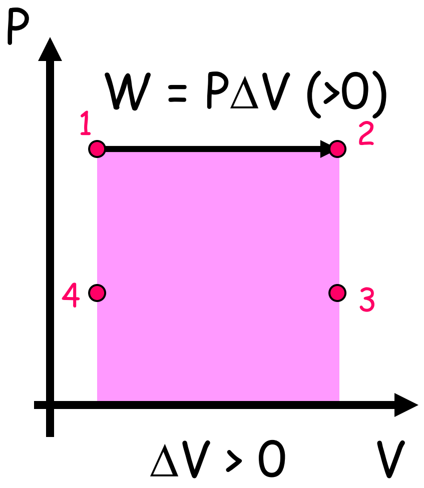
A gas expands from state I to state f. The work done by the gas equals the area under the PV curve.

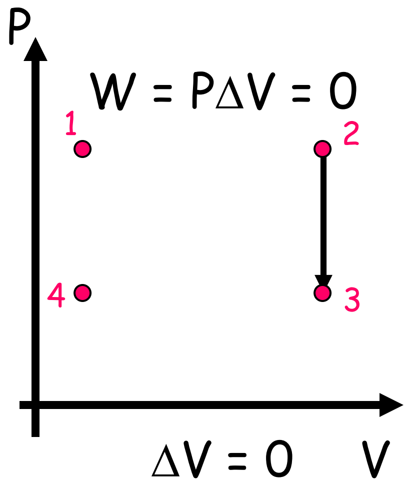
Observations from PV diagram 1 and 2

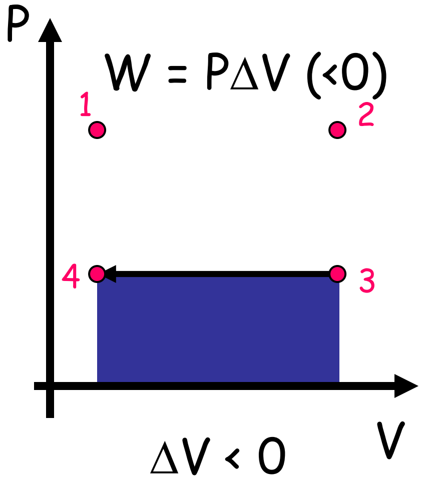
- Although initial and final sates are same work done by the system is different.
- Work done by the system depends on the initial, final and intermediate states of the system.
- These observations are very important in the designing of engines.

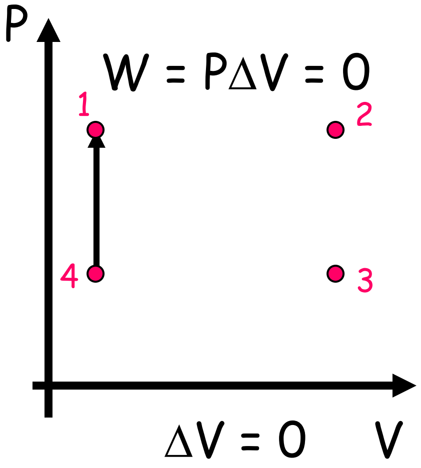
Isobaric Process: P=constant

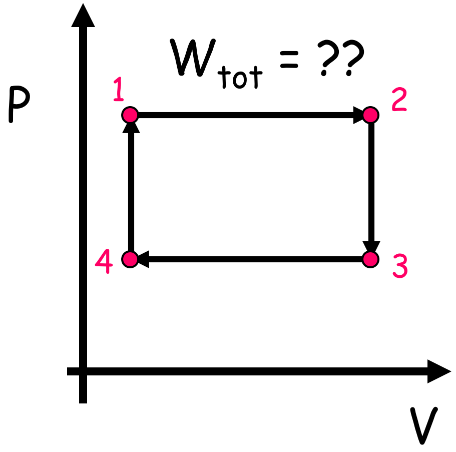
Isochoric Process: V=constant

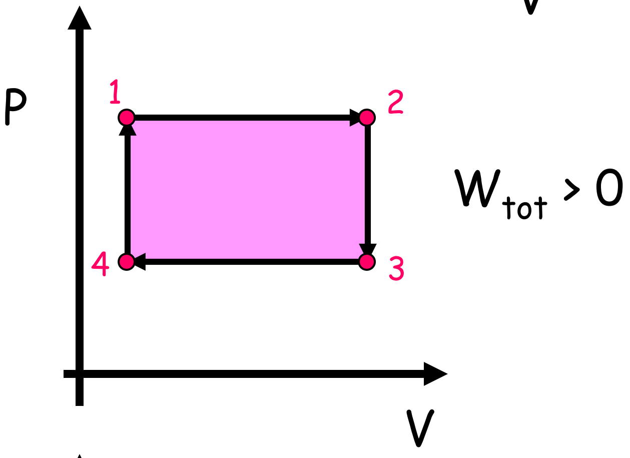


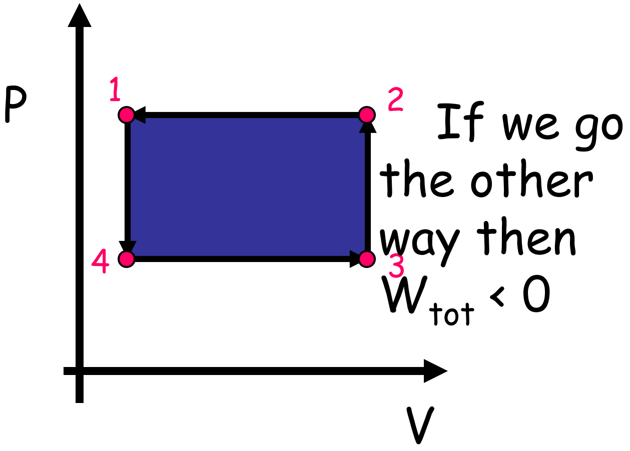






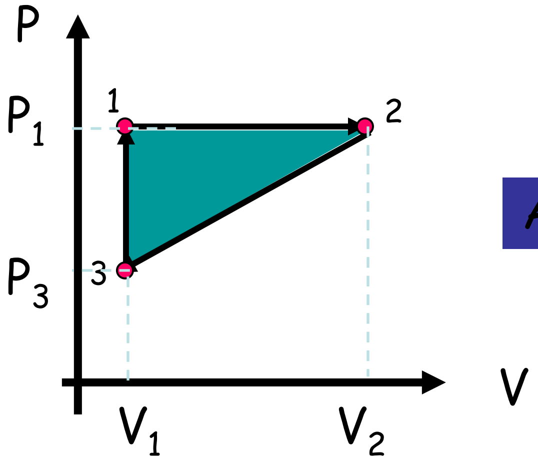






If we go the other way then $W_{tot} < 0$

Now try this: What is the total work done by system when going from state 1 to state 2 to state 3 and back to state 1 ?

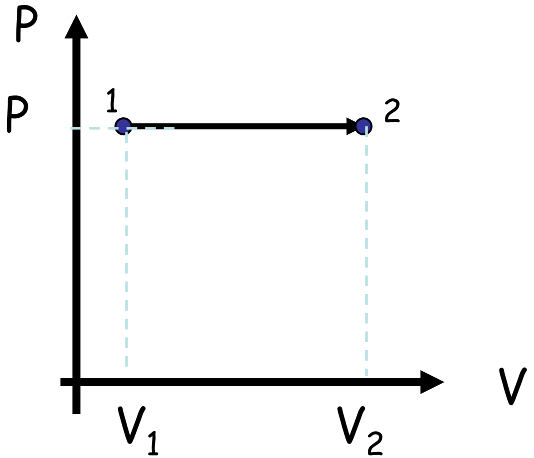


Area = $(V_2-V_1)\times(P_1-P_3)/2$

Different processes in a PV Diagram →

First Law of Thermodynamics Example-1

2 moles of monatomic ideal gas is taken from state 1 to state 2 at constant pressure $P=1000$ Pa, where $V_1=2m^3$ and $V_2=3m^3$. Find T_1, T_2, ΔU, W, Q.



1. $P V_1 = n R T_1 \quad \Rightarrow T_1 = P V_1/(nR) = 120K$
2. $P V_2 = n R T_2 \quad \Rightarrow T_2 = P V_2/(nR) = 180K$

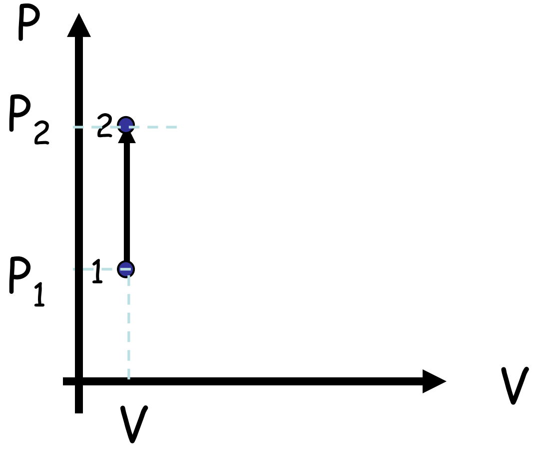
3. $\Delta U = (3/2)\, n R \Delta T = 1500$ J or $\Delta U = (3/2)\, P \Delta V = 1500$ J

4. $W = P \Delta V = 1000 \text{ J} > 0$ Work done by the system (gas)

5. $Q = \Delta U + W = 1500 \text{ J} + 1000 \text{ J} = 2500 \text{ J} > 0$ heat gained by system (gas)

First Law of Thermodynamics
Example-2

2 moles of monatomic ideal gas is taken from state 1 to state 2 at <u>constant volume</u> $V=2m^3$, where $T_1=120K$ and $T_2=180K$. Find Q.



1. $P V_1 = n R T_1 \Rightarrow P_1 = n R T_1/V = 1000$ Pa

2. $P V_2 = n R T_1 \Rightarrow P_2 = n R T_2/V = 1500$ Pa

3. $\Delta U = (3/2) n R \Delta T = 1500$ J

4. $W = P \Delta V = 0$ J

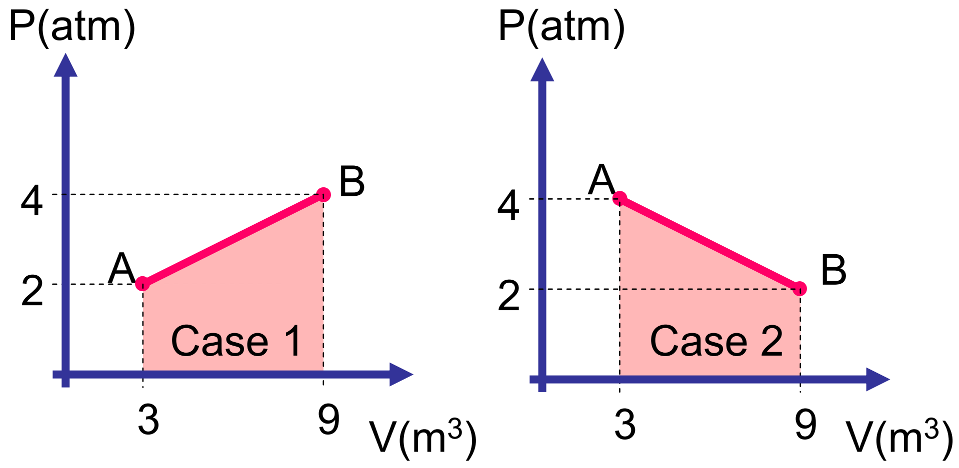
5. $Q = \Delta U + W = 0 + 1500 = 1500$ J

=> It requires less heat to raise T at const. volume than at const. pressure.

Concept Question

Shown in the picture below are the pressure versus volume graphs for two thermal processes, in each case moving a system from state A to state B along the straight line shown. In which case is the work done by the system the biggest?

1. Case 1
2. Case 2
3. Same ← correct



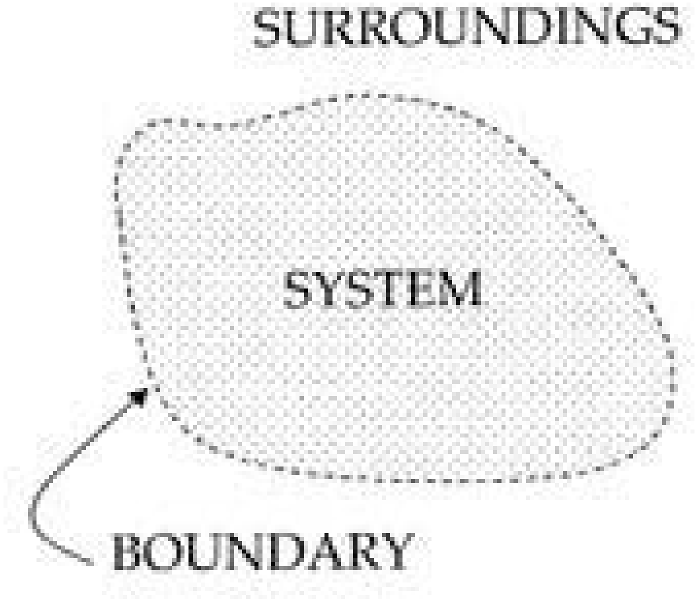
Net Work = area under P-V curve

Area the same in both cases!

Thermodynamic Processes

(for gases)

Thermodynamic systems



- A system (region) is **separated** from the remainder of the universe **by a boundary** which may be imaginary or not, but which having finite volume.
- The possible exchanges of work, heat, or matter between the system and the surroundings take place across this boundary.
- There are five dominant classes of systems:

Closed Systems – matter may not cross the boundary.
Open Systems – heat, work, and matter may cross the boundary.

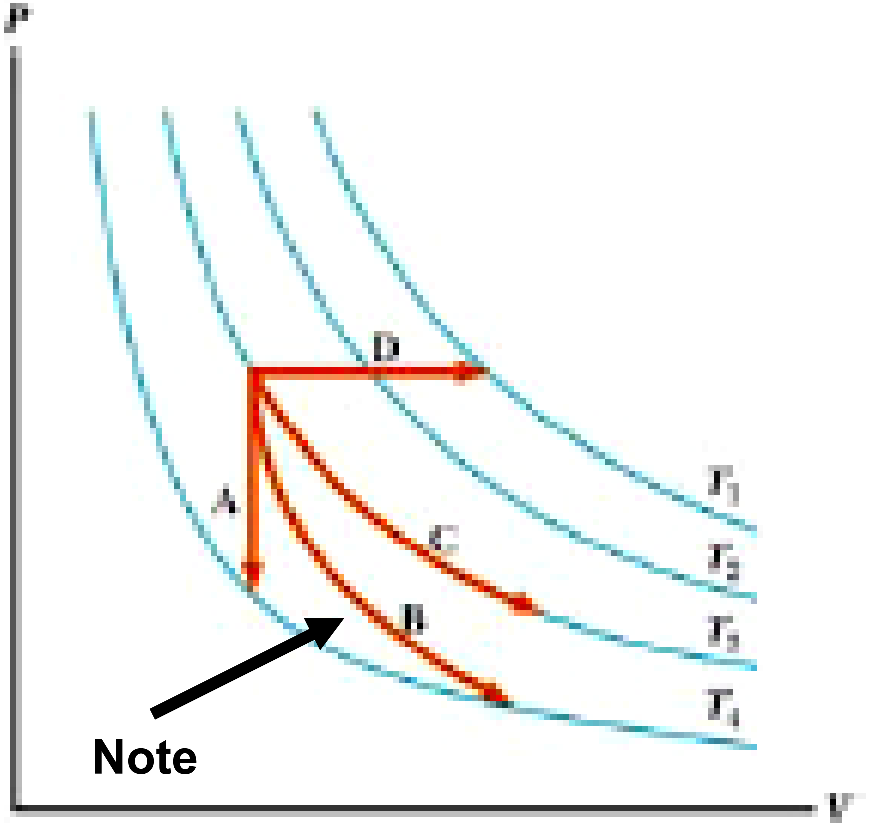
Isolated Systems – matter and energy may not cross the boundary.
Adiabatic Systems – heat may not cross the boundary.
Diathermic Systems - heat may cross boundary.

Quick Quiz

Identify the paths A, B, C, and D in Figure as

isobaric,
isothermal,
isovolumetric,
or adiabatic.

For path B, $Q = 0$.



Thermodynamic Processes (for gases)

- Isothermic: constant temperature
  - $\Delta T = 0$ means $\Delta U = 0$ (U is constant!)
- Adiabatic: no gain/loss of heat energy (Q)
  - $Q = 0$ means $\Delta U = W$

Note: Isothermal and Adiabatic are important for Carnot Engine (Ideal heat Engine)

- Isochoric (or isovolumetric): constant volume
  - $\Delta V = 0$ means $W = 0$ (no work performed on/by system)
- Isobaric: constant pressure
  - $\Delta P = 0$ means $W = P\Delta V$

Note: Isochoric and Isobaric are important for specific heat of Gases.

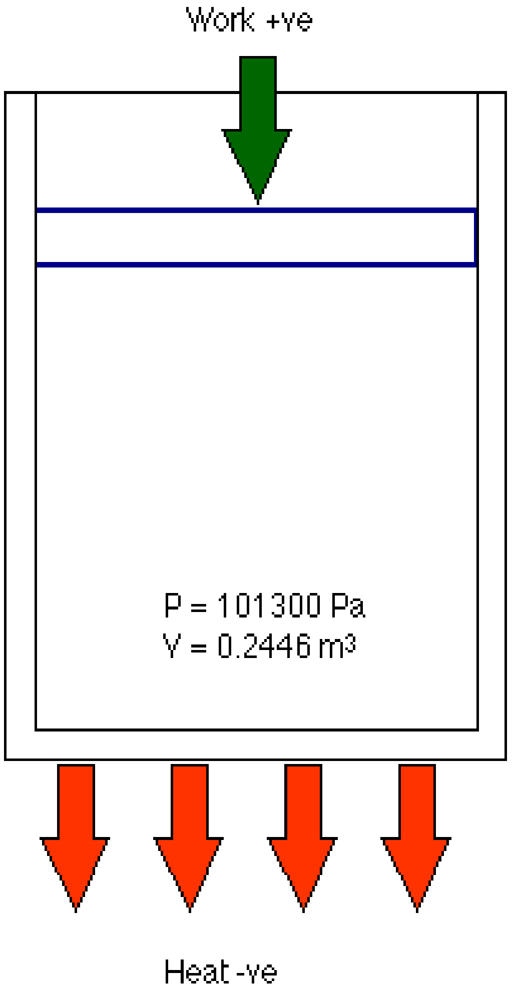
Isothermal Process:

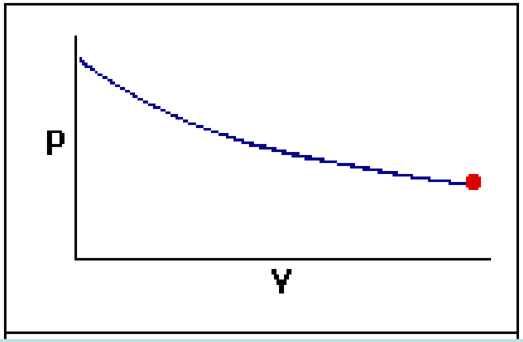
Note:

- An **isothermal process is a** thermodynamic process in which the temperature of the system stays constant: $\Delta T = 0$.

