Unit 7

Answers: Gas Laws

Quick checks

1 c By Boyle's law, PV stays the same. If P becomes 4 times bigger, V must become 4 times smaller, a quarter of what it was.

2 c Doubling the volume needs double the **kelvin** temperature: 0 °C = 273 K, and 2 × 273 = 546 K, which is 546 − 273 = **273 °C**. (546 °C is the trap: 546 is the answer in kelvin, not in degrees Celsius.)

3 b STP is 0 °C (273 K) and 1 atm (760 mmHg, 76 cmHg). 25 °C is room temperature, used for other standards, and 0 K is absolute zero.

4 c The average kinetic energy of the molecules is directly proportional to the absolute temperature. Heating them makes them move faster; the molecules themselves don't grow.

5 c The lightest gas diffuses fastest, since the rate goes as $1/\sqrt{M}$. Methane, at 16 g/mol, is the lightest of the four.

1 a. **b** By Boyle's law, $P = k \times \frac{1}{V}$: P is directly proportional to $\frac{1}{V}$, and a direct proportion plots as a straight line through the origin. Against V itself, the graph would be a falling curve.

1 b. **c** By Charles's law, the volume is proportional to the kelvin temperature. 200 K is twice 100 K, so the volume doubles.

1 c. **b** For a fixed mass of gas, $\frac{PV}{T}$ stays constant, since $V \propto \frac{1}{P}$ (Boyle) and $V \propto T$ (Charles).

1 d. **c** At absolute zero, 0 K, which is −273 °C (more exactly −273.15 °C), the volume of a gas would shrink to zero by Charles's law, and its molecules would have the least energy possible.

1 e. **c** The kinetic theory assumes the molecules are so small that their own volume can be ignored, that they don't attract each other, that collisions are perfectly elastic and that they are always moving.

1 f. **c** At low pressure the molecules are far apart, so their volume doesn't matter; at high temperature they move fast, so their weak attraction hardly affects them.

1 g. **b** $\frac{r_2}{r_2} = \sqrt{\frac{32}{2}} = \sqrt{16} = 4$. The rate goes as the square root of the molar masses, not the molar masses themselves, so 16 is the trap.

1 h. **c** Standard pressure is 1 atm = 760 mmHg = 76 cmHg = 101,325 Pa.

2 a. By Charles's law, the volume of a gas at constant pressure is directly proportional to its absolute temperature. Outside, the air in the balloon cools, its molecules slow down and hit the rubber less often and less hard, so the gas contracts and the balloon shrinks. Brought back indoors, it swells again.

2 b. The gas laws say that volume (or pressure) is proportional to the **absolute** temperature, measured from absolute zero, where the volume of a gas would be zero. The kelvin scale starts there; the Celsius scale starts at the melting point of ice, 273 degrees higher. Doubling a temperature in °C doesn't double the volume (10 °C to 20 °C raises it by only 3.5%), and a temperature of 0 °C or below would give a zero or negative volume, which is impossible.

2 c. As the balloon rises, the air pressure around it falls. By Boyle's law, the gas inside expands as the pressure on it falls, so the balloon grows many times bigger as it climbs. If it were filled full at the ground, it would burst soon after launch; partly filled, it can rise to about 30 km before it bursts.

2 d. By Graham's law, the rate of diffusion of a gas is inversely proportional to the square root of its molar mass. Ammonia (17 g/mol) is lighter than hydrogen chloride (36.5 g/mol), so its molecules move faster at the same temperature, and it diffuses about $\sqrt{(36.5/17)} = 1.47$ times faster.

2 e. After a drive, the tyres and the air in them are warm. The tyre's volume hardly changes, so by the pressure law ($P \propto T$ at constant volume) the warm air's pressure is higher than it will be once the tyres cool. A reading taken warm would be too high, and a tyre filled to the right pressure while warm would be too soft once it cooled.

3 i.

Boyle's law	Charles's law
Relates the pressure and volume of a gas.	Relates the volume and temperature of a gas.
The temperature is kept constant.	The pressure is kept constant.
$V \propto \frac{1}{P}$: inverse proportion.	$V \propto T$: direct proportion.
$P_1V_1 = P_2V_2$	$\frac{V_1}{T_1} = \frac{V_2}{T_2}$
A graph of P against V is a curve.	A graph of V against T (in K) is a straight line through the origin.

