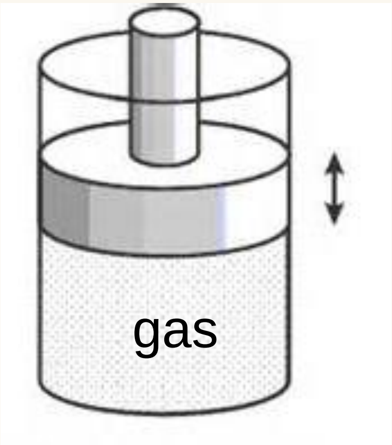
# PHAS1000 – THERMAL PHYSICS

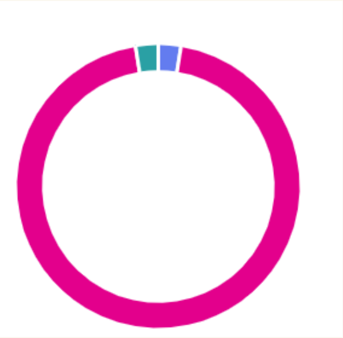
## Lecture 11

## First Law of Thermodynamics

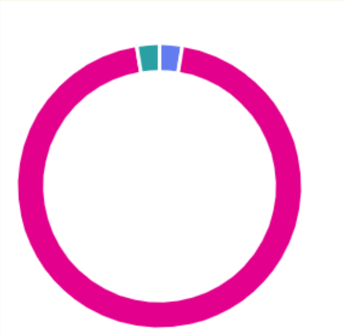


# Feedback summary

1. The volume of work

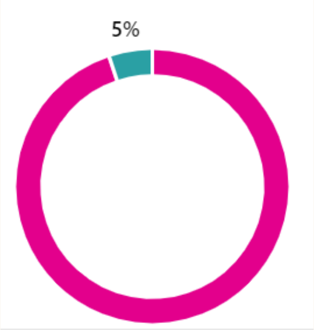


2. The pace

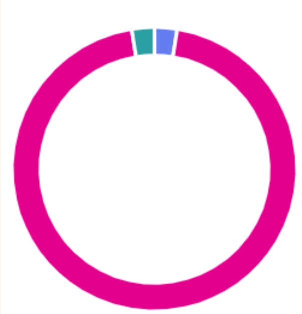


- too much
- about right
- too little

3. The level of difficulty or challenge




6. The level of difficult of the coursework



# Feedback comments

## You like…

Very engaging and understandable

Good notes and example questions

Gives us time to write stuff down

Working together in groups within the workshops.

## Could be better…

Upload full PowerPoint before (without question answers)

Amount of Vevox questions slows down the lecture.

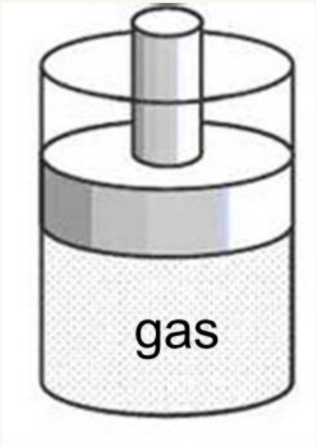
More questions to do by ourselves

# Overview

This lecture covers:

- 1st law of thermodynamics
- Work and internal energy
- Molar heat capacity at constant pressure $c_p'$
- Mayer's equation
- Joule-Thompson effect for real gases

# First Law of Thermodynamics




$Q\ (heat)$

$PV = nRT$

Heating at constant volume (rigid container)

- *T* and *P* increase
- All heat goes into <u>internal energy</u>, $U$ (degrees of freedom)

Heating at constant pressure (allows for expansion)

- *T* and *V* increase
- heat goes into <u>internal energy</u> and <u>work</u> (expanding against the atmosphere)