- This typically occurs when a system is in contact with an outside thermal reservoir (heat bath),

- and processes occur slowly enough to allow the system to continually adjust to the temperature of the reservoir through heat exchange.





ALL the heat added to the system Is used to work

Isothermal Processes

- Process where the temperature (T) of the working substance remains constant
- There are 2 possible outcomes

1. As work is performed on the working substance, it releases the energy as heat (Q) {Q is released}
2. All heat energy (Q) absorbed is converted to work by the working substance {Q is absorbed}

- Since $\Delta T = 0$, then $\Delta U = 0$ so

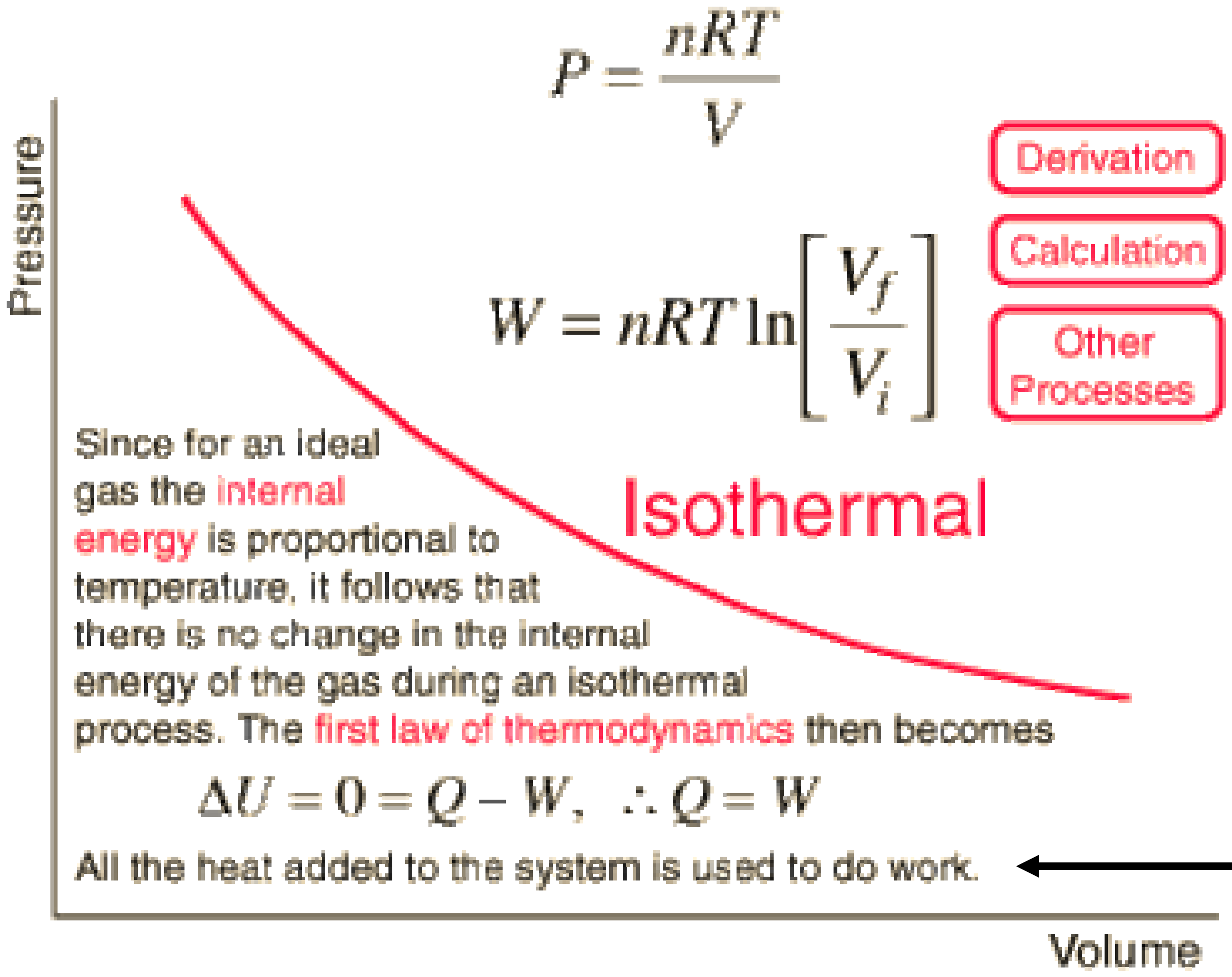
$$\Delta U = Q - W = 0$$

becomes

$$W = Q = (nRT)\ln(V_f/V_i)$$

{work performed by working substance}

For a constant temperature process involving an ideal gas, pressure can be expressed in terms of the volume:



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

$$W = nRT\ln\left[\frac{V_f}{V_i}\right]$$

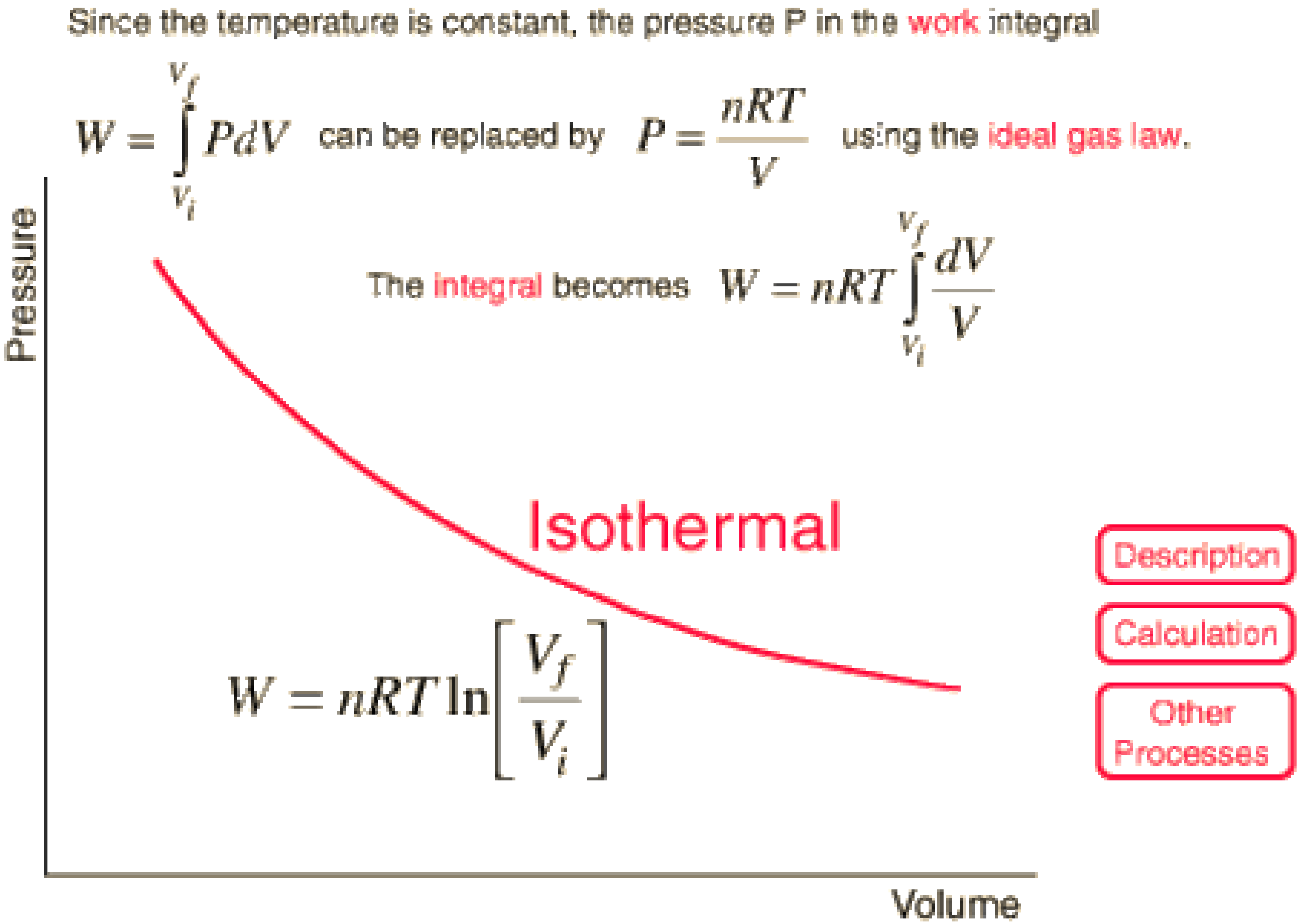
Since for an ideal gas the internal energy is proportional to temperature, it follows that there is no change in the internal energy of the gas during an isothermal process. The first law of thermodynamics then becomes

$$\Delta U = 0 = Q - W, \quad \therefore Q = W$$

All the heat added to the system is used to do work.

Derivation:

$$\Delta W = P\Delta V$$



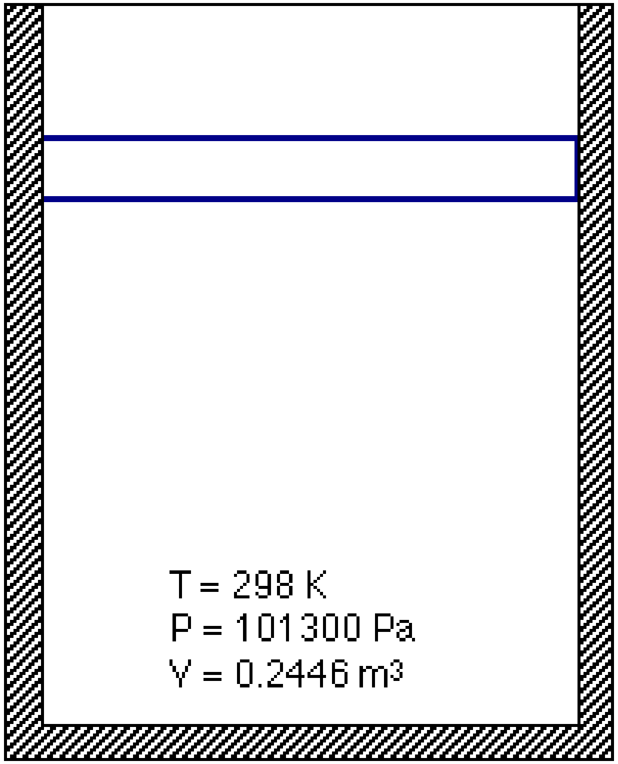
Since the temperature is constant, the pressure P in the work integral

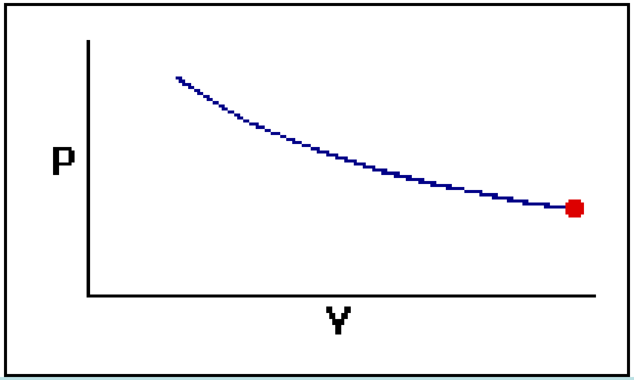
$$W = \int_{V_i}^{V_f} P\,dV$$ can be replaced by $$P = \frac{nRT}{V}$$ using the ideal gas law.

The integral becomes $$W = nRT\int_{V_i}^{V_f}\frac{dV}{V}$$

$$W = nRT\ln\left[\frac{V_f}{V_i}\right]$$

Adiabatic Process





Only Q=0

Insulated wall

$\Delta U = -W$

$W = -(3/2)nR\Delta T$

Work performed on the working substance increases its internal energy by exactly the same amount.

Adiabatic Processes

- Process where no heat energy (Q) is allowed to enter or leave the system, Q = 0 ($\Delta U = Q - W = -W$)
- Two outcomes:
  1. Work performed on the working substance increases its internal energy by exactly the same amount
  2. Worked performed by the working substance decreases its internal energy by exactly the same amount
- Since $\Delta U = -W$ & ΔU depends on ΔT,
  - For a monatomic gas:

$$W = -(3/2)nR\Delta T$$

  - For a diatomic gas:

$$W = -(5/2)nR\Delta T$$

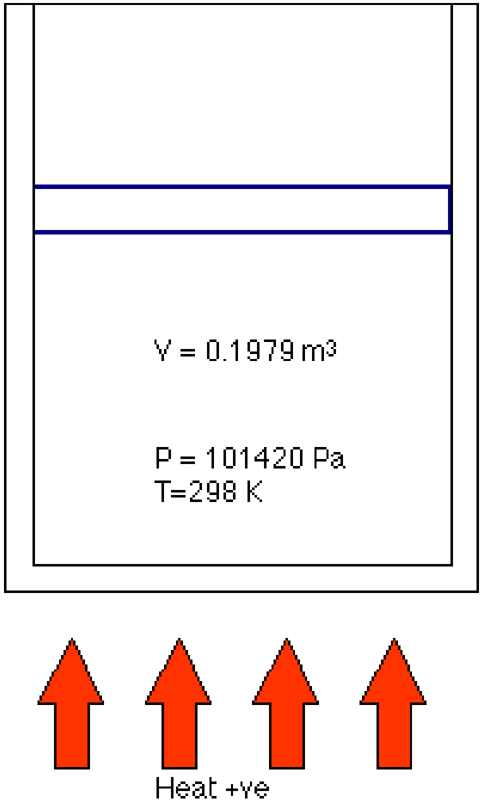
P-V relation for Adiabatic Processes

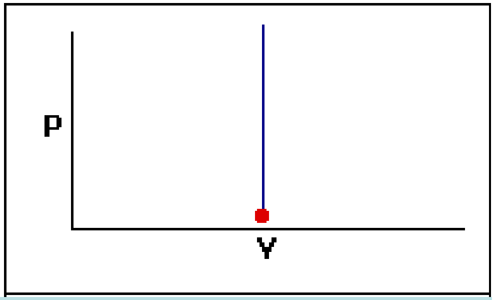
- When a gas undergoes an adiabatic expansion/contraction the relationship between pressure and volume is

  $$P_iV_i^{\gamma} = P_fV_f^{\gamma}$$

  where γ **is C_P/C_V** (the **ratio the molar heat capacities** at constant P and V, respectively)
- For monoatomic gases, γ is 5/3
- For Diatomic gases, γ is 7/5

Isochoric Process:





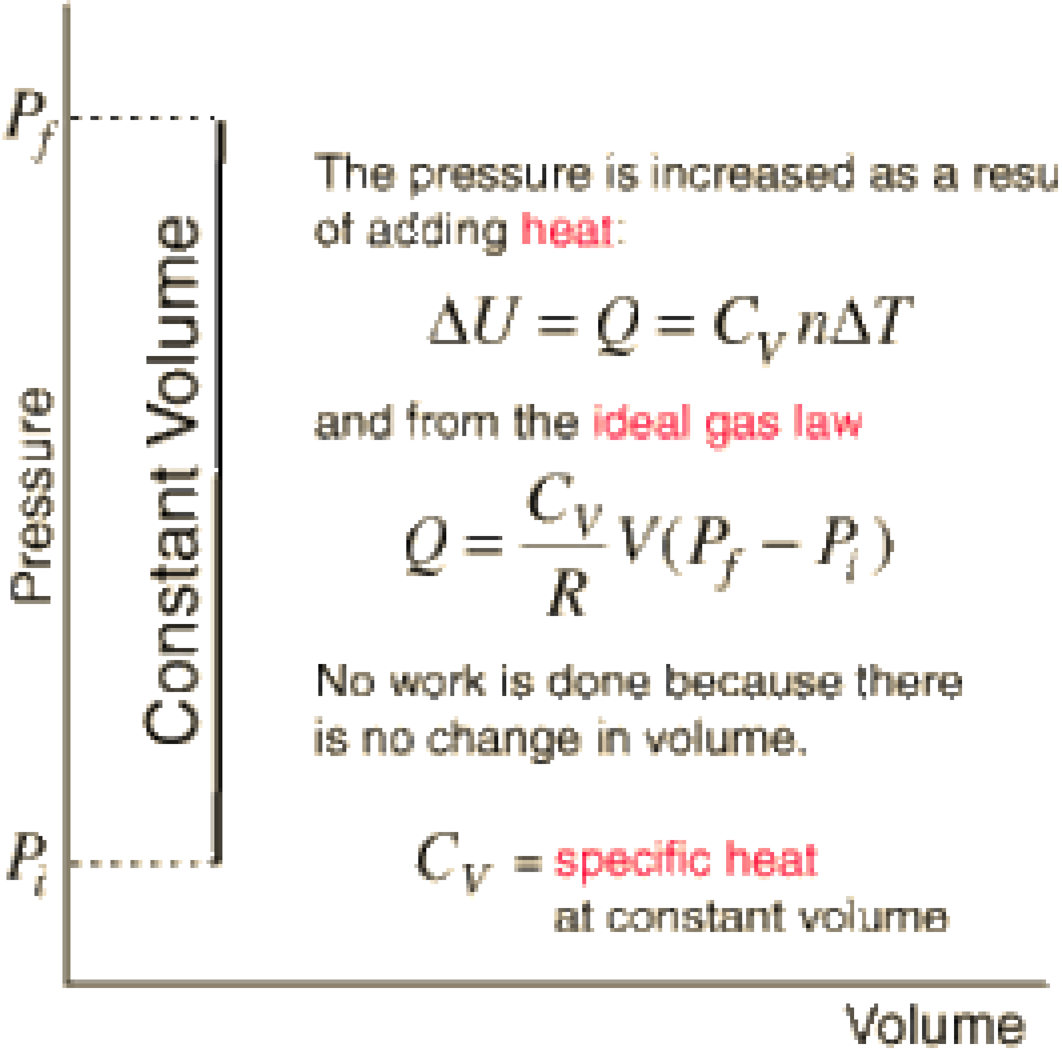
$$Q = n\int_{T_1}^{T_2} C_V \, dT$$

Internal energy (U) increases as heat energy (Q) is absorbed by the working substance

Isochoric Processes

- Process where the volume (V) of the working substance remains constant
- No work is performed during this process since $\Delta V = 0$ {area under PV curve is zero}
- Two outcomes:
  - Internal energy (U) increases as heat energy (Q) is absorbed by the working substance
  - Internal energy (U) decreases as heat (Q) is released by the working substance
- Since $\Delta V = 0$ then $W = 0$, so

$$\Delta U = Q$$



The pressure is increased as a result of adding heat:

$$\Delta U = Q = C_V n \Delta T$$

and from the ideal gas law

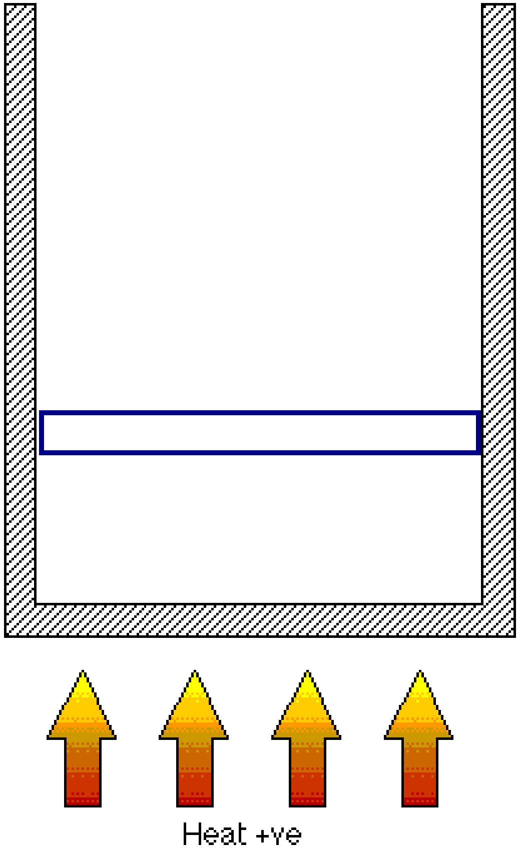
$$Q = \frac{C_V}{R} V (P_f - P_i)$$

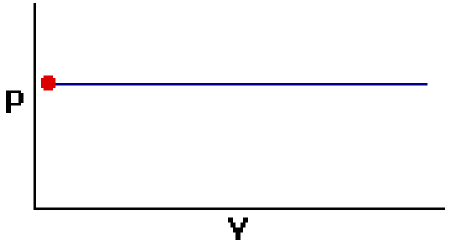
No work is done because there is no change in volume.