3 ii.

Real gas	Ideal gas
Obeys the gas laws only at low pressure and high temperature.	Would obey the gas laws exactly at every pressure and temperature.
Its molecules have a volume of their own.	Its molecules would have no volume.
Its molecules attract each other weakly.	Its molecules would not attract each other at all.
Can be turned into a liquid.	Could never be turned into a liquid.
Every gas that exists.	A model; no such gas exists.

3 iii.

Diffusion	Effusion
A gas spreads through another gas, or into any space open to it, by the random motion of its molecules.	A gas escapes, molecule by molecule, through a very small hole into an empty space or a lower pressure.
Example: the smell of incense spreading through a room.	Example: helium leaking out of a party balloon through the rubber.
Graham's law holds only roughly (the molecules are jostled by the other gas).	Graham's law holds very closely.

4 a. **Boyle's law:** the volume of a fixed mass of a gas is inversely proportional to its pressure, provided its temperature stays the same: $PV = \text{constant}$.

Explanation: the pressure of a gas is caused by its molecules hitting the walls of the container. At a constant temperature, their average kinetic energy, and so their average speed, stays the same. If the volume is halved, the same number of molecules, moving at the same speed, travel only half as far between one wall and the next, so they hit each part of the walls twice as often. Twice the number of hits each second on each unit area means twice the pressure. So halving the volume doubles the pressure.

4 b. **Charles's law:** the volume of a fixed mass of a gas is directly proportional to its absolute temperature, provided its pressure stays the same: $\frac{V}{T} = \text{constant}$.
At constant pressure, a gas contracts by $\frac{1}{273}$ of its volume at 0 °C for every 1 °C it is cooled. If it could go on contracting at that rate, then at −273 °C it would have lost all of its volume. A graph of volume against temperature in °C is a straight line which, extended backward, reaches zero volume at −273 °C. Nothing can have less than zero volume, so −273 °C (−273.15 °C, more exactly) is the lowest temperature possible: absolute zero, the start of the kelvin scale. (Real gases turn liquid before they get there, so the line is extended, not measured, near absolute zero.)

4 c. Let a fixed mass of gas go from (P_1, V_1, T_1) to (P_2, V_2, T_2).
First, at constant temperature T_1, change the pressure from P_1 to P_2; the volume becomes V. By Boyle's law, $P_1V_1 = P_2V$, so $V = \frac{P_1V_1}{P_2}$ … (i)
Then, at constant pressure P_2, change the temperature from T_1 to T_2; the volume goes from V to V_2. By Charles's law, $\frac{V}{T_1} = \frac{V_2}{T_2}$, so $V = \frac{V_2T_1}{T_2}$ … (ii)
From (i) and (ii), $\frac{P_1V_1}{P_2} = \frac{V_2T_1}{T_2}$. Multiplying both sides by $\frac{P_2}{T_1}$:

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

This is the combined gas equation: $\frac{PV}{T}$ is constant for a fixed mass of gas.

4 d. **STP** (standard temperature and pressure) is 0 °C (273 K) and 1 atm (760 mmHg, 101,325 Pa).
The volume of a gas changes with its temperature and pressure, so a volume alone doesn't tell how much gas there is. Quoting every volume at the same agreed conditions lets us compare amounts of gases fairly, and at STP one mole of any gas occupies 22.4 L.

4 e. Any four of:

- A gas is made of a very large number of tiny molecules, all alike for one gas.
- The volume of the molecules is negligible compared with the volume of the container.
- The molecules move all the time at random, in straight lines.
- Their collisions with each other and with the walls are perfectly elastic.
- There is no force of attraction or repulsion between them, except during collisions.
- The pressure of a gas is caused by its molecules hitting the walls.
- The average kinetic energy of the molecules is proportional to the absolute temperature.

4 f. Two assumptions of the kinetic theory stop being true:

- **The molecules' own volume.** At high pressure the molecules are packed close, and their own volume becomes a real part of the gas's volume, so the gas can't be squeezed as much as Boyle's law predicts.
- **Attraction between molecules.** At low temperature the molecules move slowly, and at high pressure they are close together, so their weak attraction pulls on them. They hit the walls less hard, the pressure is less than predicted, and the gas can finally turn into a liquid.

A real gas therefore follows the gas laws closely only at low pressure and high temperature.