# First Law of Thermodynamics

$$\boxed{Q_{in} = \Delta U + W_{by}}$$

1st Law

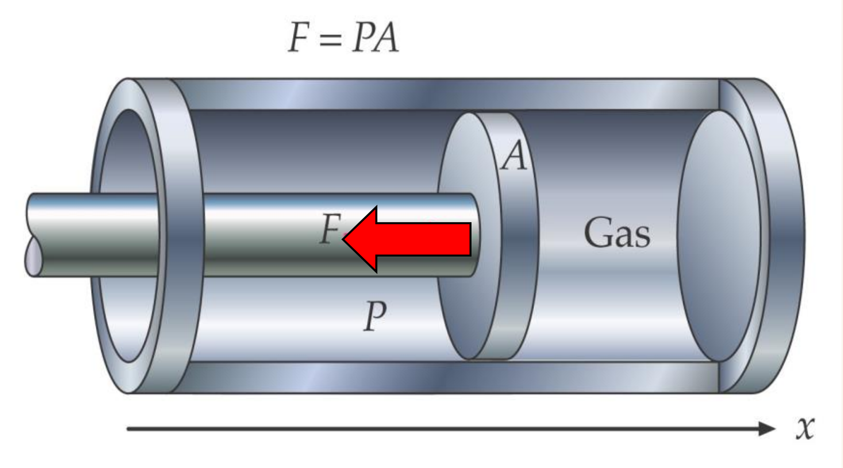
$Q_{in}$ heat transferred into the system

$\Delta U$ increase in internal energy of the system

$W_{by}$ work done by the system

# Work

$W_{by}$ = work done by the system (the gas) in expanding:




Gas at pressure *P* expands quasi-statically

It exerts force *F* on piston of area *A*, *so* $F = PA$

Work is done by the gas when piston moves distance $dx$

$$dW_{by} = F_x dx = PAdx = PdV$$

So $W_{by} = \int_{V_i}^{V_f} PdV$

If volume constant: $W_{by} = 0$

If pressure constant: $W_{by} = P\Delta V$

Note: $W_{by} = -W_{on}$

# Constant volume and constant pressure

$Q_{in} = nc'\Delta T$

For the same $\Delta T$ we need more heat when heating at constant pressure than at constant volume (because we also do work).

$$Q_{in} = \Delta U + W_{by}$$

molar heat capacity at constant volume = $c_v'$

molar heat capacity at constant pressure = $c_p'$

$c_p' > c_v'$ for gases since work is done against the surroundings in expanding when volume not fixed.

$c_p' \sim c_v'$ for liquids and solids (as expansion is small)

# Mayer's Equation

Ideal gases

Heating at constant volume: $Q_{in} = nc_v'\Delta T$

Pressure will increase as the gas is heated, but $\Delta V = 0$ so there is no work done.

1st law: $Q_{in} = \Delta U + W_{by}$ so $Q_{in} = \Delta U + 0$ i.e. $\Delta U = nc_v'\Delta T$ Eqn 1

Heating at constant pressure: $Q_{in} = nc_p'\Delta T$

The heat added increases the internal energy and makes the gas do work to expand.

1st law: $Q_{in} = \Delta U + W_{by}$ so $\Delta U = Q_{in} - W_{by}$ i.e. $\Delta U = nc_p'\Delta T - P\Delta V$ Eqn 2

Relationship between $c_v'$ and $c_p'$

For the same increase in internal energy we can equate Eqn 1 and Eqn 2. i.e. $nc_v'\Delta T = nc_p'\Delta T - P\Delta V$

But $PV = nRT$ so at constant pressure $P\Delta V = nR\Delta T$, Thus $nc_v'\Delta T = nc_p'\Delta T - nR\Delta T$