C_V = specific heat at constant volume

Other Processes

Isobaric process





$$Q = n\int_{T_1}^{T_2} C_P \, dT$$

P = 250000 Pa
T = 298 K
V = 0.0991 m³

Isobaric Processes

- Process where the pressure (P) of the working substance remains constant
- Since $\Delta P = 0$, then the area under the PV curve (the work performed) is equal to $P \cdot \Delta V$ or

$$W = P \cdot \Delta V$$

{work performed by working substance}

- **The internal energy change of the system is equal to the difference between heat energy absorbed & work performed**, or

$$\Delta U = Q - W = Q - P \cdot \Delta V$$

- The internal energy change (ΔU) is also related to the change in temperature (ΔT):

$$\Delta U = (3/2) nR \cdot \Delta T \text{ \{monatomic gas\}}$$

Or $$\Delta U = (5/2) nR \cdot \Delta T \text{ \{diatomic gas\}}$$

Specific Heat Capacity & 1st Law of Thermodynamics (for monatomic gases)

- The heat (Q) absorbed by a gas can be expressed as:

  $$\mathbf{Q = Cn\Delta T} \quad \text{------------------------------}$$

  where C is the molar heat capacity (J/mol·K)
- Since gases it is necessary to distinguish between molar heat capacity at constant pressure (C_P) and constant volume (C_V)
- Let's begin with the 1st Law of Thermodynamics:

  $$\mathbf{Q = \Delta U + W}$$

- At **constant pressure**: $\{\Delta U = (3/2)nRT \;\&\; W = P\Delta V = nR\Delta T\}$

  $$\mathbf{Q = (3/2)nR\Delta T + nR\Delta T = (5/2)nR\Delta T \rightarrow C_P = (5/2)R}$$

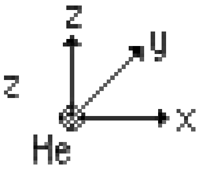
- At **constant volume**: $\{\Delta U = (3/2)nRT \;\&\; W = 0\}$

  $$\mathbf{Q = (3/2)nR\Delta T + 0 = (3/2)nR\Delta T \;\rightarrow C_V = (3/2)R}$$

Selected Specific Heats

Degrees
of
freedom

3

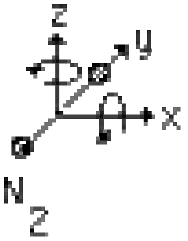


Monoatomic

$$C_v = \frac{3}{2}R = 12.5\ \frac{\mathrm{J}}{\mathrm{mol\ K}}$$

Helium	12.5
Argon	12.6

5

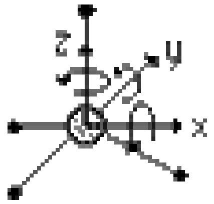


Diatomic

$$C_v = \frac{5}{2}R = 20.8\ \frac{\mathrm{J}}{\mathrm{mol\ K}}$$

Nitrogen (N_2)	20.7
Oxygen (O_2)	20.8

6



Polyatomic

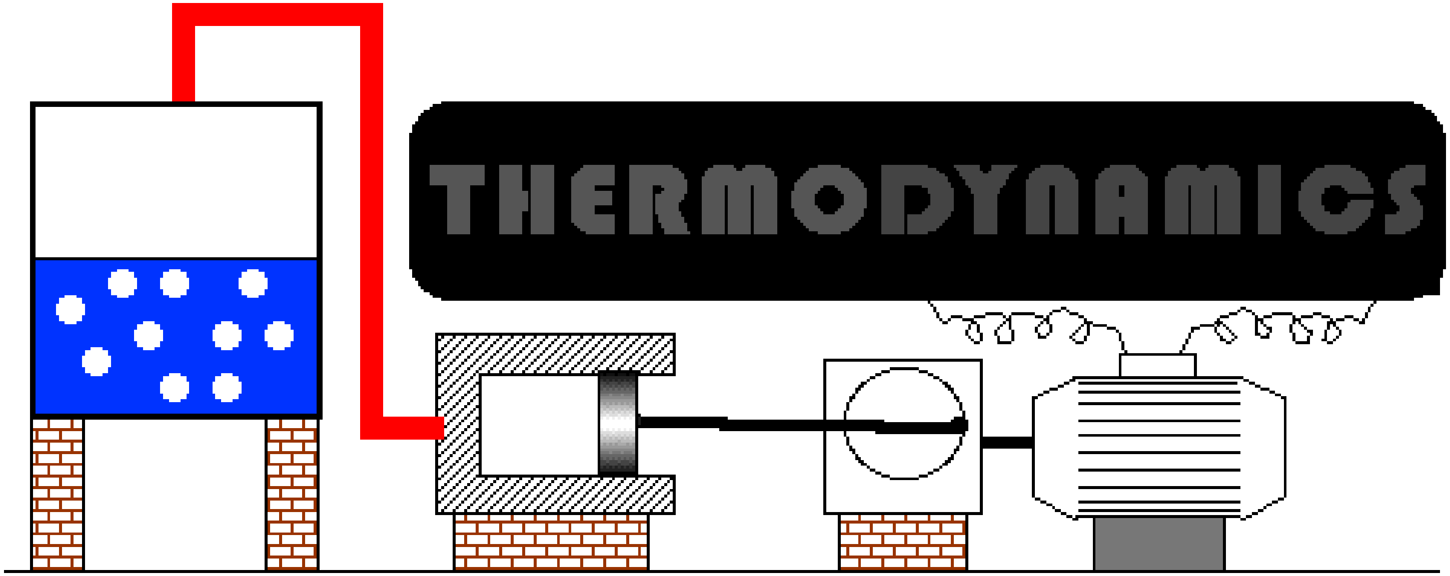
$$C_v = \frac{6}{2}R = 24.9\ \frac{\mathrm{J}}{\mathrm{mol\ K}}$$

Ammonia (NH_4)	29.0
Carbon dioxide (CO_2)	29.7

Study material on Thermodynamics

- Book: Basic Thermodynamics - Evelyn Guha (Cahpter-3,4 & 5)
- **Worked Examples on first Law: Page-57,58,59,60 &61 (chapter-3)**

THERMODYNAMICS



Lecture-3

Section -3

- Heat Engine
- Second Law of Thermodynamics
- Carnot Engine(P-V cycle)

Thermodynamics

- **Thermodynamics** (from the Greek *thermos* meaning heat and *dynamics* meaning power) is a **branch of physics** that studies the effects of changes in temperature, pressure, and volume on physical systems .

•Roughly, heat means "energy in transit" and dynamics relates to "movement"; thus, in essence **thermodynamics studies the movement of energy.**

History:
Sadi Carnot (1796-1832):
“Father" of thermodynamics.

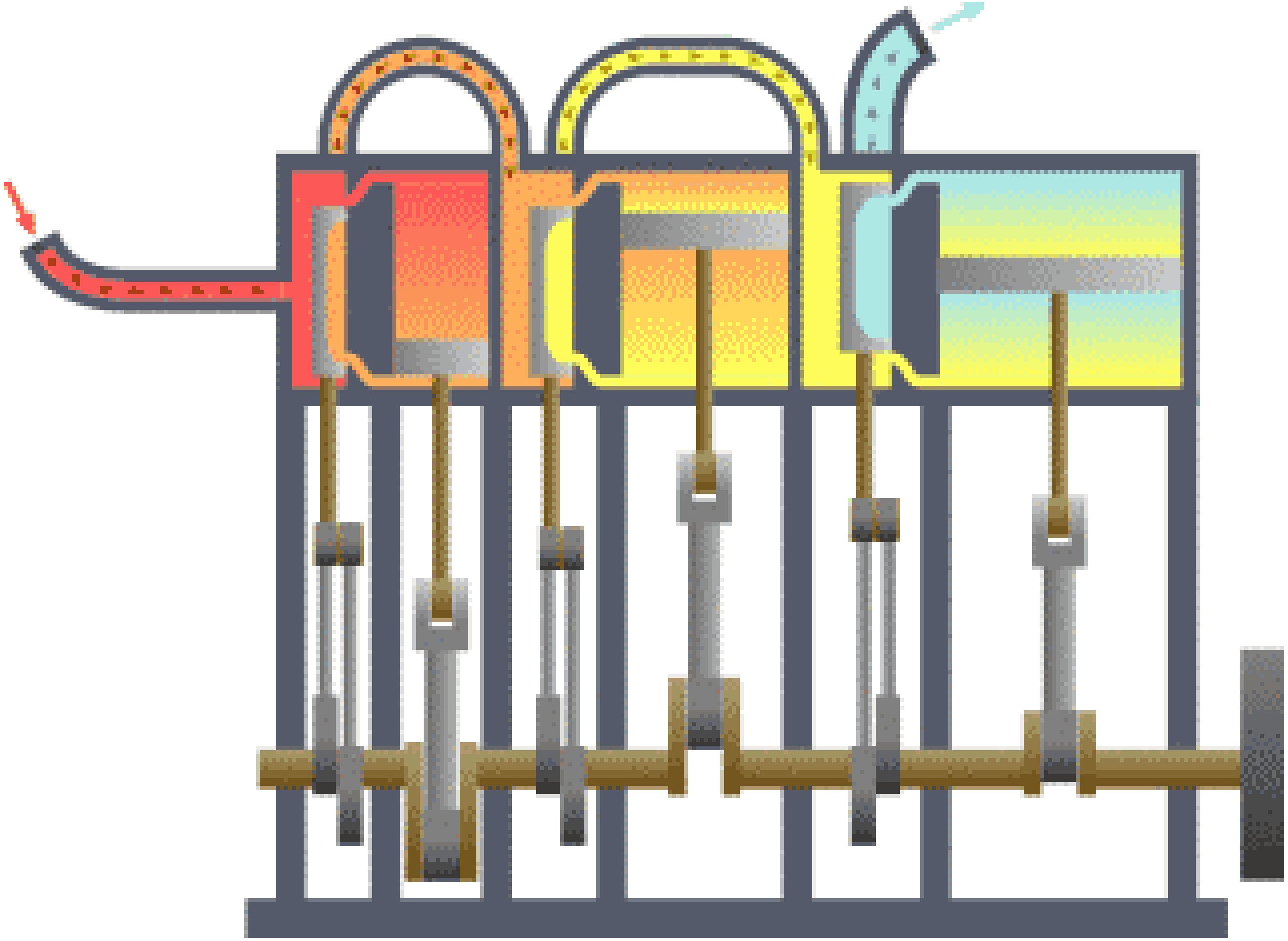
http://en.wikipedia.org/wiki/Image:Carnot2.jpg

Sadi Carnot (1796-1832)

- French engineer
- Published only 1 work during his lifetime
    - Described the details of the "Carnot" engine (an "ideal" heat engine)
- Fascinated with steam engines
    - Resented the advancements made in rival England
    - The bulk of his work focused on understanding heat and steam engine design/efficiency
    - Work based on the "caloric" theory

- Contracted cholera and died the next day, at the age of 36

thermodynamic system



- Typical **thermodynamic system** - heat moves from hot (boiler) to cold (condenser) and work is extracted.

Thermodynamic Processes (for gases)

- Isothermic: constant temperature

  $\Delta T = 0$ means $\Delta U = 0$ (U is constant!)

  $W = Q = (nRT)\ln(V_f/V_i)$
- Adiabatic: no gain/loss of heat energy (Q)

  $Q = 0$ means $\Delta U = W$

Note: Isothermal and Adiabatic are important for Carnot Engine (Ideal heat Engine)

- Isochoric (or isovolumetric): constant volume

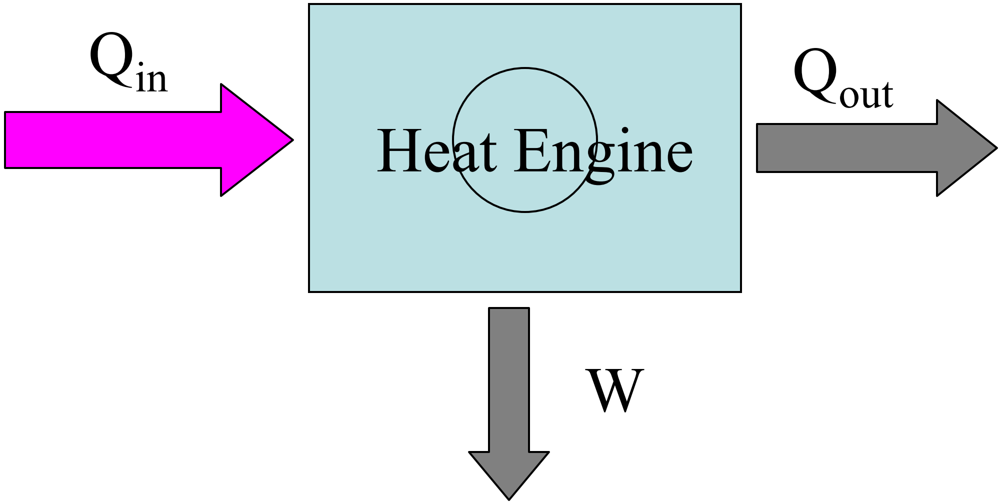
  $\Delta V = 0$ means $W = 0$ (no work performed on/by system)
- Isobaric: constant pressure

  $\Delta P = 0$ means $W = P\Delta V$

Note: Isochoric and Isobaric are important for specific heat of Gases.

Heat Engines

- A process that utilizes heat energy input (Q_{in}) to enable a working substance perform work output

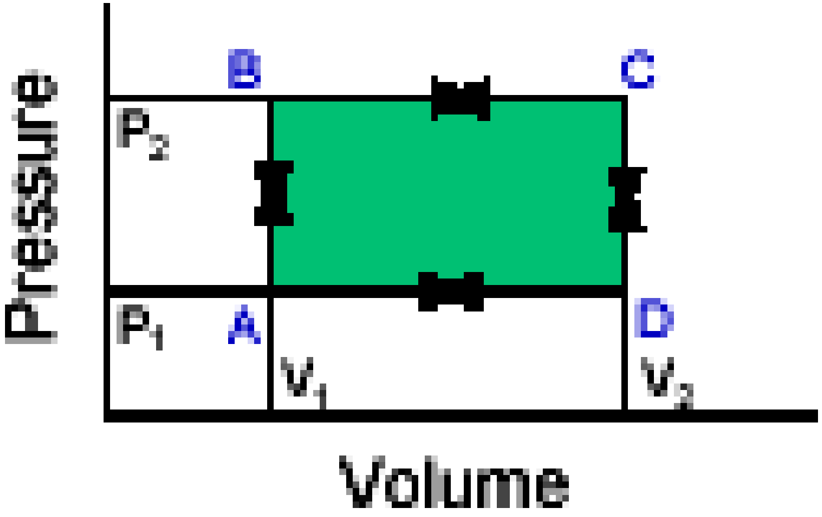


- Heat energy input equals the work performed plus the heat energy discarded:

$$Q_{in} = Q_{out} + W$$

Cyclic Processes

Definition: A process that starts and ends at the same state.



$\Delta E_{int} = 0$ → from 1st law of thermo: $\boxed{W = -Q}$

- Clockwise: Heat Engine … Q → W.
- Counterclockwise: Heat Pump … W → Q.

The 2nd law of thermodynamics

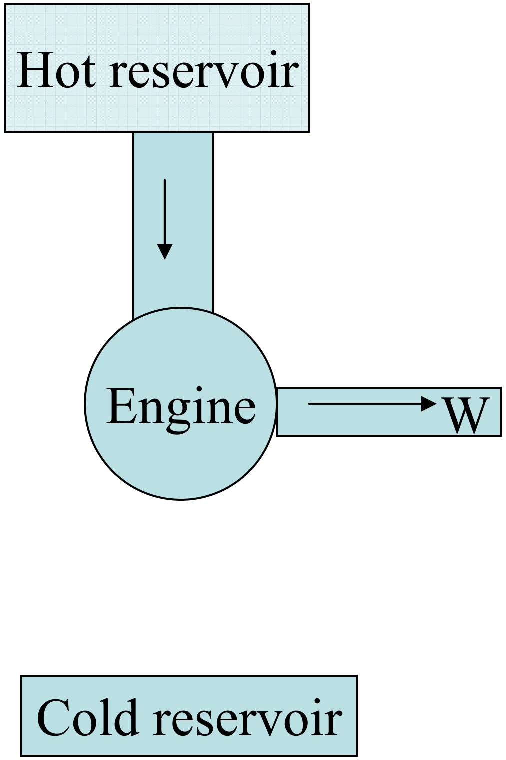
1st law: $\Delta U = Q + W$
In a cyclic process ($\Delta U = 0$) $Q = W$: we cannot do more work than the amount of energy (heat) that we put inside

2nd law: It is impossible to construct an engine that, operating in a cycle produces no other effect than the absorption of energy from a reservoir and the performance of an equal amount of work: we cannot get 100% efficiency

What is the most efficient engine we can make given a heat and a cold reservoir?

