Class 20: Thermodynamics

AP Physics

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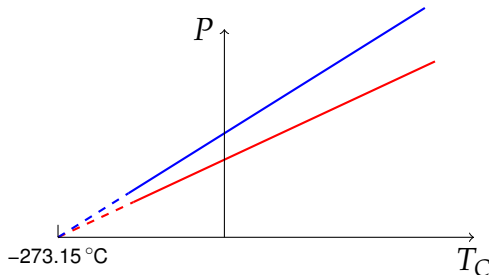
Olympiads School

April 2018

Review: Absolute Temperature Scale

aka the Kelvin Scale

Relationship between the absolute temperature scale and the Celsius scale is a constant:

$$T = T_C + 273.15$$

Plotting pressure vs. temperature at *constant volume* for gases gives a straight line that appear to intersect the x-axis at $-273.15\,^{\circ}$C:

Review: Absolute Temperature Scale

$$T = T_C + 273.15$$

Quantity	Symbol	SI Unit
Absolute temperature	T	K (Kelvin)
Temperature in degree Celsius	T_C	°C is not an SI unit

- Developed by William Thomson (Lord Kelvin) and James Joule
- Until the 1960's, absolutely temperature used the unit "degree kelvin"
- The temperature *change* of 1 K is the same as 1 °C
- The two scales differ in where *zero* is (called the "null point")

Relationship Between Temperature and Pressure

The relationship between absolute temperature T and pressure P of a gas at constant volume is defined using its triple point:

$$T = \frac{T_{\text{tp}}}{P_{\text{tp}}} P$$

Triple point is a combination of pressure and temperature where all phases of a substance (solid, liquid and vapour) may coexist in thermal equilibrium.

- The triple point temperature for water is at $T_{\text{tp}} = 273.16 \, \text{K}$, or $0.01 \, ^\circ\text{C}$
- Triple point pressure for water is $P_{\text{tp}} = 611.2 \, \text{Pa}$

Thermal Expansion

When temperature T of an object with length L increases, the object *usually* expands. The *thermal strain* $(\Delta L / L)$ is proportional the change in temperature:

$$\boxed{\frac{\Delta L}{L} = \alpha \Delta T}$$ where $$\boxed{\alpha = \frac{1}{L}\frac{dL}{dT}}$$

Quantity	Symbol	SI Unit
Length	L	m (meter)
Temperature	T	K (kelvin)
Coefficient of linear expansion	α	K^{-1} (per kelvin)

α is independent of pressure for solids and liquids, but may vary with T.

Thermal Expansion

There is also a similar expression for **coefficient of volume expansion**:

$$\frac{\Delta V}{V} = \beta \Delta T \quad \text{where} \quad \beta = \frac{1}{V}\frac{dV}{dT}$$

β is also independent of pressure for solids and liquids, but may vary with T.

Quantity	Symbol	SI Unit
Volume	V	m^3 (cube meter)
Temperature	T	K (kelvin)
Coefficient of volume expansion	β	K^{-1} (per kelvin)

Careful application of calculus will show that for isotropic material (where α is the same in all direction)

$$\beta = 3\alpha$$

Ideal Gas Law for Low-Density Gases

Boyle's Law: Physicist Robert Boyle (1627-1691) discovered that, when a gas is allowed to expand or compress at *constant temperature*, the product of pressure P and V remain constant, i.e.:

$$PV = \text{constant}$$

We also know that at *constant volume*, temperature is proportional to pressure. This is how we got the absolute temperature scale discussed earlier, i.e.:

$$PV = CT$$

where "C" is some constant to be determined.

Ideal Gas Law

Thought experiment:

- Two identical containers with volume V with same amount of same kind of gas at same pressure P and temperature T.
- When the containers are combined and the molecules are free to move, P and T remain the same, but volume is increased by factor of 2.