Cancelling $n$ and $\Delta T$ gives: $c_v' = c_p' - R$ *or* $c_p' - c_v' = R$

Mayer's equation

# Testing Mayer's equation

**Molar Heat Capacities in J/mol·K of Various Gases at 25°C**

| Gas | $c'_p$ | $c'_v$ | $c'_v/R$ | $c'_p - c'_v$ | $(c'_p - c'_v)/R$ |
|---|---|---|---|---|---|
| *Monatomic* | | | | | |
| He | 20.79 | 12.52 | 1.51 | 8.27 | 0.99 |
| Ne | 20.79 | 12.68 | 1.52 | 8.11 | 0.98 |
| Ar | 20.79 | 12.45 | 1.50 | 8.34 | 1.00 |
| Kr | 20.79 | 12.45 | 1.50 | 8.34 | 1.00 |
| Xe | 20.79 | 12.52 | 1.51 | 8.27 | 0.99 |
| *Diatomic* | | | | | |
| $N_2$ | 29.12 | 20.80 | 2.50 | 8.32 | 1.00 |
| $H_2$ | 28.82 | 20.44 | 2.46 | 8.38 | 1.01 |
| $O_2$ | 29.37 | 20.98 | 2.52 | 8.39 | 1.01 |
| CO | 29.04 | 20.74 | 2.49 | 8.30 | 1.00 |
| *Polyatomic* | | | | | |
| $CO_2$ | 36.62 | 28.17 | 3.39 | 8.45 | 1.02 |
| $N_2O$ | 36.90 | 28.39 | 3.41 | 8.51 | 1.02 |
| $H_2S$ | 36.12 | 27.36 | 3.29 | 8.76 | 1.05 |

$$c'_p - c'_v = R$$

# Success of the Equipartition Theorem

Ideal gases

| | Degrees of Freedom (f) | U per mole | $c_v'$ | $c_p'$ | $\gamma = \frac{c_p'}{c_v'}$ |
|---|---|---|---|---|---|
| monatomic | 3 | $\frac{3}{2}RT$ | $\frac{3}{2}R$ | $\frac{5}{2}R$ | $\frac{5}{3} = 1.67$ |
| diatomic | 5 | $\frac{5}{2}RT$ | $\frac{5}{2}R$ | $\frac{7}{2}R$ | $\frac{7}{5} = 1.40$ |
| polyatomic | 6 | $\frac{6}{2}RT$ | $\frac{6}{2}R$ | $\frac{8}{2}R$ | $\frac{8}{6} = 1.33$ |

Ignoring vibration which does not contribute to heat capacity until high temps.

From Equipartition Theorem

$$c_v' = \frac{1}{n}\frac{dU}{dT}$$

$$c_p' = c_v' + R$$

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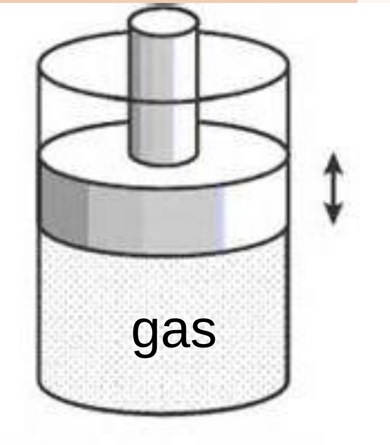
Two identical samples of hydrogen are heated: one at constant volume and one at constant pressure.

If the same amount of heat is added to each sample, what can you say about their temperature rises?

A Both samples have the SAME temperature rise

B Heating at constant VOLUME yields a greater temperature rise

C Heating at constant PRESSURE yields a greater temperature rise



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Results slide

A Both samples have the SAME temperature rise

##.##%

B Heating at constant VOLUME yields a greater temperature rise

##.##%

C Heating at constant PRESSURE yields a greater temperature rise

##.##%

# Answer Q1

Two identical samples of hydrogen are heated: one at constant volume and one at constant pressure. If the same amount of heat is added to each sample, what can you say about their temperature rises?

A Both samples have the SAME temperature rise

B Heating at constant VOLUME yields a greater temperature rise

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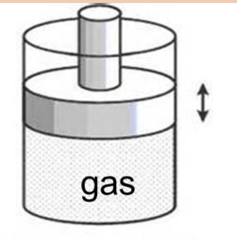



$Q = nc' \Delta T$ $\Delta T = \frac{Q}{nc'}$

in this Question $\Delta T \propto \frac{1}{c'}$

$c_p' > c_v'$ $\therefore \Delta T_p < \Delta T_v$ ANS $\boxed{B}$

# Question 2

Two moles of oxygen gas are heated from a temperature of 20°C and a pressure of 1 atm to a temperature of 100°C. Assume that oxygen is an ideal gas.

(i) How much heat must be supplied if the *volume* is kept constant during heating?

(ii) How much heat must be supplied if the *pressure* is kept constant during heating?

(iii) What is the increase in internal energy in each case?

(iv) How much work is done in part (ii)?