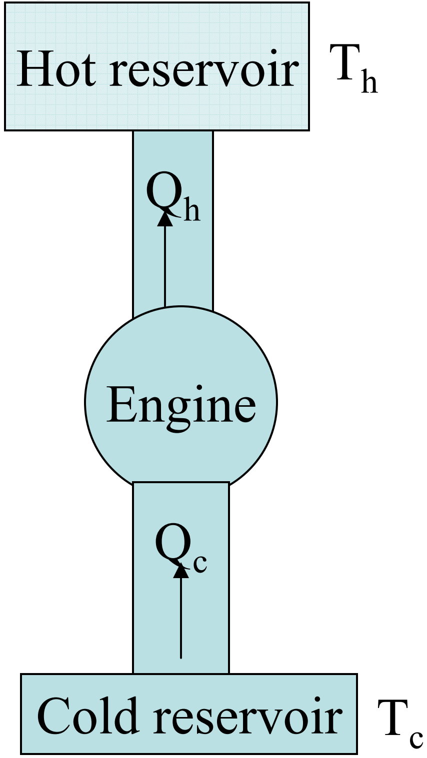
Second Law of Thermodynamics

- Kelvin-Planck statement: It is impossible to construct a heat engine that, operating in a cycle, produces no other effect than the absorption of thermal energy from a reservoir and the performance of equal amount of work.



Impossible engine

- Impossible refrigerator

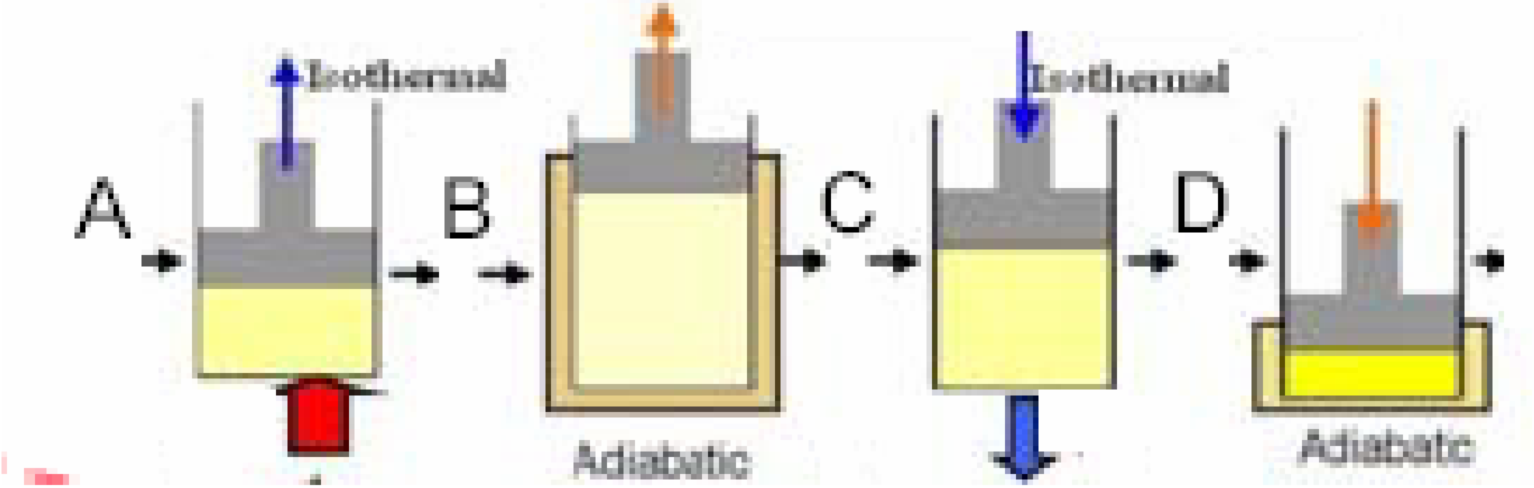


•Clausius statement (in a simpler form) **Heat will not flow spontaneously from a cold object to a hot object.**

Example of Heat Engine

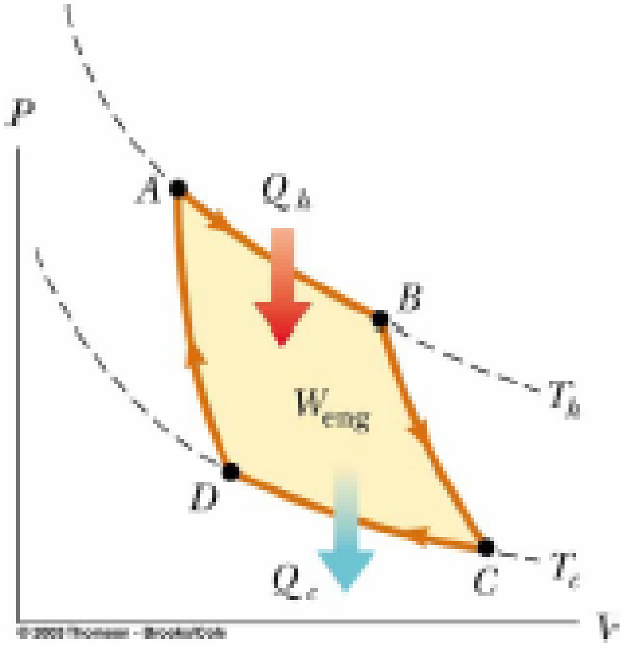
- The Carnot Cycle (Engine)
  - An “ideal” reversible heat engine (no heat engine can be more efficient than a Carnot engine)
  - A 4 stage engine that operates between 2 temperature reservoirs (T_{hot} and T_{cold}) consisting of
    - 2 isothermic phases
    - 2 adabatic phases

Carnot Cycle



- No engine can be more efficient than the Carnot engine.
- A→B: Heat added from hot reservoir, work extracted.
- B→C: No heat transfer, work extracted.
- C→D: Work added, heat extracted to cold reservoir.
- D→A: No heat transfer, work added.
- Total: Net work extracted is area inside cycle.

Carnot cycle

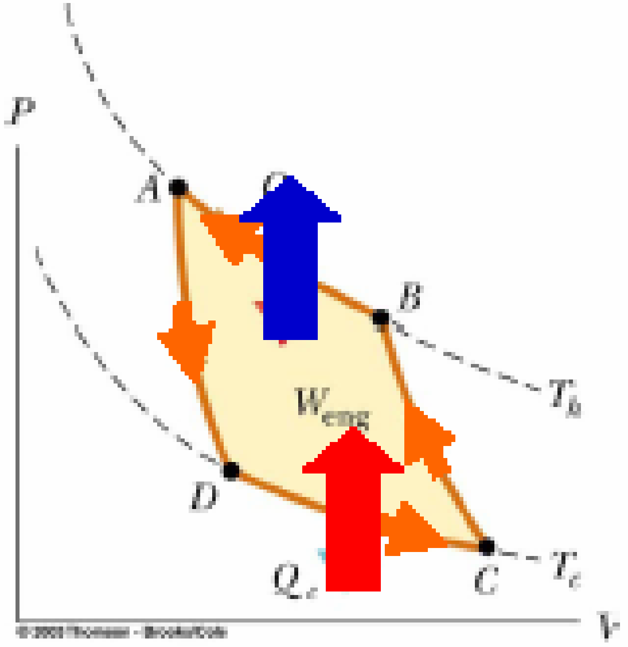


Work done by engine: W_{eng}

$W_{eng}=Q_{hot}-Q_{cold}$

efficiency: $1-T_{cold}/T_{hot}$

inverse Carnot cycle



A heat engine or a fridge!

By doing work we can transport heat

Efficiency of a Heat Engine

- A measure of the effectiveness of a **heat engine** is its thermodynamic efficiency:

Efficiency = $\varepsilon = W_{performed}/Q_{input} = (Q_{input} - Q_{out})/Q_{input}$

or

% Efficiency = % $\varepsilon = (W_{performed}/Q_{input})\cdot 100\%$

- **For the Carnot ("ideal") engine:**

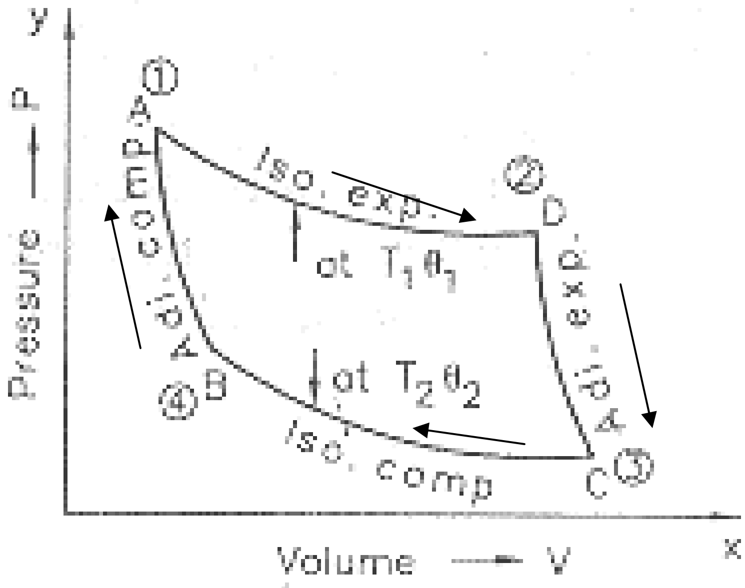
% Efficiency = % $\varepsilon_{Carnot} = (Q_{input} - Q_{out})/Q_{input}$

since $Q_{input}/Q_{out} = T_{hot}/T_{cold}$ the efficiency can be written as

Show that

$$\% \varepsilon_{Carnot} = [(T_{hot}-T_{cold})/T_{hot}]\cdot 100\%$$

Proof:



adiabatic expansion

$$W_2 = \frac{P_2 V_2 - P_3 V_3}{\gamma - 1}$$

$$W_2 = \frac{mR\,(T_1 - T_2)}{\gamma - 1}$$

Adiabatic compression

$$W_4 = -\frac{mR\,(T_1 - T_2)}{\gamma - 1}$$

Isothermal expansion

Work done by the air

$$W_1 = mRT_1 \log_e \left(\frac{V_2}{V_1}\right)$$

$$Q_1 = \frac{mRT_1 \log_e \left(\frac{V_2}{V_1}\right)}{J}$$

where $1/J = A$, is constant.

Conversion constant (joule effect due to cyclic process)

Isothermal compression

$Q_2 = W_3/J$

$$Q_2 = \frac{mRT_2}{J} \log_e \left(\frac{V_3}{V_4}\right)$$

$$\eta = \frac{Q_1 - Q_2}{Q_1}$$

It can be shown that $V_2/V_1 = V_3/V_4$. Consider the adiabatic expansion BC. Since temperature and volume at B and C are T_1, T_2 and T_2, T_3 respectively.

$$\frac{V_3}{V_2} = \left(\frac{T_1}{T_2}\right)^{1/(\gamma-1)}$$

From adiabatic compression curve DA, similarly we get

$$\frac{V_4}{V_1} = \left(\frac{T_1}{T_2}\right)^{1/(\gamma-1)}$$

Hence →

$$\frac{V_4}{V_1} = \frac{V_3}{V_2} \quad \text{or} \quad \frac{V_2}{V_1} = \frac{V_3}{V_4} = r$$

where r is the ratio called isothermal expansion or compression ratio (both are same for Carnot cycle). Substituting these values in the expression for heat received and rejected, we get

$$Q_1 = mART_1 \log_e \frac{V_2}{V_1} = mART_1 \log_e r$$

$$\text{and} \quad Q_2 = mART_2 \log_e \frac{V_3}{V_4} = mART_2 \log_e r$$

$$\therefore \quad Q_1 - Q_2 = mAR \log_e r \times (T_1 - T_2)$$

Hence we have for the efficiency of the Carnot engine

$$\boxed{\eta = \frac{Q_1 - Q_2}{Q_1}} = \frac{mAR\,(T_1 - T_2) \log_e r}{mART_1 \log_e r}$$

$$\text{or} \qquad \eta = \frac{T_1 - T_2}{T_1}$$

$$\text{or} \quad \boxed{\eta = 1 - \frac{T_2}{T_1}} \qquad \ldots($$

Example-1

The efficiency of a Carnot engine is 30%. The engine absorbs 800 J of energy per cycle by heat from a hot reservoir at 500 K. Determine a) the energy expelled per cycle and b) the temperature of the cold reservoir. c) How much work does the engine do per cycle?

a) Generally for an engine: efficiency: $1-|Q_{cold}|/|Q_{hot}|$
$0.3=1-|Q_{cold}|/800$, so $|Q_{cold}|=-(0.3-1)*800=560$ J

b) for a Carnot engine: efficiency: $1-T_{cold}/T_{hot}$
$0.3=1-T_{cold}/500$, so $T_{cold}=-(0.3-1)*500=350$ K

c) $W=|Q_{hot}|-|Q_{cold}|=800-560=240$ J

Example-2

An engine is operated between a hot and a cold reservoir with Q_{hot}=400J and Q_{cold}=300J. a) what is the efficiency of the engine?
The engine is modified and becomes a carnot engine. As a result the efficiency is doubled. b) what is the ratio T_{cold}/T_{hot}. c) what is the maximum efficiency of this engine?

a) efficiency=$1-Q_{cold}/Q_{hot}=1-300/400=0.25$
b) new efficiency: $0.5=1-T_{cold}/T_{hot}$ $T_{cold}/T_{hot}=0.5$
c) 0.5 (Carnot engine has maximum efficiency).

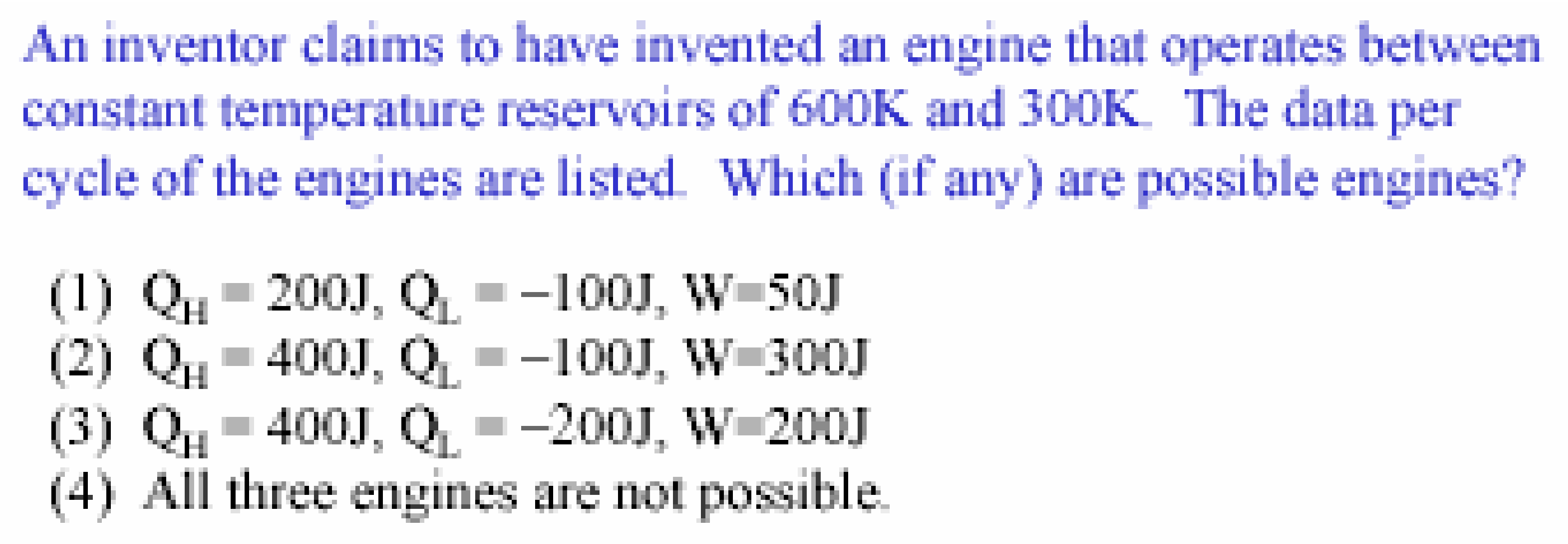
Example-3

A new powerplant is designed that makes use of the temperature difference between sea water at 0m (20^0) and at 1-km depth (5^0). A) what would be the maximum efficiency of such a plant? B) If the powerplant produces 75 MW, how much energy is absorbed per hour? C) Is this a good idea?

a) maximum efficiency=carnot efficiency=$1-T_{cold}/T_{hot}=$ $1-278/293=0.051$ efficiency=5.1%

b) $P=75*10^6$ J/s $W=P*t=75*10^6*3600=2.7\times10^{11}$ J
efficiency$=1-|Q_{cold}|/|Q_{hot}|=(|Q_{hot}|-|Q_{cold}|)/|Q_{hot}|=$ $W/|Q_{hot}|$ so $|Q_{hot}|=W/$efficiency$=5.3\times10^{12}$ J

c) Yes! Very Cheap!! but… $|Q_{cold}|=|Q_{hot}|-W=5.0\times10^{12}$ J every hour 5E+12 J of waste heat is produced:
$Q=cm\Delta T$ 5E+12=4186*m*1 m=1E+9 kg of water is heated by 1^0C…perhaps not!



An inventor claims to have invented an engine that operates between constant temperature reservoirs of 600K and 300K. The data per cycle of the engines are listed. Which (if any) are possible engines?

(1) Q_H ■ 200J, Q_L ■ −100J, W■50J
(2) Q_H ■ 400J, Q_L ■ −100J, W■300J
(3) Q_H ■ 400J, Q_L ■ −200J, W■200J
(4) All three engines are not possible.

1st Law of Thermodynamics: $W = Q_H - Q_L$

Engine 1 violates this law, but 2 & 3 obey it.

2nd Law of Thermodynamics:

$$\varepsilon_{max} = W/Q_H = 1 - Q_L/Q_H = 1 - T_L/T_H = 1 - 300/600 = 1/2$$

An inventor claims to have invented an engine that operates between constant temperature reservoirs of 600K and 300K. The data per cycle of the engines are listed. Which (if any) are possible engines?