C must scale with the number of molecules of gas N, which modifies the equation to this, the **ideal gas law**:

$$\boxed{PV = NkT}$$

The constant $k = 1.381 \times 10^{-23}$ J/K is called **Boltzmann's constant**. It is found experimentally to have the same value for any kind or amount of gas.

Ideal Gas Law

The ideal gas law can also be written a more familiar way:

$$\boxed{PV = nRT}$$

where

- $n = N/N_A$ is the number of moles of the gas
- $R = kN_A = 8.314\,\text{kg}/\text{mol K}$ is the universal gas constant, and
- $N_A = 6.022 \times 10^{23}$ is Avagadro's number

The ideal gas law is an *equation of state*, because it relates all the quantities that define the *state* of a gas: pressure P, volume V and temperature T.

Kinetic Theory of Gases

Assumptions for the kinetic theory of gases:

1. The gas consists of a large number of molecules that make *elastic* collisions with each other and with the walls of the container.

2. The molecules are separated, on average, by distances that are large compared to their diameters, and they exert no force (gravitational, electrostatic etc) on each other except when they collide.[1]

3. In the absence of external forces, there is no preferred position for a molecules in the container, and there is no preferred velocity vector.

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[1] This means that the density of the gas is low, i.e. assume ideal gas behaviour.

Average Kinetic Energy of a Gas

We note that pressure is force of the gas molecules exerts when colliding with the container, given by

$$P = \frac{F}{A}$$

By Newton's second law of motion: the collision changes the momentum of the gases

$$\mathbf{F} = \frac{d\mathbf{p}}{dt}$$

We can then relate the change momentum, to force to pressure and to the ideal gas law. After some calculus. . .

Average Kinetic Energy of a Gas

We find the average kinetic energy $\langle K \rangle$ of a molecule of gas in a container, given by:

$$\langle K \rangle = \frac{3}{2}kT$$

i.e. temperature is a measurement of the average kinetic energy.

Often it is advantageous to calculate the root mean square ("rms") velocity of the molecules, which measures the speeds that the majority of the particles are below:

$$v_{\mathrm{rms}} = \sqrt{\frac{3kT}{m}}$$

P-V Diagram

Thermodynamic processes is usually plotted on a "*P-V* diagram".
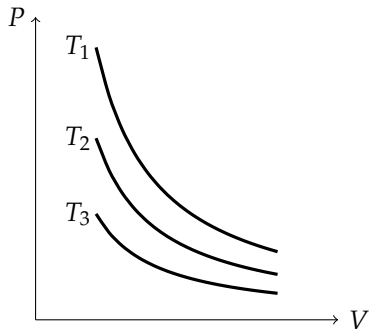
- Under constant temperature, the relationship between pressure and volume is a hyperbolic curve.
- Each line is called an **isotherm**; it represents a different constant temperature
- $T_3 > T_2 > T_1$

Note: Aside from P-V diagrams, there are many similar diagrams in thermodynamics.

Real Gases

Most gases behave like ideal gas at most ordinary pressures, but the equation breaks down when the density of gas is high and molecules are not far apart:

- pressure is sufficiently high
- temperature is low

In this situation the **van der Waal equation** provides a more accurate description of the behaviour of real gases:

$$\left(P + \frac{an^2}{V^2} \right) (V - bn) = nRT$$

- The term an^2/V^2 is from the attraction of the gas molecules to each other
- The term b is approximately the volume occupied by one mole of the gas

Real Substances

Neither the **ideal gas law** nor the **van der Waal equation** can capture the exact relationship between pressure and volume, because neither can account for phase changes. The P-V diagram of a real substance is like this:
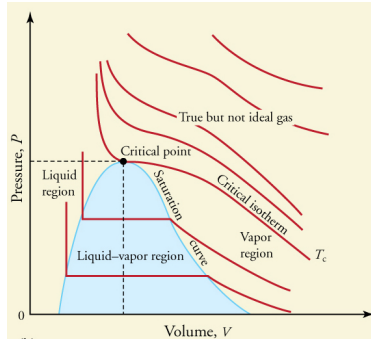
Phase Diagrams