(i) $Q_v = nC_v' \Delta T$

$= 2 \times \frac{5}{2} R \times (100 - 20)$

$= 2 \times \frac{5}{2} \times 8.31 \times 80$

$= 3.33 \text{ kJ}$

(ii) $Q_p = nC_p' \Delta T$

$= 2 \times \frac{7}{2} R \times 80$

$= 4.66 \text{ kJ}$

(iii) $\Delta U = nC_v' \Delta T$

$= 3.33 \text{ kJ}$

(iv) $Q_{in} = \Delta U + W_{by}$

$W_{by} = Q_{in} - \Delta U$

$= 4.66 - 3.33$

$= 1.33 \text{ kJ}$

<u>OR</u> $W_{by} = P\Delta V$

$PV = nRT$

$\therefore P\Delta V = nR\Delta T$

so $W_{by} = nR\Delta T$

$= 2 \times 8.31 \times 80$

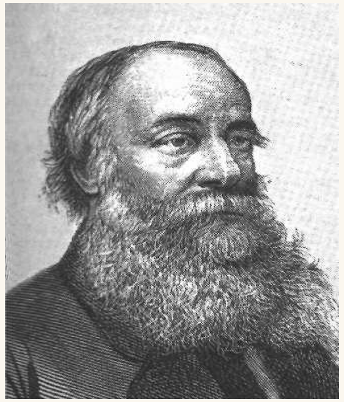
$= 1.33 \text{ kJ}$

# Summary

| | $Q_{in} = \Delta U + W_{by}$ |
|---|---|
| At constant VOLUME | $nc_v'\Delta T = nc_v'\Delta T + 0$ |
| At constant PRESSURE | $nc_p'\Delta T = nc_v'\Delta T + P\Delta V$ |

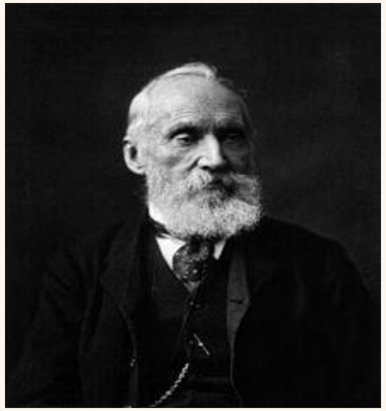
Thus $\Delta U = nc_v'\Delta T$

# Joule-Thompson Effect



James Joule
1818-1889

- born in Salford, Lancashire, brewer.
- Investigated electricity; Joule heating = $I^2R$
- Established that different forms of energy could be converted into each other.



William Thompson
(Lord Kelvin)
1824-1907

- Born in Belfast.
- Worked at the University of Glasgow
- Knighted by Queen Victoria for work on transatlantic telegraph
- Admitted to the House of Lords as Lord Kelvin
- Worked with Joule to really establish ideas about kinetic theory
- Determined the correct value of Absolute Zero as -273.15°C

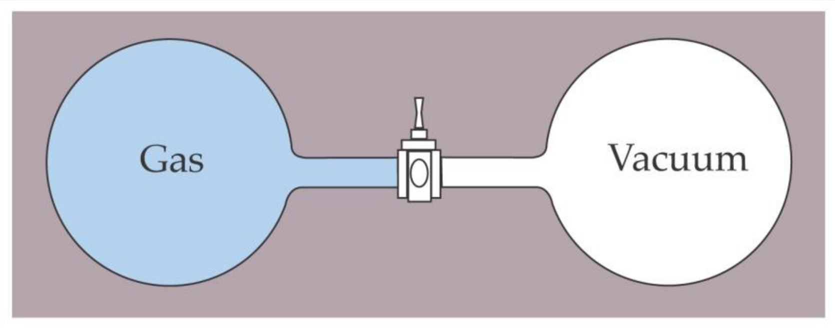
# Joule


https://www.youtube.com/watch?v=HqbcZz-p7IQ

Watch the short clip (35:18 – 37:35) about the studies of James Joule, fundamental to our understanding of work, heat and energy.

Or view clip on Mediasite: Joule_10/31/2024

# (a) Expansion of ideal gas into vacuum




$$Q_{in} = \Delta U + \ W_{by}$$

Apparatus: insulated from surroundings by rigid walls (to eliminate heat flow or work being done).

Gas allowed to do free expansion into vacuum.

When gas reaches equilibrium, temp is found to have remained constant (for gases at low density, ideal gases).