~~(1) $Q_H = 200J$, $Q_L = -100J$, $W=50J$~~

~~(2) $Q_H = 400J$, $Q_L = -100J$, $W=300J$~~

(3) $Q_H = 400J$, $Q_L = -200J$, $W=200J$

~~(4) All three engines are not possible.~~

$\varepsilon_2 = W/Q_H = 3/4$

$\varepsilon_3 = W/Q_H = 2/4 = 1/2$

More Examples

An engine absorbs 1600 J from a hot reservoir and expels 1000 J to a cold reservoir in each cycle.

(a) What's the efficiency of the engine?

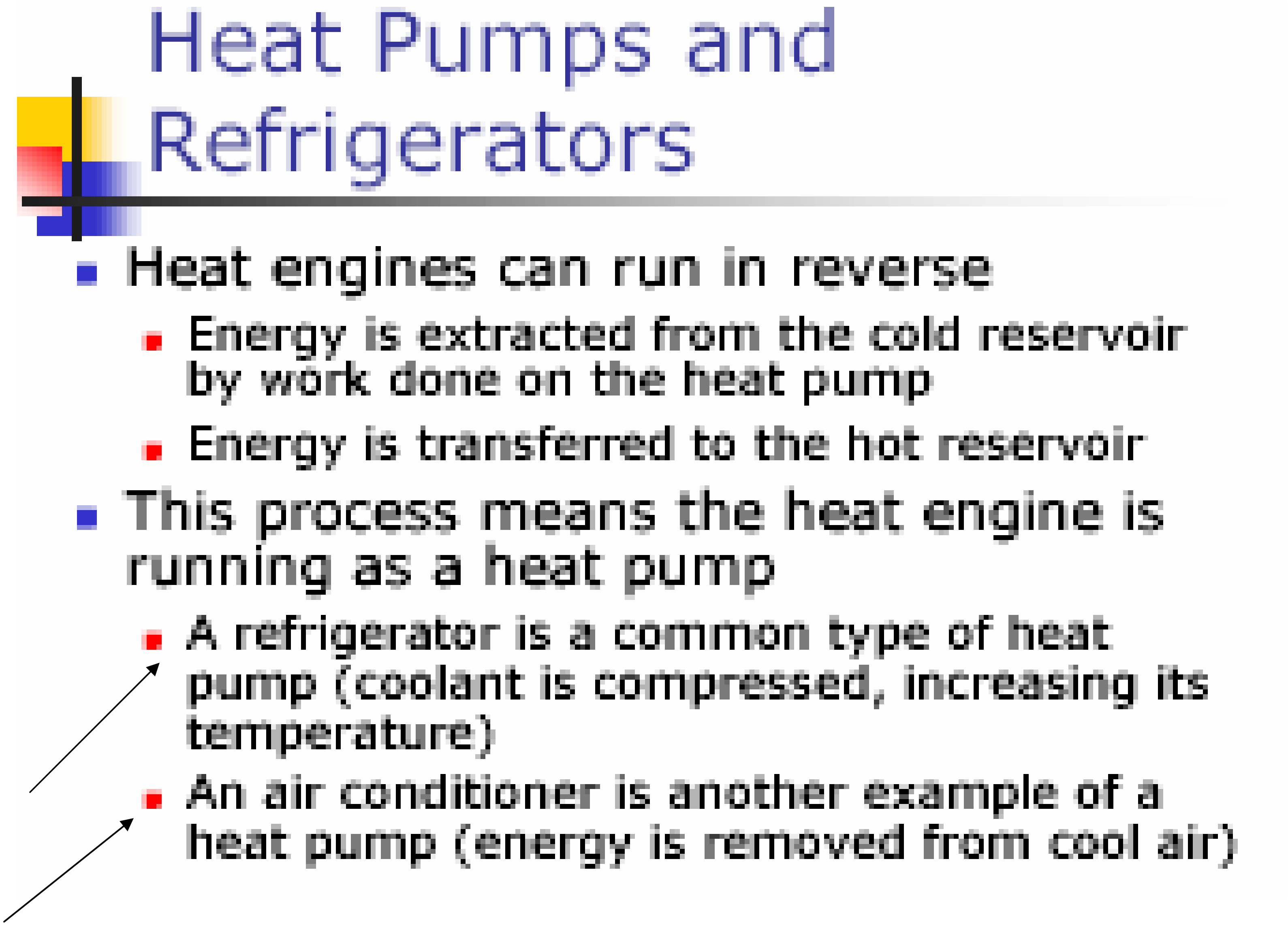
(b) How much work is done in each cycle?

(c) What's the power output of the engine if each cycle lasts for 0.300 s?

$$e = 1 - \frac{|Q_c|}{|Q_h|} = 1.00 - \frac{1000\,\mathrm{J/cycle}}{1600\,\mathrm{J/cycle}} = 0.375$$

$$W_{\mathrm{eng}} = |Q_h| - |Q_c| = (1600 - 1000)\,\mathrm{J/cycle} = 600\,\mathrm{J/cycle}$$

$$P = \frac{W_{\mathrm{eng}}}{T} = \frac{600\,\mathrm{J/cycle}}{0.300\,\mathrm{s/cycle}} = 2000\,\mathrm{J/s}\,[\mathrm{W}]$$

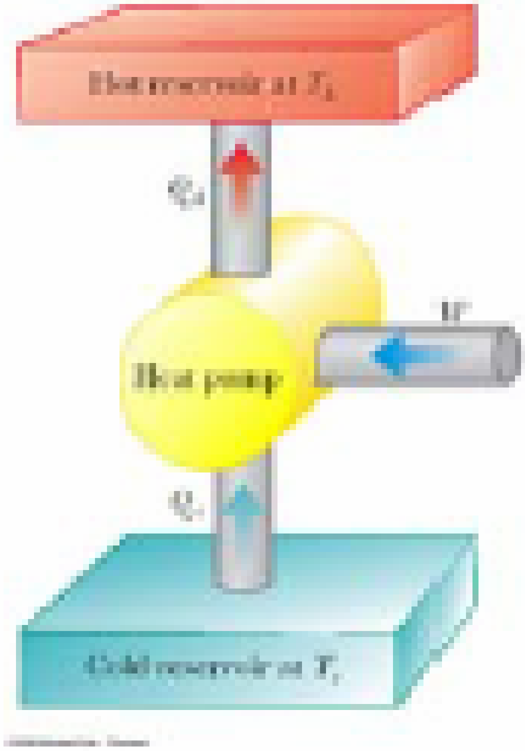


Heat Pumps and Refrigerators

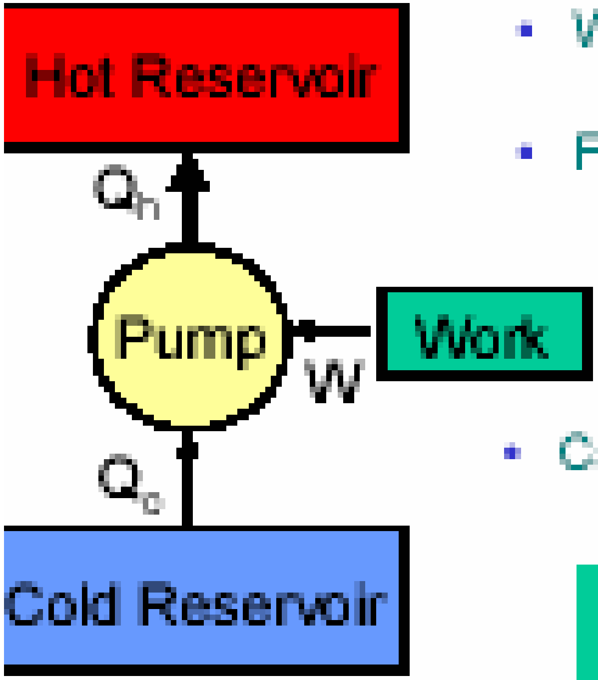
- Heat engines can run in reverse
    - Energy is extracted from the cold reservoir by work done on the heat pump
    - Energy is transferred to the hot reservoir
- This process means the heat engine is running as a heat pump
    - A refrigerator is a common type of heat pump (coolant is compressed, increasing its temperature)
    - An air conditioner is another example of a heat pump (energy is removed from cool air)

Heat Pump, cont

- The work is what you pay for
- The Q_C is the desired benefit
- The coefficient of performance (COP) measures the performance of the heat pump running in cooling mode



Coefficient of Performance



- W is work done *on* engine (normal).
- From 1st law of thermo with $\Delta E_{int} = 0$:

$$|Q_h| = |Q_c| + W$$

- Can define pump coef. of performance:

Heating mode

$$COP = \frac{|Q_h|}{W}$$

Cooling mode

$$COP = \frac{|Q_c|}{W}$$

- Can exceed unity! ($COP < \infty$)

Heat Pump, COP

- In cooling mode, $COP = \frac{|Q_c|}{W}$
- In heating mode, $COP = \frac{|Q_H|}{W}$
- The higher the number, the better
- A good refrigerator or air conditioner typically has a COP of 5 or 6

Example

The energy entering an electric heater by electrical transmission can be converted to heat energy with an efficiency of 100%. By what factor does the cost of heating your home change when you replace your electrical heating system with an electric heat pump that has a COP of 4.00? Assume the motor running the heat pump is 100% efficient.

You pay for electricity. With electric heater 100% of electrical energy is converted to heat.

With an electric heat pump, 100% of electrical energy is converted to work and then 400% of that work is converted to heat (COP = 4.00). It therefore takes less electrical energy (& $) to get the same heat.

Your heating bill will go down by a factor of 4.00.

Reversible and irreversible processes

- In nature almost all the processes have a preferred direction.

  For example heat flows hotter to cooler bodies, a ball moving on a rough surface stops but the opposite phenomenon never occur without the influence of external forces.

  A process is irreversible if the the system and its surroundings can not be returned to its initial state.

Reversible and irreversible processes-2

- In **irreversible process** we pass through **a series of nonequilibrium states** while going from initial to final state, so irreversible **process can not be represented by a** line **on PV diagram.**
- A process may be **reversible** if the **system passes** from the initial state to the final state through a **succession of equilibrium states.**
- If a **process occur quasi-statistically**, that is **slowly enough**, so that each state departs only infinitesimally from equilibrium, it **can be considered reversible** and can be represented by a line on a PV diagram.

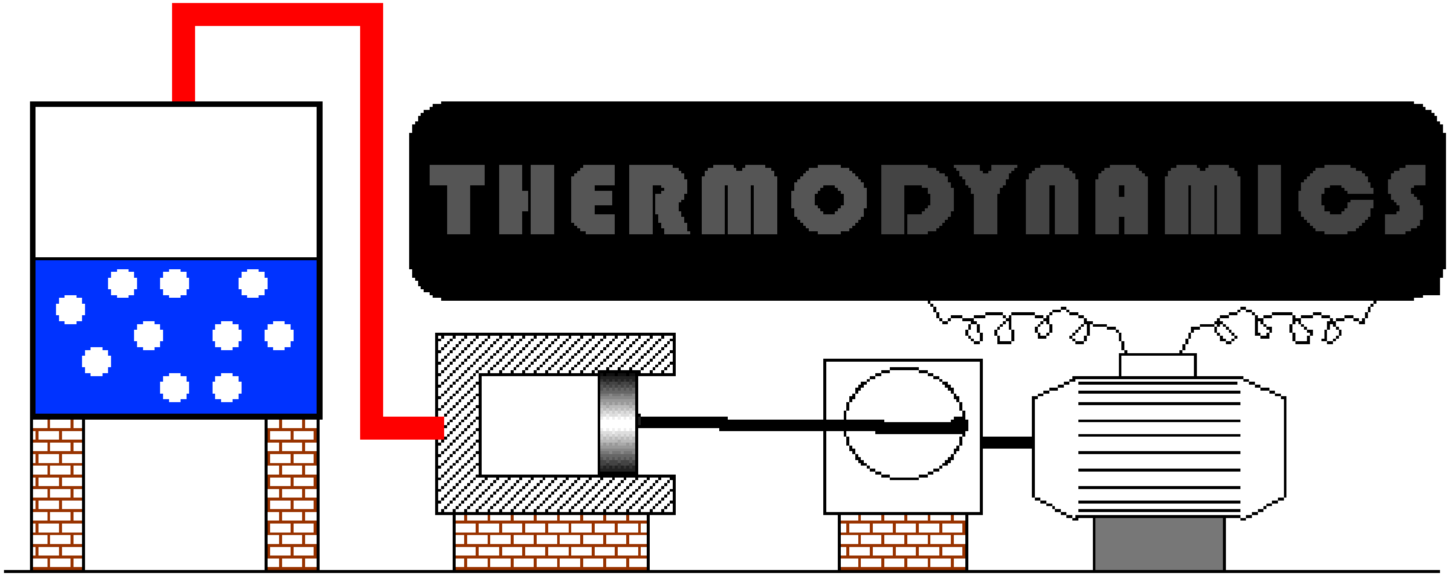
Carnot Theorem

- No real heat engine operating between two heat reservoirs can be more efficient than a Carnot engine operating between the same two reservoir (Carnot Theorem).

- All Carnot engines operating between the same two temperature in a reversible manner have the same efficiency.
- Efficiency of any reversible engine operating in a cycle between two temperatures is greater than the efficiency of any irreversible (real) engine operating between the same temperatures. Actually friction, heat loses by conduction and other practical difficulties make all the real engine irreversible and thus less efficient compared to a Carnot engine.

Study material on Thermodynamics

- Book: Basic Thermodynamics - Evelyn Guha (Cahpter-4)
- **Worked Examples on Carnot Cycle: Page-77,78,79,80,81 & 82.(chapter-4)**



THERMODYNAMICS

Lecture-4

Second Law of Thermodynamics

- Not all processes that are allowed by energy conservation occur in nature. Why ?

- Ice melts but water does not spontaneously freeze,
- heat flows from hot to cold but never from cold to hot.

$\Rightarrow$ **We need a new concept which makes these (reversed) processes**

highly unlikely.

New concept: Entropy (S)

- A measure of “disorder” or probability of state of a system.
- A property of a system (=state function, just like P, V, T, U)
  - related to number of different “thermodynamic states” of system
  - Examples of increasing entropy:
    - ice cube melts
    - gases expand into vacuum

- In 1850 Clausius introduced a new thermodynamic state variable **Entropy** (it’s a Greek word meaning ‘turning into’).
- Entropy is a measure of how much heat is unavailable for conversion into work.
- A thermodynamic system can described by a temperature T, an internal energy U and an entropy S. **The entropy provides a relation between heat and temperature.**

Entropy-2

- The change in entropy, dS, between two equilibrium states is given by the heat transferred, dQ, divided by the absolute temperature T, of the system in this interval ,that is

$$dS = \frac{dQ}{T}$$

- In any **spontaneous process** the entropy can not decrease.

$$dS \geq 0.$$

- This is the second law of thermodynamics, with equality holding for a reversible process.

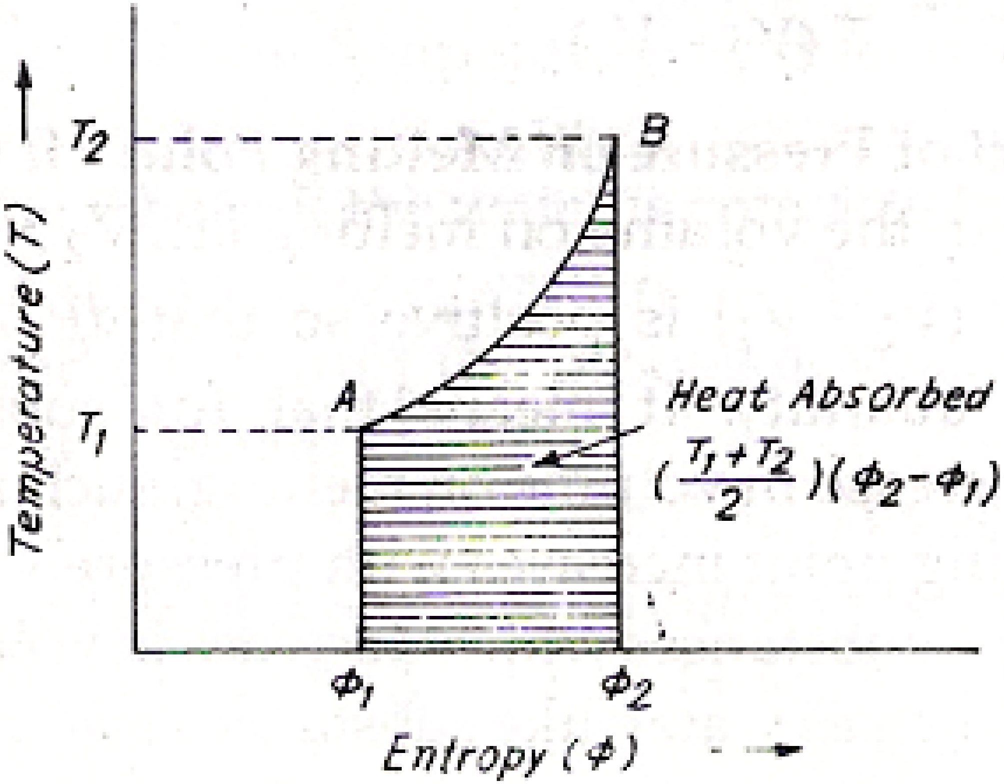
If we give a very small quantity of heat *dQ* to the substance at *TK*, there will be practically no change in *T* as *dQ* is infinitely small. Then minute change in entropy.

$$d\phi = \frac{dQ}{T} \qquad \text{...(15.35)}$$

By integrating the above equation we can get the total change in entropy

$$\int_{\phi_1}^{\phi_2} d\phi = \int_{T_1}^{T_2} \frac{dQ}{T} \qquad \text{...(15.36)}$$

A graph between entropy and temperature is known as temperature entropy or $T - \phi$ or $T - S$ diagram. Such a graph for heating process is shown in Fig. 15.13. The area under the $T - \phi$ diagram gives the total heat rejected or received.