The phase diagram plots pressure against temperature to show when the different phases of matter exist. For water:
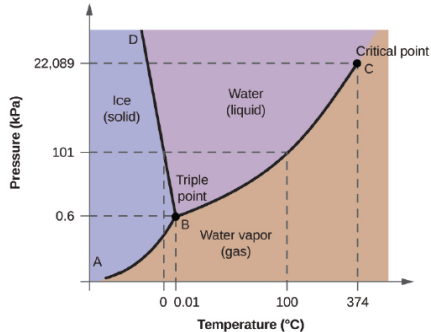
- At **triple point** B, all three phases of matter can exist in equilibrium
- At **critical point** C, liquid and vapour (gas) are indistinguishable, and the gas laws can model their behaviour

First Law of Thermodynamics

First Law of Thermodynamics

The change in the internal energy of a system is the sum of the work and heat exchanged between a system and its surroundings.

$$\Delta U = Q - W$$

Quantity	Symbol	SI Unit
Change in internal energy of a system	ΔU	J (joules)
Work done *by* the system	W	J (joules)
Heat into the system	Q	J (joules)

IMPORTANT NOTE: Sometimes the equation is written as $\Delta U = Q + W$, where W is the work done *to* the system, rather than *by* the system. Both conventions are commonly use. You have to be very careful.

First Law of Thermodynamics

$$\boxed{\Delta U = Q - W}$$

Internal energy U is the sum of kinetic and potential energies, but does *not* include

- The bulk kinetic energy of the system, i.e. if the entire container of gas moves at speed v
- The potential energy inside a force field, e.g. gravitational, electrostatic, magnetic

For an ideal gas, the internal energy is just the total kinetic energy of the gas:

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

First Law of Thermodynamics

$$\Delta U = Q - W$$

Q is the *thermal energy* (heat) *into* the system, through conduction, convection and radiation.

- $+$ if heat is added to the system
- $-$ if heat leaves the system

For conduction, the rate of heat transfer $\Delta Q / \Delta t$ (aka "thermal current") is given by:

$$H = \frac{\Delta Q}{\Delta t} = kA\frac{\Delta T}{\Delta x}$$

where k is the thermal conductivity of the material
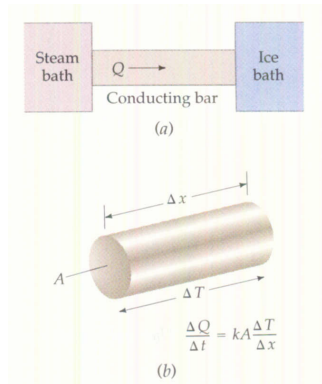
First Law of Thermodynamics

$$\Delta U = Q - W$$

W is the mechanical work done by the system to the surrounding

- $+$ done *by* the system, e.g. using steam pressure to push a piston or shaft
- $-$ done *to* the system, e.g. pushing a piston to compress gas in an engine
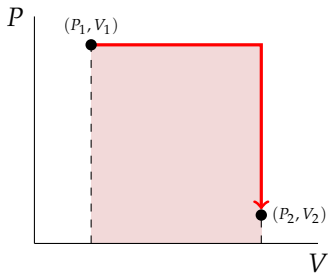
$$W = \int_{P_1}^{P_2} P dV$$

It's up to you to show that this equation is derived from the definition of work, $W = \int \mathbf{F} \cdot d\mathbf{s}$.

Work Done To a Gas

On the P-V diagram, W is the area under the curve.