Shows that internal energy does not depend on the volume of an ideal gas.

For an ideal gas $U$ depends only on temperature.

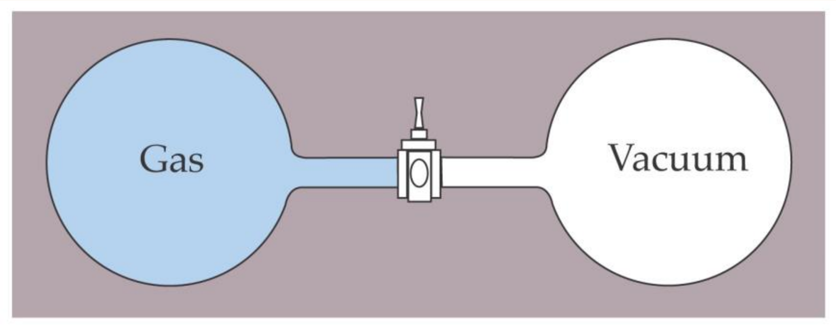
$$U = nf\frac{1}{2}RT \qquad KE_{av} = \frac{3}{2}nRT$$

$$\Delta U = nc_v'\Delta T$$

# (b) Expansion of real gas into vacuum

What temperature effects do you notice when you release a fire extinguisher, or aerosol?

# (b) Expansion of real gas into vacuum




Real gases have attractions between molecules

As the gas expands the potential energy of the molecules is increased as they get further apart.

For a rigid, insulated container, this increase in PE can only come from the KE. So the temperature is reduced slightly.

Joule-Thompson effect:
A real gas cools when undergoing a free expansion.

For a real gas $U$ has KE and PE terms.

# Summary

$$Q_{in} = \Delta U + W_{by}$$

1st law of thermodynamics (always true)

$$W_{by} = \int_{V_i}^{V_f} P dV$$

(always true)

If volume constant: $W_{by} = 0$

If pressure constant: $W_{by} = P\Delta V$

$$W_{by} = -W_{on}$$

$$\Delta U = nc_v' \Delta T$$

$$\Delta U = C_v \Delta T$$

(only for ideal gas)

$$c_p' - c_v' = R$$

Mayer's equation

$$C_v = nc_v'$$

$$C_p = nc_p'$$

$$\gamma = \frac{c_p'}{c_v'}$$

$$U = nf\frac{1}{2}RT$$

$$KE_{av} = \frac{3}{2}nRT$$

(only for ideal gas)

For a real gas $U$ has both KE and PE terms, and the gas cools on free expansion.
Joule-Thompson effect.

# Question 3

Two moles of nitrogen at 450°C is mixed with 0.5 moles of argon at 350°C. What is the final temperature of the mixture, if the mixing is done at (a) constant volume, and (b) constant pressure?

# ANSWERS

# Answer Q3

Two moles of nitrogen at 450°C is mixed with 0.5 moles of argon at 350°C. What is the final temperature of the mixture, if the mixing is done at (a) constant volume, and (b) constant pressure?

$\boxed{\text{2 moles } N_2 \text{ @ } 450^\circ C}$ $\boxed{\text{0.5 moles Ar @ } 350^\circ C}$

a) heat lost by $N_2$ = heat gained by Ar

$$Q = (n c_v \Delta T)_{N_2} = (n c_v \Delta T)_{Ar}$$

$$2 \times \frac{5}{2} R \times (450 - T_f) = 0.5 \times \frac{3}{2} R \, (T_f - 350)$$

$$10(450 - T_f) = 1.5\,(T_f - 350)$$

$$4500 - 10T_f = 1.5T_f - 525$$

$$4500 + 525 = 11.5\,T_f$$

$$\underline{T_f = 437^\circ C}$$

(b) $Q = (n c_p' \Delta T)_{N_2} = (n c_p' \Delta T)_{Ar}$

$$2 \times \frac{7}{2} R\,(450 - T_f) = 0.5 \times \frac{5}{2} R\,(T_f - 350)$$

$$14(450 - T_f) = 2.5\,(T_f - 350)$$

$$6300 - 14T_f = 2.5T_f - 875$$

$$6300 + 875 = 16.5\,T_f$$

$$\underline{T_f = 435^\circ C}$$