15.22 GENERAL EXPRESSION FOR THE CHANGE OF ENTROPY OF A PERFECT GAS

Let the initial conditions of a gas be represented by P_1, V_1, T_1 and ϕ_1 and the final condition be represented by P_2, V_2, T_2 and ϕ_2. From energy equation,

First Law: $$dQ = dW + dU$$

$$d\phi = \frac{dQ}{T} = \frac{PdV}{JT} + C_v \frac{dT}{T}$$

[assume m=1, n=1]

$$\int_{\phi_1}^{\phi_2} d\phi = \frac{R}{J}\int_{V_1}^{V_2} \frac{dV}{V} + C_v \int_{T_1}^{T_2} \frac{dT}{T}$$

as $PV = RT$

$$\boxed{\phi_2 - \phi_1 = \frac{R}{J}\log_e \frac{V_2}{V_1} + C_v \log_e \frac{T_2}{T_1}}$$

In terms of V and T

………..(1)

Where J is a constant (conversion factor), mass of gas m=1kg

Expression in terms of pressure and volume:

From (1)

$$\phi_2 - \phi_1 = \frac{R}{J}\log_e\frac{V_2}{V_1} + C_v\log_e\left(\frac{V_2}{V_1}\times\frac{P_2}{P_1}\right)$$

as

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \text{ or } \frac{T_2}{T_1} = \frac{V_2}{V_1}\times\frac{P_2}{P_1}$$

$$= \left(C_v + \frac{R}{J}\right)\log_e\frac{V_2}{V_1} + C_v\log_e\left(\frac{P_2}{P_1}\right)$$

$$\boxed{\text{or } \phi_2 - \phi_1 = C_p\log_e\left(\frac{V_2}{V_1}\right) + C_v\log_e\left(\frac{P_2}{P_1}\right)}$$

Expression in terms of pressure and Temperature:

From (1)

$$\phi_2 - \phi_1 = \frac{R}{J}\log_e\left(\frac{P_1}{P_2}\times\frac{T_2}{T_1}\right) + C_v\log_e\left(\frac{T_2}{T_1}\right)$$

as

$$\frac{V_2}{V_1} = \frac{P_1}{P_2}\times\frac{T_2}{T_1}$$

$$\boxed{= C_p\log_e\left(\frac{T_2}{T_1}\right) - \frac{R}{J}\log_e\left(\frac{P_2}{P_1}\right)}$$

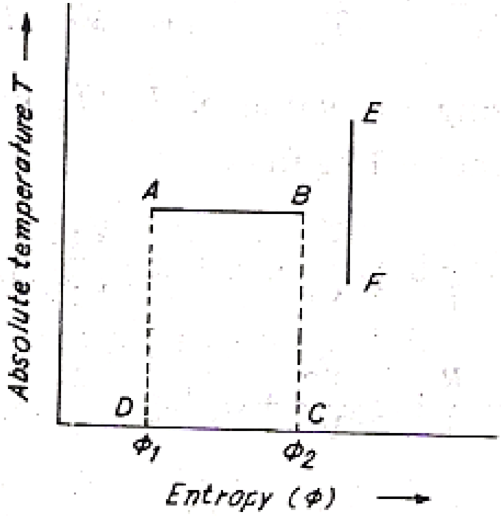
$$\text{or } \phi_2 - \phi_1 = 2.3\left[C_p\log_{10}\left(\frac{T_2}{T_1}\right) - \frac{R}{J}\times\log_{10}\left(\frac{P_2}{P_1}\right)\right]$$

15.23 ISOTHERMAL AND ADIABATIC PROCESSES ON T-φ DIAGRAM

$$\phi_2 - \phi_1 = \frac{Q}{T_1} = \frac{P_1 V_1 \log_e\left[\frac{V_2}{V_1}\right]}{JT_1}$$

$$= \frac{mRT_1}{JT_1} \log_e\left[\frac{V_2}{v_1}\right]$$

$$= \frac{mR}{J} \log_e\left[\frac{V_2}{V_1}\right]$$



Can also be obtained from equation (1).

$$d\phi = \frac{dQ}{T} = 0$$

The vertical line EF represents a reversible adiabatic expansion from condition E to F. As no heat is absorbed or rejected during this process, the T – φ diagram gives no area under the curve EF. This means that during reversible adiabatic process entropy remains constant and thus the process is known as isentropic.

HEATING AT CONSTANT PRESSURE

$$d\phi = \frac{dQ}{T} = mC_p \frac{dT}{T}$$

$$\phi_2 - \phi_1 = mC_p \log_e \left(\frac{T_2}{T_1}\right)$$

HEATING AT CONSTANT VOLUME

$$d\phi = \frac{dQ}{T} = mC_v \frac{dT}{T}$$

$$\int_{\phi_1}^{\phi_2} d\phi = mC_v \int_{T_1}^{T_2} \frac{dT}{T}$$

$$\phi_2 - \phi_1 = mC_v \log_e \left(\frac{T_2}{T_1}\right)$$

EXAMPLE 27 *Calculate the change in entropy when 10 gram of ice at 0°C is converted into water at the same temperature.*

Solution : We know change in entropy $\phi_2 - \phi_1 = Q/T$ and in this problem

$$Q = ML = 10 \times 80 = 800 \text{ and } T = 273$$

Change in entropy = 2.93.

EXAMPLE 28 *Calculate the change in entropy of 2 g of* O_2 *when its temperature is raised from 20°C to 100°C and its volume is doubled.*

given

For oxygen

$$R = 260 \text{ J/kg/K}, \quad C_v = 0.19 \text{ k cal/kg/k}$$

Note:

$$AR = \frac{R}{J} = \frac{260}{4200} = 0.062$$

solution

$$\phi_2 - \phi_1 = 2.3\text{ m}\left[C_v \log_{10}\left(\frac{T_2}{T_1}\right) + AR \log_{10}\left(\frac{V_2}{V_1}\right)\right]$$

$$= \mathbf{0.1777 \times 10^{-3} \text{ k cal/K.}}$$

Imp

EXAMPLE 29 *Calculate the increase in entropy when 1 g of ice at –10°C is converted into steam at 100°C.*

Specific heat of ice = 0.5, latent heat of ice = 80 cal/g, latent heat of steam = 540 cal/g.

Solution : (*i*) Increase in entropy when the temperature of 1 g of ice increases from – 10 to 0°C.

$$= \int_{T_1}^{T_2} \frac{dQ}{T} = \int_{T_1}^{T_2} \frac{mCdT}{T}$$

$$= mC \int_{T_1}^{T_2} \frac{dT}{T} = mC \log_e \left(\frac{T_2}{T_1}\right)$$

$$= 1 \times 0.5 \times 2.3026 \times \log_{10}\left(\frac{273}{263}\right)$$

$$= \mathbf{0.01865\ cal/K.}$$

(*ii*) Increase in entropy when 1 g of ice at 0°C is converted into water at 0°C.

$$d\phi = \frac{dQ}{T} = \frac{80}{273} = \mathbf{0.293\ cal/K.}$$

(*iii*) Increase in entropy when the temperature of 1 g of water is raised from 0°C to 100°C.

$$d\phi = \int_{T_1}^{T_2} \frac{dQ}{T} = mC \int_{T_1}^{T_2} \frac{dT}{T}$$

$$= \mathbf{0.312\ cal/K.}$$

(*iv*) Increase in entropy when 1 g of water at 100°C is converted into steam at 100°C

$$d\phi = \frac{dQ}{T} = \frac{540}{373} = 1.447 \text{ cal /K}$$

Total increase in entropy

$$= 0.01865 + 0.293 + 0.312 + 1.447$$

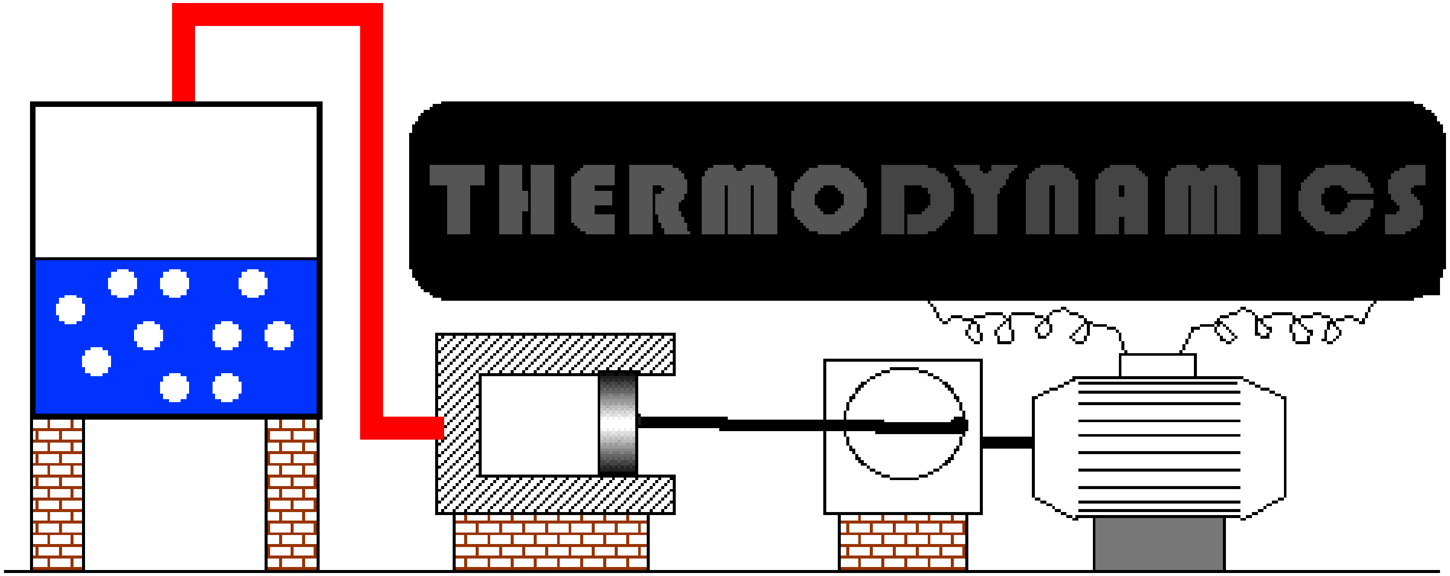
$$= \mathbf{2.07065\ cal/K.}$$

Study material on Thermodynamics

- Book: Basic Thermodynamics - Evelyn Guha (Cahpter-5)
- **To Read:Page-91,92,93,94,95 and 96**
- **Worked Examples: Page-112,113,114 and 115 (for Entropy) Chapter – 5.**

References:

- Basic Thermodynamics – Evelyn Guha (Chapter-3,4 &5 theory and Problems)
- Engineering Thermodynamics – P. K. Nag (third edition) (Solved Problems: pages-66,67, 130,131,170,171,172(Imp),179)
- Thermodynamics- Cengel-Boles (Ch. 5 & 6)



Lecture-5

More on Entropy (S)

- A measure of “disorder” or probability of state of a system.
- A property of a system (=state function, just like P, V, T, U)
  - related to number of different “states” of system
- Examples of increasing entropy:
  - ice cube melts
  - gases expand into vacuum
- Change in entropy:
  - $\Delta S = Q/T$ (T in K !) SI unit: [J/K]
    - >0 if heat flows into system (Q>0)
    - <0 if heat flows out of system (Q<0)

Reversible vs. Irreversible changes in a thermodynamic system:

- **Definition given by Fermi (1936), in Thermodynamics:**

"A transformation is said to be reversible when the successive states of the transformation differ by infinitesimals from equilibrium states."

$$\Delta S_{rev} = 0$$

- Irreversible: **Processes in which new entropy is "created". A system spontaneously changes, or energy is transformed in a way that creates new entropy.** This does not allow complete recovery of all aspects of previous thermodynamic states.

$$\Delta S_{irrev} > 0$$

Processes that happen spontaneously are irreversible.

- **The entropy change (Q/T) of the system+environment ≥ 0**
  - **never < 0**
  - **order to disorder**

  The entropy of the universe increases whenever an irreversible process occurs. All real processes in nature are irreversible.
- Consequences:
  - A “disordered” state cannot spontaneously transform into a more “ordered” state.
  - No engine operating between two reservoirs can be more efficient than one that produces zero change in entropy. The latter is called a “Carnot engine” (no real engine can ever be perfectly reversible but Carnot is a useful idealization, since it represents the limiting case) .
  - Heat cannot be transferred spontaneously from cold to hot.

Entropy

- Microscopic origin of entropy was essentially explained by Maxwell, Boltzmann and Gibbs around 1870.
- Let ‘i ‘ index the possible states of a system, p_i be the probability to be in the i-th state and let there be Ω total states. Then the **microscopic definition** of the entropy is

$$S = -k \sum_{i=0}^{\Omega} p_i \ln p_i ,$$

- Where k is Boltzmann’s constant

Entropy

- If all the states are equally likely then

$$p_i = \frac{1}{\Omega}$$

$$therefore \quad , \; S = k \ln \Omega$$

- This equation was so important to Boltzmann that it appears on his grave.

Change of Entropy in a Carnot cycle

- In a Carnot cycle

$$dS = \frac{Q_{hot}}{T_h} - \frac{Q_{cold}}{T_c}$$

$$but \quad \frac{Q_{hot}}{Q_{cold}} - \frac{T_h}{T_c}$$

$$Therefore \quad , \; dS = 0$$

- The entropy of the universe remains constant in a reversible process. So the entire energy is available to do work and after a complete reversible cycle. If we have a computer made up of reversible gates only we can do our computation without expensing energy.

Phase diagram and Clausius Clapeyron equation

Reference:

Page- 292, Heat and Thermodynamics by

Zemansky & Dittman (7th Edition)

Three dimensional Phase diagram for a pure substance

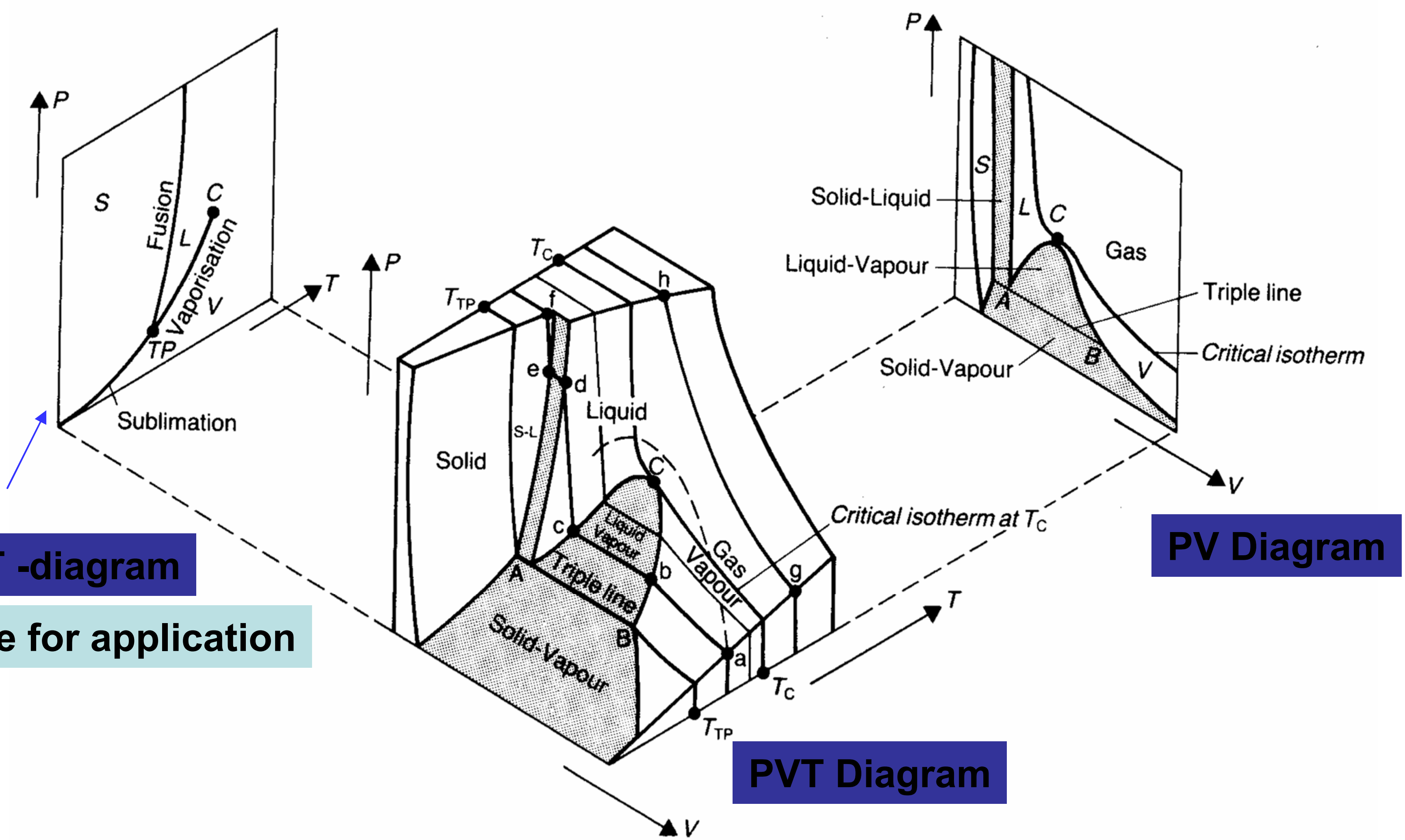


Fig. 9.1 A typical *PVT* surface together with its *P–T* and *P–V* projections.

