THE GAS LAWS

Note: The IUPAC (International Union of Pure and Applied Chemistry) definition of STP conditions given on page 82 of *Hebden: Chemistry 11* has been changed as follows.

STANDARD TEMPERATURE AND PRESSURE (STP) = 0^oC and 100 kPa

Which therefore changes the molar volume of a gas at STP.

1 mol of ANY GAS at STP has a volume of 22.7 L

(There are, in fact, several different "standards" of both temperature and pressure currently in use by various organizations, but the IUPAC standard is used here.)

There is a further IUPAC standard which can be used:

STANDARD AMBIENT TEMPERATURE AND PRESSURE (SATP) = 25^oC and 100 kPa

Which has an associated molar volume:

1 mol of ANY GAS at SATP = 24.8 L

This latter standard was adopted because 25^oC better reflects temperature conditions in chemical laboratories: "ambient" means "surrounding area or environment". (Although different laboratories are kept at different temperatures in different countries, and in different regions of the same country, everyone would probably agree that working at 0^oC is a bit chilly!)

A. BOYLE'S LAW

In 1660, Robert Boyle proposed the first of the experimentally-determined gas laws.

Boyle's Law states that the volume of a gas decreases when the pressure increases.

Using the proportionality symbol, " $\propto$ ", we can show this **inverse** relationship as:

$$V \propto \frac{1}{P} \qquad \text{or} \qquad V = \frac{\text{constant}}{P} \qquad \text{or} \qquad P \bullet V = \text{constant}$$

If either of the pressure or volume is changed, the resulting product of P•V remains constant and hence:

$$P_1 \bullet V_1 = \text{constant} = P_2 \bullet V_2 \qquad \text{where "1"= before the change} \quad \text{and} \quad \text{"2" = after the change}$$

that is: $\boxed{P_1 \bullet V_1 = P_2 \bullet V_2}$

EXAMPLE: A gas at 50.0 kPa pressure was expanded to 3.50 L and 8.50 kPa. What was the previous volume of the gas?

Let P_1 = previous pressure = 50.0 kPa, V_1 = previous volume = ?
P_2 = new pressure = 8.50 kPa , V_2 = new volume = 3.50 L

$$P_1 \bullet V_1 = P_2 \bullet V_2 \quad \text{so that} \quad V_1 = \frac{P_2 \cdot V_2}{P_1} = \frac{8.50\,\text{kPa} \times 3.50\,\text{L}}{50.0\,\text{kPa}} = \mathbf{0.595\ L}$$

EXERCISES:

1. A cylinder contains a movable piston and has a pressure of 82.6 kPa in a volume of 0.575 L. Calculate the pressure if the piston compresses the gas in the cylinder to a volume of 0.275 L.
2. A gas is compressed in a cylinder to a pressure of 1.50×10^5 kPa and a volume of 25.0 mL. If the gas is allowed to expand such that its pressure is 1.00×10^2 kPa, what volume will the gas occupy?

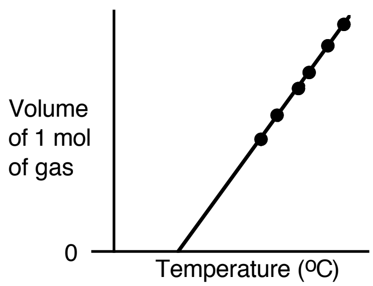
B. CHARLES' LAW

In 1787 the French physicist Jacques Charles, who was the first person to design a balloon and fly in it, found that an increase in temperature causes an increase in the volume of a gas.

Charles' Law states that if the pressure of a gas is held constant, then increasing the temperature of a gas increases its volume.

This statement has an interesting consequence: if the temperature is decreased, then the volume also decreases. But, you can't keep decreasing the volume of a gas indefinitely. At some point the gas particles will be so close together that they will form a liquid or a solid. In 1848, William Thompson (later known as Lord Kelvin) noted that Charles' Law implies a **lowest temperature** exists, and that a gas thermometer can establish an ABSOLUTE TEMPERATURE SCALE, now known as the Kelvin scale.

Plotting volume–vs–temp(^{o}C) for many gases gives the following graph.



Experimentally, it is found that the line extrapolates to zero volume at –273^{o}C. Zero degrees on the Kelvin temperature scale is defined as follows.

Definition: $\boxed{\mathbf{0\ K = -273^{o}C} \quad \text{and} \quad \mathbf{T(K) = T(^{o}C) + 273}}$

Note: "0 K" is pronounced "zero Kelvin", **not** "zero degrees Kelvin".