- W is done *by* the system (positive) if the path moves right, and
- done *to* the system (negative) if it moves left

In the example below, the gas is changed from point 1 to 2, but the work done is different.
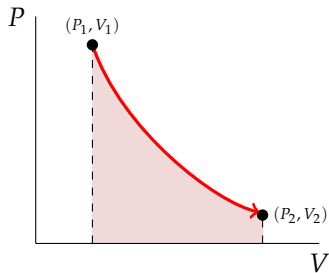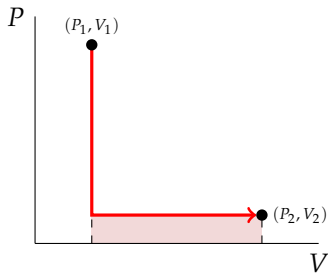
Quasi-Static Processes

In thermodynamics, a **quasi-static process** is a thermodynamic process that happens slowly enough for the system to remain in internal equilibrium. We are concerned with 4 of these process:

- Isobaric process - constant pressure
- Isochoric process - constant volume
- Isothermal process - constant temperature
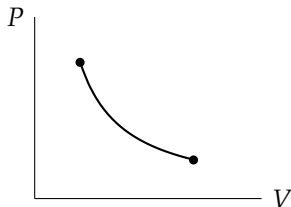- Adiabatic process - "isolated", no heat exchanged with surrounding
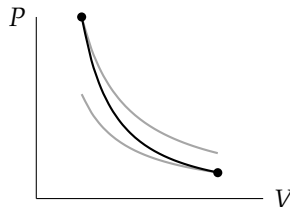
Quasi-Static Processes
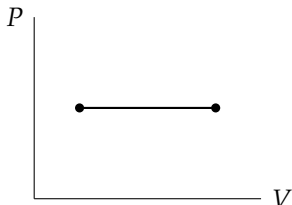
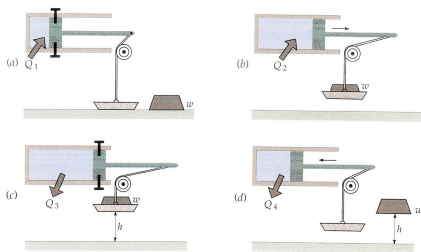Isobaric (constant pressure)
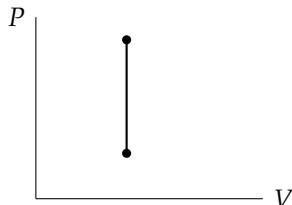
Isochoric (constant volume)

Isothermal (constant temperature)

Adiabatic (constant heat)
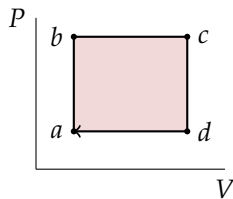
A Simple Heat Engine Cycle

P-V diagram of the simple heat engine shown on the left.

1. Heat is added at constant volume; no work done.
2. Heat is added as gas expands at constant pressure; work is done by the gas to lift the weight.
3. Heat is extracted at constant volume; no work done.
4. Heat is extracted at constant pressure; work is done on the gas to compress it.

Efficiency of Heat Engine

In a heat engine, the internal energy at the beginning and end of the cycle are the same (same point on the P-V diagram), so the work done is just the difference between heat added and taken out:

$$W = Q_{\text{in}} - Q_{\text{out}}$$

Efficiency is defined as the ratio between work done and heat added:

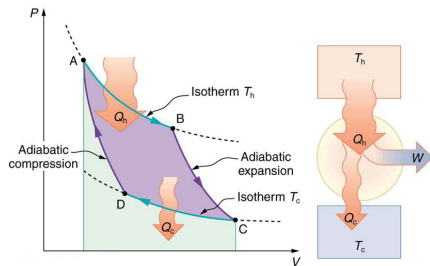$$\boxed{\eta = \frac{W}{Q_{\text{in}}} = 1 - \frac{Q_{\text{out}}}{Q_{\text{in}}}}$$

Second Law of Thermodynamics

Kelvin-Planck Statement

It is impossible for heat engine working in a cycle to produce no other effect than that of extracting heat from a reservoir and performing an equivalent amount of work.

Carnot Engine

The Carnot engine cycle is the most efficient.

The efficiency of a Carnot engine is:

$$\eta_C = 1 - \frac{Q_{\text{out}}}{Q_{\text{in}}} = 1 - \frac{T_c}{T_h}$$