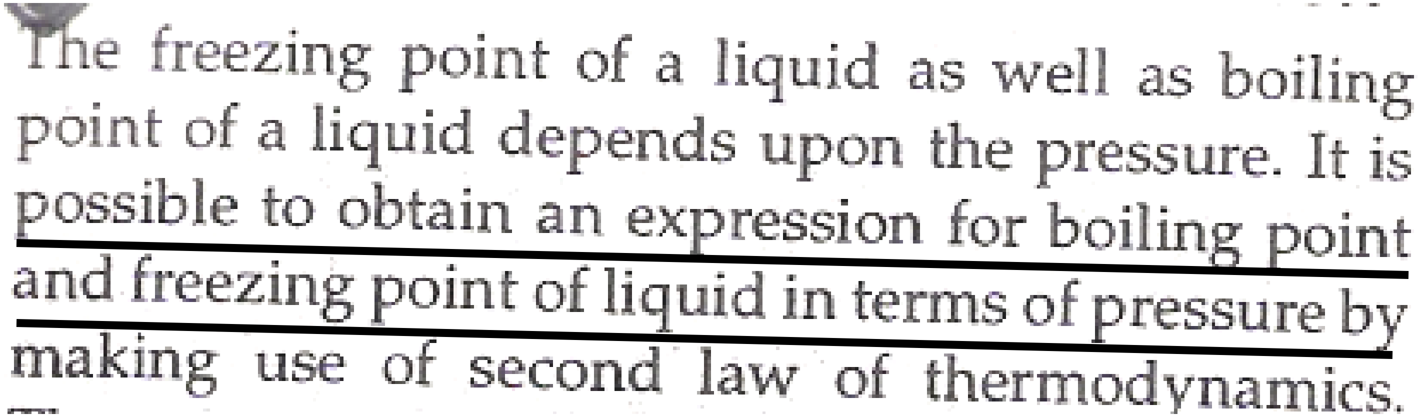
PT -diagram

Use for application

PV Diagram

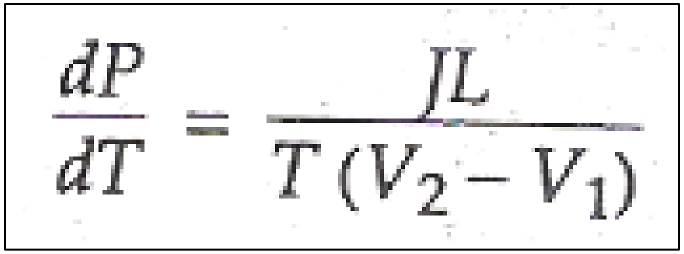
PVT Diagram

Clausius - Clapeyron Equation



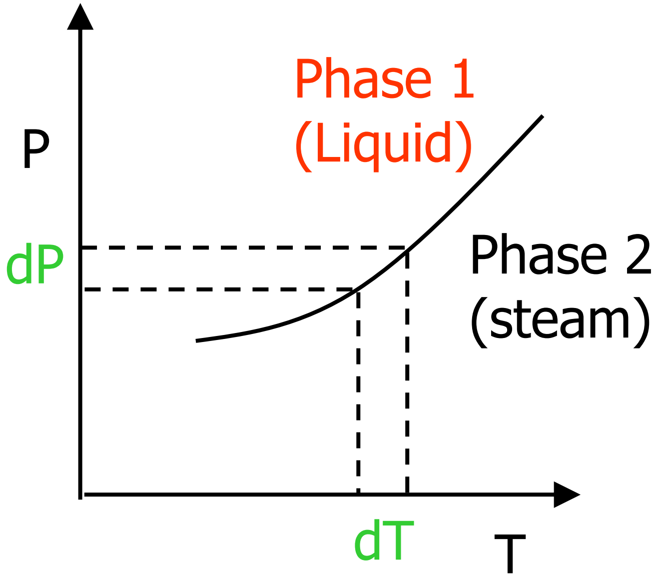
The freezing point of a liquid as well as boiling point of a liquid depends upon the pressure. It is possible to obtain an expression for boiling point and freezing point of liquid in terms of pressure by making use of second law of thermodynamics.

Equation is called Clausius-Clapeyron Equation



$$\frac{dP}{dT} = \frac{JL}{T(V_2 - V_1)}$$

Where J is joule constant, L is Latent heat



Clapeyron used steam as working substance in a Carnot cycle and derived relation between pressure, temperature, latent heat and volume. A P-V diagram of such a cycle is shown in Fig.

Consider one gram of water at boiling temperature T represented by point A in Fig. . If we bring in contact with the cylinder containing water a hot body having temperature T, then water will start evaporating at the given pressure P. After some time whole of the water is converted into dry saturated steam at temperature T. The amount of heat absorbed during the process is equal to the latent heat of water, say L.

At B, the steam expands adiabatically so that its pressure slightly decreases *i.e.* it becomes equal to $P - dP$ and temperature falls to $T - dT$. Towards the end of the adiabatic expansion *i.e.*, at point C, the cylinder is brought in contact with a cold body at $T - dT$ temperature and steam is subject to a constant pressure operation CD. This operation continues till point D *i.e.*, till it is completely liquefied. Now the water is adiabatically compressed back to its original condition as shown by point A. Let

Specific volume of water at pressure $P = V_w$

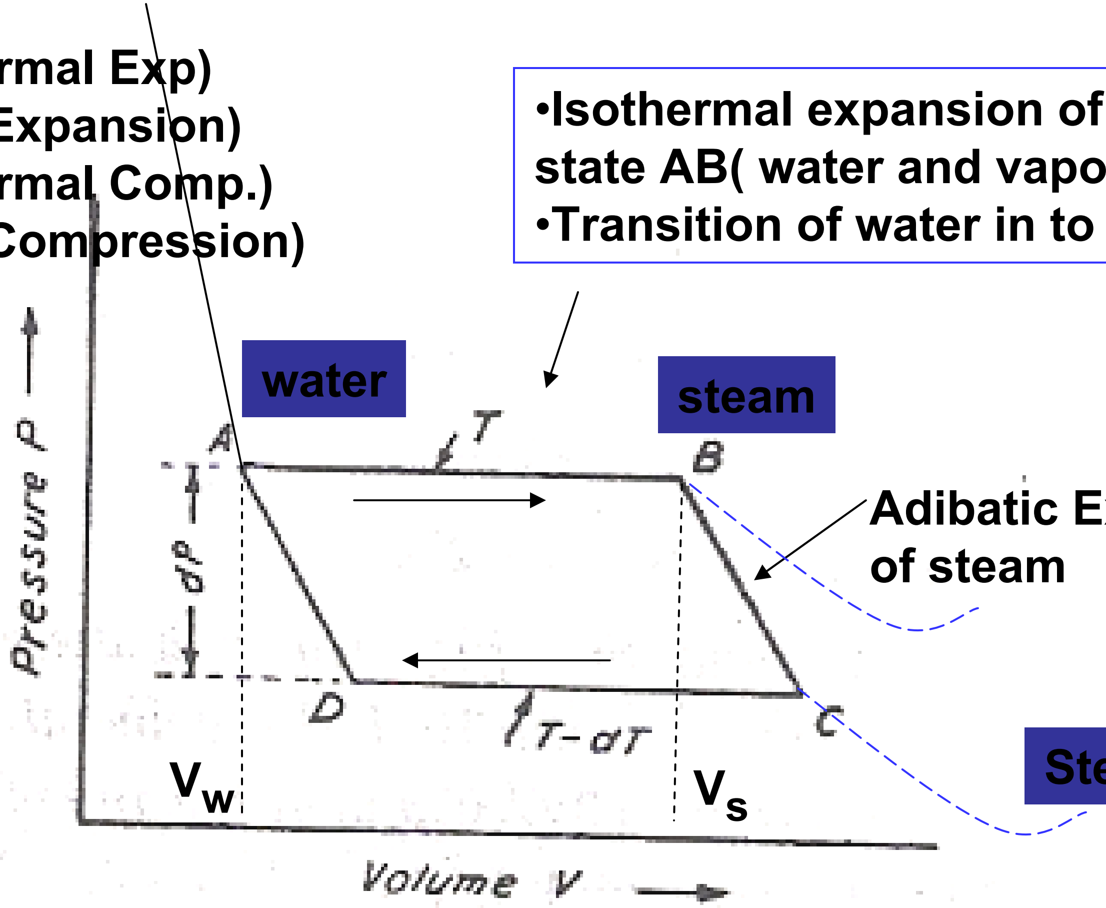
Specific volume of dry steam at pressure $P = V_s$

Latent heat at point A of water $= L$

(1) AB (Isothermal Exp)
(2) BC (Adia. Expansion)
(3) CD (Isothermal Comp.)
(4) DA (Adia. Compression)

- Isothermal expansion of mixed state AB(water and vapour)
- Transition of water in to steam

- Reversible process
- Carnot cycle



water

steam

Adibatic Expension of steam

Steam phase

Note

Specific volume of water at pressure $P = V_w$
Specific volume of dry steam at pressure $P = V_s$
Latent heat at point A of water $= L$

Note: Specific volume means Volume per unit mass, hence heat Q=L

For reversible cycle the efficiency is given by

$$\eta = \frac{T_1 - T_2}{T_1}$$

In this case

$$T_1 - T_2 = T - (T - dT) = dT; \text{ and } T_1 = T$$

$$\rightarrow \quad \eta = \frac{dT}{T}$$

→ Amount of heat absorbed per cycle = L cal. **[Q=m L= L]**

As m=1 gm

$$\frac{\text{Work done or output}}{\text{Input}} = \eta$$

[Q=W/J]

→ Output or work done $= J \times L \times \eta$ - - - - - - - - - - - - - **(1)**

Also work done W = Area under P-V diagram

$$W = AB \times \text{Pressure change } (= dP)$$

$$W = (V_s - V_w)\, dP$$ - - - - - - - - - - - - - **(2)**

$$J.L\,\eta = (V_s - V_w)\, dP$$

$$\text{or} \quad \frac{JL\,dT}{T} = (V_s - V_w)\, dP$$

$$\boxed{\begin{aligned} \frac{dP}{dT} &= \frac{JL}{T\,(V_s - V_w)} \\ \frac{dP}{dT} &= \frac{JL}{T\,(V_2 - V_1)} \end{aligned}} \leftarrow$$

Effect of Pressure on Melting Point. If there is increase in the volume on melting *i.e.*, $V_2 > V_1$, the quantity $(V_2 - V_1)$ is positive so that dP/dT is a positive quantity. It means that for substances which increase in volume on melting, such as wax, the melting point increases with pressure.

For the substances which decrease in volume on melting such as water, like substances $(V_2 < V_1)$ *i.e.*, the quantity $(V_2 - V_1)$ is a negative quantity. Hence dP/dT is negative which means that melting point of water like substances decrease with increase in pressure.

Effect of pressure on Boiling Temperature. When a liquid changes from liquid to gas its volume always increases *i.e.*, $V_2 > V_1$. Hence from

dP/dT **Is positive , hence increase**

In terms of Entropy

$$\boxed{\frac{dp}{dT} = \frac{L}{T\Delta v}} \longrightarrow \boxed{\frac{dp}{dT} = \left(\frac{s_2 - s_1}{v_2 - v_1}\right) = \frac{\Delta s}{\Delta v}}$$

As ΔS=ΔQ=L/T as m=1

Using the C-C equation: fusion

Example:
Calculate the melting temperature of ice at a pressure of 1000 atmospheres……

$$\boxed{\frac{dp}{dT} = \frac{\Delta p}{\Delta T} = \frac{L}{T\Delta v}}$$

L_{fusion} = 3.4 x 10^5 J kg^{-1}
v_{ice} = 1.091 x 10^{-3} m^3 kg^{-1}
v_{water} = 1.000 x 10^{-3} m^3 kg^{-1}
$\Delta v = v_{water} - v_{ice}$ = -9.1 x 10^{-5} m^3 kg^{-1}
T_{melt} (1 atmosphere) = 273K

$$\frac{\Delta p}{\Delta T} = \frac{3.4\times10^5}{273\times(-9.1\times10^{-5})} = -1.36\times10^7\,\mathrm{Pa\,K^{-1}}$$

$$\frac{\Delta T}{\Delta p} = -7.35\times10^{-7}\,\mathrm{K\,Pa^{-1}} = -7.4\times10^{-3}\,\mathrm{K/atm}$$

T_{melt} (1000 atm) = 273-7.4 = 265.6

Laws of Thermodynamics

0th Law: when 2 objects are in thermodynamic equilibrium independently with a 3rd object, they are in fact in thermodynamic equilibrium with each other or in other words,

You can use a thermometer to measure the temperature of something

1st Law: ***conservation of energy***

$$\Delta U = Q - W$$

2nd Law: *thermodynamic limit of heat engine efficiency*

1. Heat only flows spontaneously from high T to cold T
2. A heat engine can never be more efficient that a “Carnot” engine operating between the same hot & cold temperature range
3. The total entropy of the universe never decreases

3rd Law: *it is not possible to lower the temperature of a system to absolute zero in a finite number of steps.*

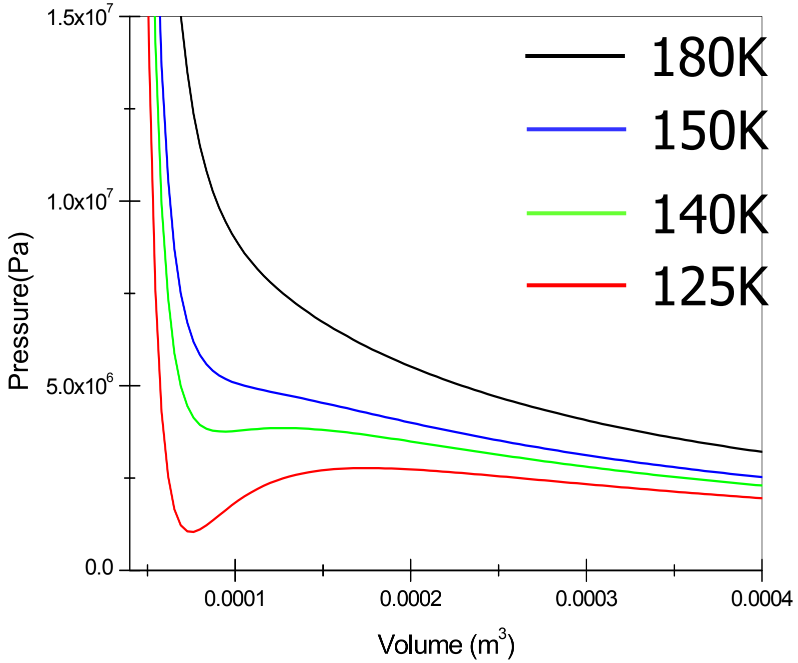
It is impossible to reach the temperature of absolute zero

PHY201: Thermodynamics

More on Clausius Clapeyron Equation (Another approach)

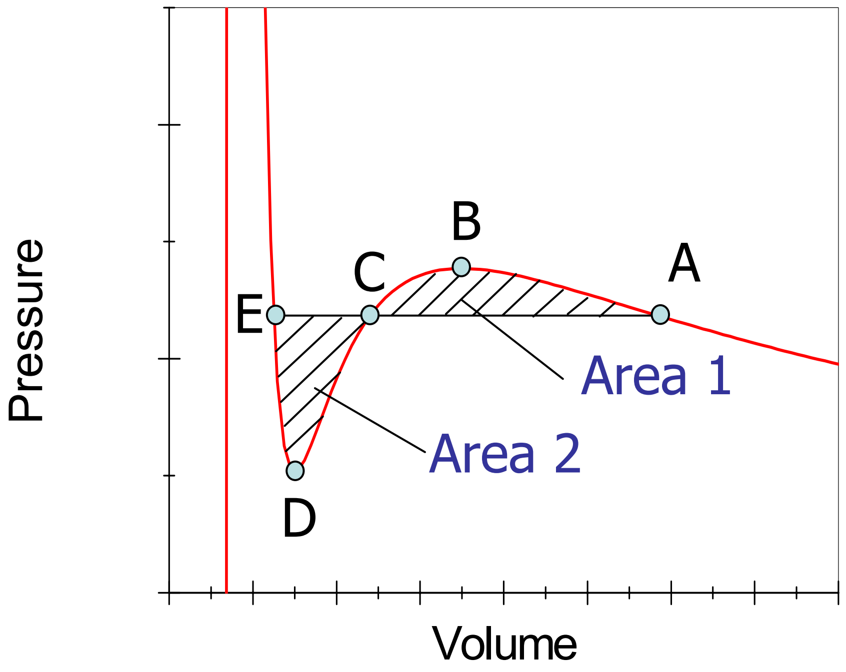
- Van der Waals isotherms (just for understanding, not in course)
- Mixed phase behaviour (just for understanding, not in course)
- **Phase transitions and the Gibbs function**
- **Derivation and use of the Clausius-Clapeyron equation (Slides 11-15 are in course)**
- **Reference: Pages 157-162, Evelyn Guha**

Van der Waals isotherms



- At higher temperatures, isotherms ideal-gas-like (hyperbolic)
- As T decreases, isotherms become progressively more distorted
- Distortion associated with formation of "condensed" phases (liquid, solid)

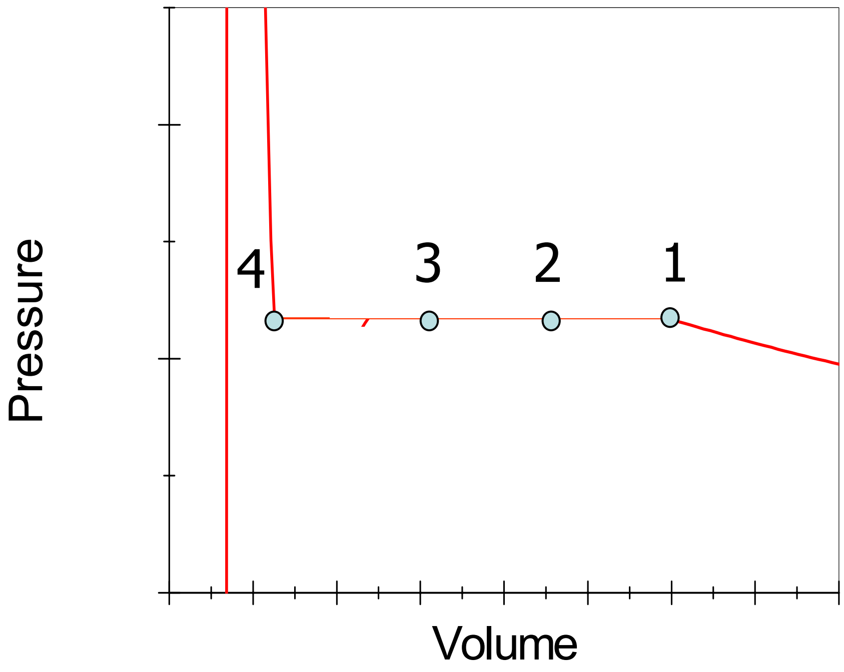
Expanded view of “distorted” isotherm

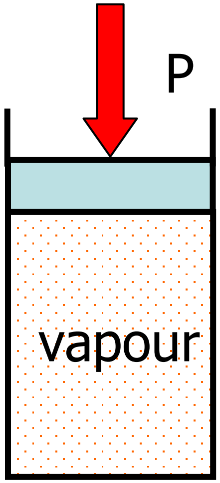


The straight line portion of the corresponds to the system in mixed phase (liquid/vapour)

- In reality, the system doesn’t exactly follow the isotherm predicted by the equation of state
- For example, along the path BCD, the volume decreases and so does the pressure: physically unrealistic
- In fact, when the system reaches point A, further compression takes the system directly along ACE
- States along the ABC and CDE portions of the isotherm are unstable
- Vertical position of straight line determined by the condition

Mixed phase region





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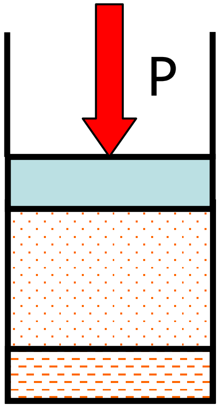

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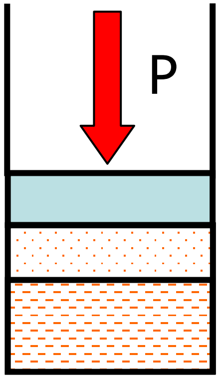