4 g. **Graham's law:** at the same temperature and pressure, the rate of diffusion of a gas is inversely proportional to the square root of its density (or of its molar mass): $\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$.
Uses (any two):

- to find the molar mass of an unknown gas, by comparing its rate of diffusion with that of a known gas;
- to separate isotopes, such as uranium-235 from uranium-238 as uranium hexafluoride gas;
- to explain why light gases (helium, hydrogen) leak out of balloons and containers faster;
- to predict where two gases will meet, as ammonia and hydrogen chloride do in a tube.

5 a.

$$V_2 = \frac{P_1 V_1}{P_2} = \frac{760 \times 600}{380} = 1{,}200\ ^3$$

1,200 cm³. Half the pressure, twice the volume.

5 b.

$$V_2 = \frac{P_1 V_1}{P_2} = \frac{101 \times 2.0}{33.7} = 6.0$$

About 6.0 L, three times bigger, since the pressure at the summit is about a third of that at sea level. (In reality it is also far colder there, which would make it a little smaller.)

5 c. $T_1 = 7 + 273 = 280$ K, $T_2 = 147 + 273 = 420$ K

$$V_2 = \frac{V_1 T_2}{T_1} = \frac{250 \times 420}{280} = 375\ ^3$$

375 cm³.

5 d.

$$T_2 = \frac{V_2 T_1}{V_1} = \frac{150 \times 273}{100} = 409.5$$

$t_2 = 409.5 - 273 = 136.5\ ^\circ$. **At 136.5 °C.**

5 e. $T_1 = 300$ K, $T_2 = 400$ K

$$V_2 = \frac{P_1 V_1 T_2}{T_1 P_2} = \frac{1 \times 2.0 \times 400}{300 \times 2} = 1.33$$

About 1.33 L. Doubling the pressure halves the volume, and heating from 300 K to 400 K makes it a third bigger again: 2.0 × ½ × 4/3 = 1.33.

5 f. At constant volume, $\frac{P_1}{T_1} = \frac{P_2}{T_2}$:

$$P_2 = \frac{P_1 T_2}{T_1} = \frac{1 \times 400}{300} = 1.33$$

About 1.33 atm.

5 g.

$$V_2 = \frac{P_1 V_1 T_2}{T_1 P_2} = \frac{700 \times 500 \times 273}{300 \times 760} = 419.1\ ^3$$

About 419 cm³ at STP.

5 h.

$$\frac{r_{_4}}{r_{_2}} = \sqrt{\frac{64}{16}} = \sqrt{4} = 2$$

Methane diffuses twice as fast as sulphur dioxide.

5 i.

$$\frac{t_{_2}}{t_{_2}} = \sqrt{\frac{M_{_2}}{M_{_2}}} = \sqrt{\frac{44}{32}} = 1.17$$

$t_{_2} = 40 \times 1.17 = 46.9$. **About 47 s.**

5 j.

$$\frac{r_X}{r_{_4}} = \sqrt{\frac{16}{M_X}} \quad \Rightarrow \quad \frac{1}{2} = \sqrt{\frac{16}{M_X}} \quad \Rightarrow \quad \frac{1}{4} = \frac{16}{M_X}$$

$M_X = 64$ g/mol. **The molar mass is 64 g/mol** (it could be sulphur dioxide).

5 k. $P_1 = 100$ kPa, $V_1 = 5.0$ m³, $T_1 = 300$ K; $P_2 = 1.2$ kPa, $T_2 = 227$ K

$$V_2 = \frac{P_1 V_1 T_2}{T_1 P_2} = \frac{100 \times 5.0 \times 227}{300 \times 1.2} = 315\ ^3$$

About 315 m³, more than 60 times the volume at launch, even though the cold makes it smaller. A balloon of 5 m³ is about 2.1 m across; one of 315 m³ would be about 8.4 m across. The rubber has to stretch to four times its width, so it is no surprise that weather balloons burst high up.

5 l. The student used degrees Celsius as if they were measured from zero volume. Charles's law needs the absolute (kelvin) temperature: 20 °C = 293 K and 40 °C = 313 K. The volume changes by the ratio $\frac{313}{293} = 1.068$, so it grows by **only about 7%**, not 100%. To double the volume, the gas would have to be heated to 2 × 293 = 586 K, which is 313 °C.