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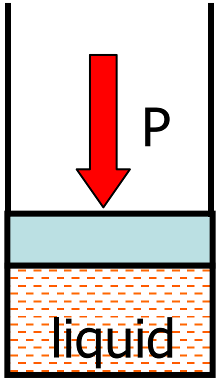
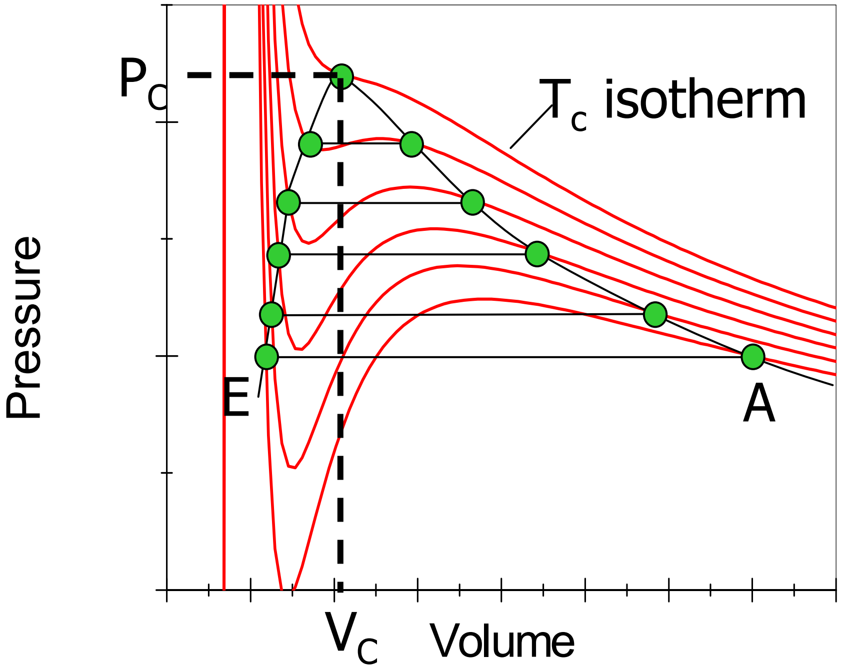


4

At all points between 1 and 4, liquid and vapour phases co-exist in equilibrium at same temperature & pressure

Liquid/vapour mixed phase region



- Locus of the equivalent "A, E" points for each isotherm defines boundary of the P-V-T region of mixed phase

- Onset of mixed phase behaviour occurs at the critical temperature T_C. This is the point at which the isotherm develops a point of inflection
- From position of point of inflection on P-V diagram, values for the critical volume (V_c) and critical pressure (P_c) can be defined
- The three parameters T_c, V_c and P_c define the critical point, C, where:

$$\left(\frac{\partial P}{\partial V}\right)_T = \left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0$$

Three dimensional Phase diagram for a pure substance

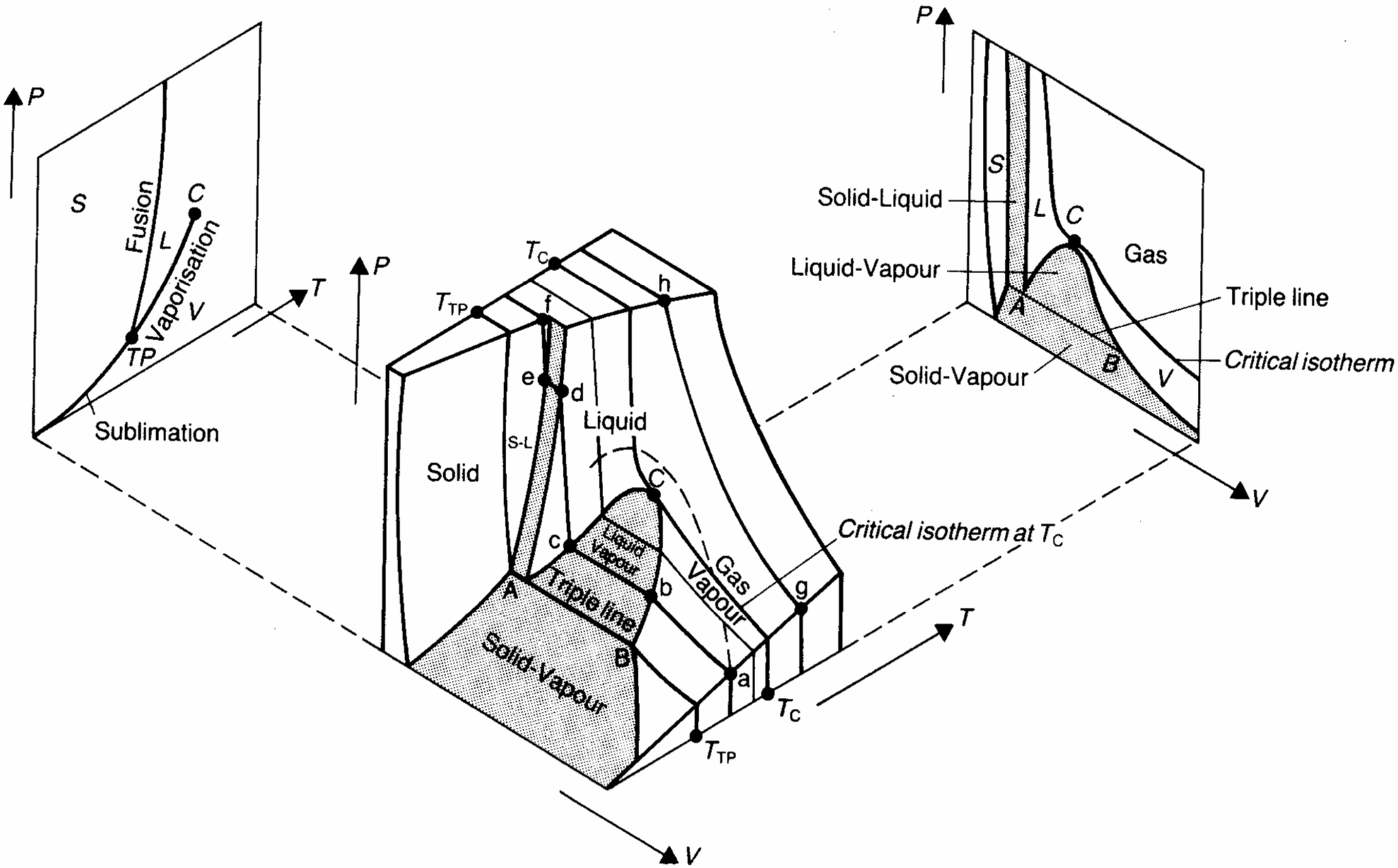
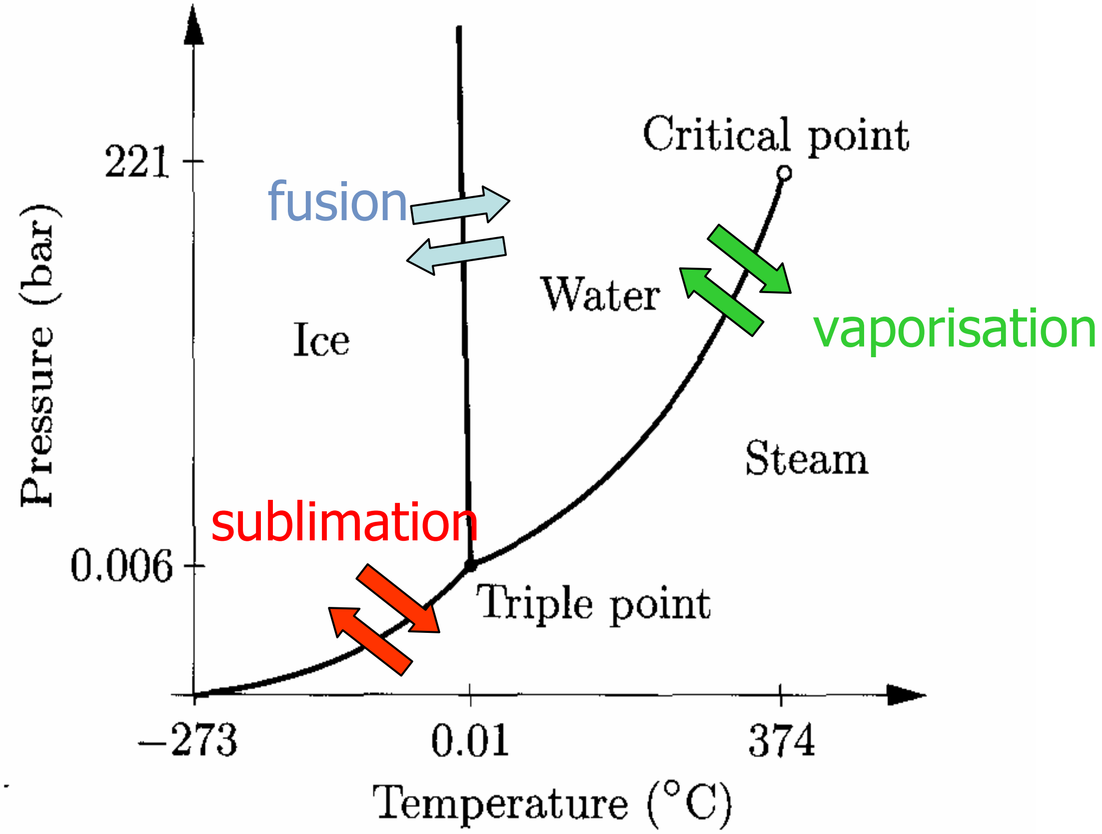


Fig. 9.1 A typical *PVT* surface together with its *P–T* and *P–V* projections.

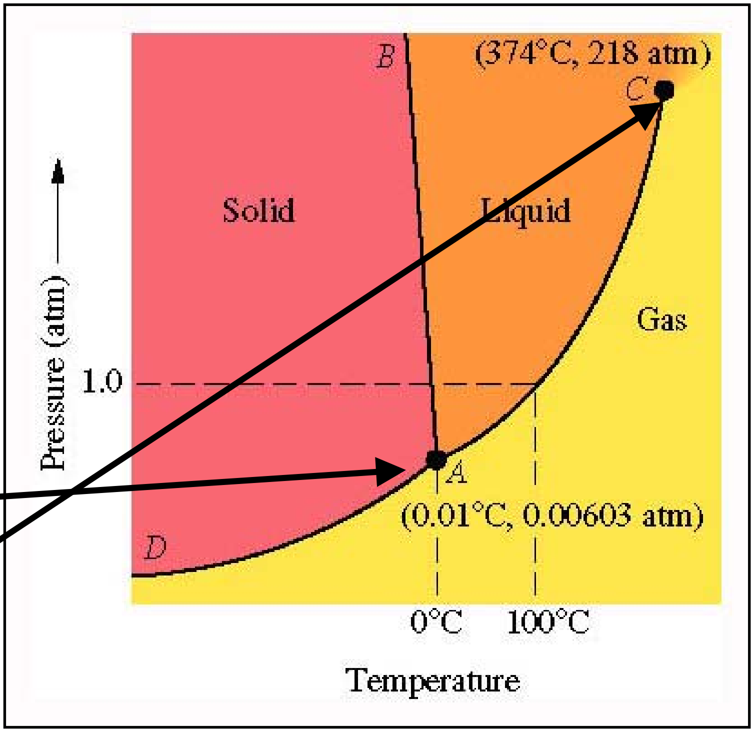
P-T projection of phase diagram



"boundary lines" between phases are where phases co-exist in equilibrium: known as <u>co-existence curves</u>

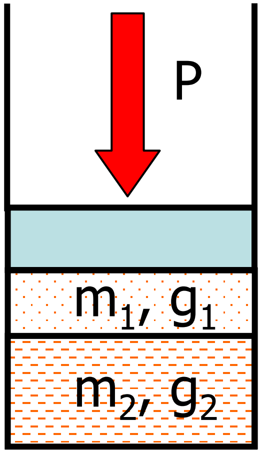
Phase Diagrams

- Graph of pressure-temperature relationship; describes when 1,2,3 or more phases are present and/or in equilibrium with each other.
- Lines indicate equilibrium state two phases.
- ***Critical pressure-*** vapor pressure at critical temp.
- ***Critical point-*** point where system is at its critical pressure and temp.
- ***Triple point-*** Temp. and press. where all three phases co-exist in equilibrium.



Phase transitions and the Gibbs function

- In general, phase transitions take place at constant temperature and pressure. Under these conditions, the Gibbs function is the appropriate thermodynamic potential.
- Consider 2 phases co-existing in equilibrium: Phase 1 and Phase 2
- Mass of phase 1 = m_1, mass of phase 2 = m_2
- Specific Gibbs function of phase 1 = g_1; Specific Gibbs function of phase 2 = g_2



$$G_{total} = m_1 g_1 + m_2 g_2$$

Consider an incremental mass of phase 1 (dm_1) undergoing a transition to phase 2.

$$dG_{total} = dm_1 g_1 + dm_2 g_2$$

$$dG_{total} = -SdT + VdP = 0 \Rightarrow \boxed{dm_1 g_1 = -dm_2 g_2}$$

But $dm_1 = -\,dm_2$ (mass conservation) $\Rightarrow$ $\boxed{g_1 = g_2}$

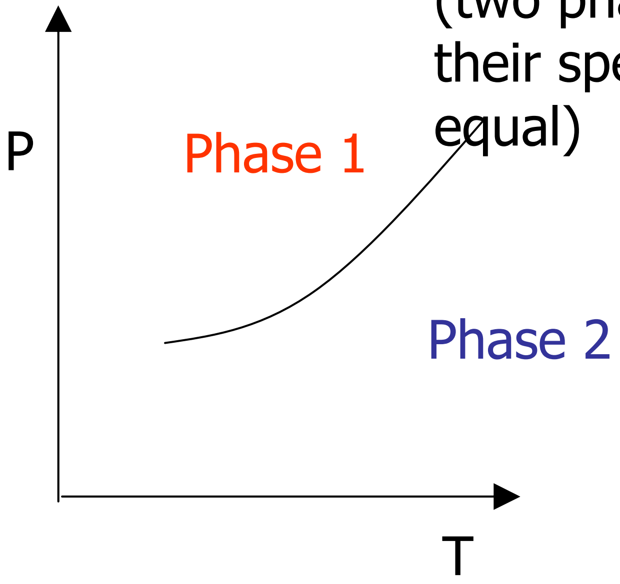
Phase transitions and the Gibbs function

CONCLUSION
When two phases co-exist in equilibrium, their specific Gibbs functions are equal

No assumptions made about the <u>nature</u> of the 2 phases: this is a <u>general</u> resu

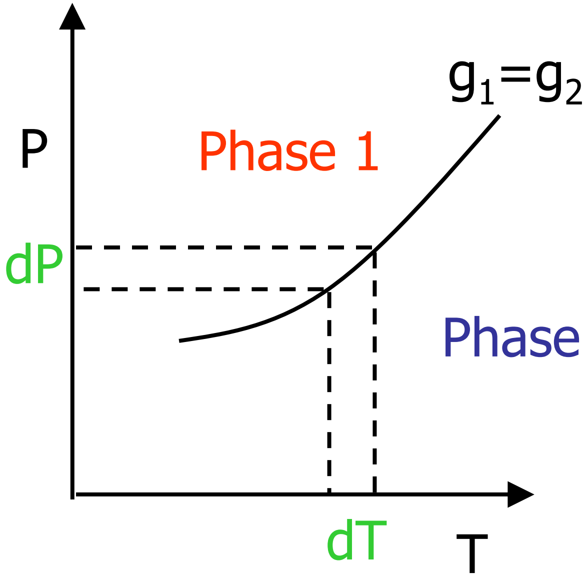
The Clausius-Clapeyron equation

The Clausius-Clapeyron equation gives an expression for the slope of the P-T co-existence curve between 2 phases. It is most commonly used to calculate how the temperature of the phase transition varies when pressure is changed



$g_1 = g_2$ along co-existence curve, (two phases co-exist in equilibrium, their specific Gibbs functions are equal)

The Clausius-Clapeyron equation



$$dg_1 = -s_1 dT + v_1 dP$$

$$dg_2 = -s_2 dT + v_2 dP$$

s, v, specific entropy, volume

Now, since $g_1 = g_2$ along co-existence curve:

$$dg_1 = dg_2 \quad \Rightarrow \quad -s_1 dT + v_1 dP = -s_2 dT + v_2 dP$$

ie

$$\frac{dp}{dT} = \left(\frac{s_2 - s_1}{v_2 - v_1} \right) = \frac{\Delta s}{\Delta v}$$

The Clausius-Clapeyron equation

$$\frac{dp}{dT} = \left(\frac{s_2 - s_1}{v_2 - v_1}\right) = \frac{\Delta s}{\Delta v}$$

Now, the specific latent heat for the transition is given by L = TΔs. Substituting in the above finally gives us our CLAUSIUS-CLAPEYRON EQUATION:

$$\boxed{\frac{dp}{dT} = \frac{L}{T\Delta v}}$$

Using the C-C equation: fusion

For melting/freezing (fusion) it's OK to assume that latent heat and specific volumes of the solid and liquid phases are constant and that the slope of the coexistence curve is therefore constant.

Example:

Calculate the melting temperature of ice at a pressure of 1000 atmospheres……

$$\boxed{\frac{dp}{dT} = \frac{\Delta p}{\Delta T} = \frac{L}{T\Delta v}}$$

L_{fusion} = 3.4 x 10^5 J kg^{-1}
v_{ice} = 1.091 x 10^{-3} m^3 kg^{-1}
v_{water} = 1.000 x 10^{-3} m^3 kg^{-1}
$\Delta v = v_{water} - v_{ice}$ = -9.1 x 10^{-5} m^3 kg^{-1}
T_{melt} (1 atmosphere) = 273K

$$\frac{\Delta p}{\Delta T} = \frac{3.4\times10^5}{273\times(-9.1\times10^{-5})} = -1.36\times10^7 \mathrm{Pa K^{-1}}$$

$$\frac{\Delta T}{\Delta p} = -7.35\times10^{-7}\ \mathrm{K\,Pa^{-1}} = -7.4\times10^{-3}\ \mathrm{K/atm}$$

T_{melt} (1000 atm) = 273-7.4 = 265.

Using the C-C equation: vaporisation

For boiling/condensing (vaporisation), the previous approach only gives reasonable results for small pressure/temperature variations. This is because the specific volume of the vapour phase is highly pressure/temperature dependent.

We need to make some (reasonable) assumptions:

➢Specific volume of vapour >> specific volume of liquid, ie $\Delta v = v_{vapour}$

$$\frac{dp}{dT} = \frac{L}{T v_{vapour}}$$