Using Kelvin's temperature scale, we can express Charles' Law by the proportional relationship

$$V \propto T(K) \quad \text{or} \quad V = \text{constant} \cdot T(K)$$

so that $$\frac{V_1}{V_2} = \frac{T_1}{T_2} \quad \text{or} \quad \frac{V_1}{T_1} = \frac{V_2}{T_2}$$

EXAMPLE: A gas has a volume of 250.0 mL at –80^{o}C. What volume does the gas occupy at 100^{o}C?

Let: V_1 = old volume = 250.0 mL , T_1 = old temperature = –80 + 273 = 193 K
V_2 = new volume = ? , T_2 = new temperature = 100 + 273 = 373 K

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad \text{so that} \quad V_2 = \frac{V_1 \cdot T_2}{T_1} = \frac{250.0\ \text{mL} \times 373\ \text{K}}{193\ \text{K}} = \mathbf{483\ mL}$$

EXERCISES:

3. On a cool winter day, a balloon is inflated with air until it has a volume of 2.50 L at 5^{o}C. The sun comes out from behind clouds and the balloon warms up until the temperature is 10^{o}C. What is the new volume of the balloon?
4. A movable piston and cylinder contains 325 mL of air at SATP. What temperature is required to shrink the volume of gas to 125 mL without changing the pressure?

C. GAY-LUSSAC'S LAW

In 1802, Joseph Louis Gay-Lussac's experiments with gases led him to propose the following law. (The law assumes that the volume and amount of gas is unchanged.)

Gay-Lussac's law states that an increase in temperature will increase the pressure.

Again, this law can be summarized as a proportion, provided we assume that temperature is measured on the Kelvin scale:

$$P \propto T(K) \quad \text{or} \quad P = \text{constant} \cdot T(K)$$

so that $$\frac{P_1}{P_2} = \frac{T_1}{T_2} \quad \text{or} \quad \frac{P_1}{T_1} = \frac{P_2}{T_2}$$

EXAMPLE: A gas in a sealed glass bulb has a pressure of 58.3 kPa at 21°C. What will be the pressure inside the bulb is the temperature is raised to 100°C?

Let: P_1 = old pressure = 58.3 kPa, T_1 = old temperature = = 21 + 273 = 294 K
P_2 = new pressure = ?, T_2 = new temperature = 100 + 273 = 373 K

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \quad \text{so that} \quad P_2 = \frac{P_1T_2}{T_1} = \frac{58.3\ \text{kPa} \times 373\ \text{K}}{294\ \text{K}} = \mathbf{74.0\ kPa}$$

EXERCISES:

5. An automobile tire is inflated to a pressure of 221 kPa at 15°C. After the car travels for 100 km, the internal temperature of the tire is 35°C. What is the new pressure inside the tire?

6. A balloon filled with helium gas is at SATP. When the balloon is cooled to liquid nitrogen temperature the pressure drops to 25.8 kPa. What is the temperature, on the Celcius scale, of liquid nitrogen?

D. DALTON'S LAW

IMPORTANT NOTE: Dalton's law is NOT considered to be part of the Chemistry 11 course but there is one important aspect of his law that is required before we can go further.

In 1801, John Dalton (whom we will meet later, in Unit VIII, as the Father of Atomic Theory), stated that his experiments had shown that if non-reacting gases are mixed, the total pressure that results is equal to the pressures created by the individual gases.

The important point for our purposes is this:

If temperature and volume are kept constant, the increase in pressure is proportional to the increase in the moles of gas particles.

Again we can express this as: $P \propto n$ or $P = \text{constant} \cdot n$, where n = moles of gas particles

E. THE IDEAL GAS LAW

Up to this point the following four laws have been investigated.

P•V = constant	(Boyle's Law)
V = constant •T	(Charles' Law)
P = constant•T	(Gay-Lussac's Law)
P = constant•n	(Dalton's Law)

All these relationships (and more) can be summarized by the **IDEAL GAS LAW:**

$$\boxed{\mathbf{PV = nRT}}$$

where **R** is a proportionality constant called the **GAS CONSTANT** or **IDEAL GAS CONSTANT.**

The value of R can be found using the known values for P, V, n and T at STP.

$$R = \frac{PV}{nT} = \frac{100\,\text{kPa} \times 22.7\,\text{L}}{1\,\text{mol} \times 273\,\text{K}} = \mathbf{8.31}\ \frac{\text{kPa}\cdot\text{L}}{\text{mol}\cdot\text{K}}$$

GAS LAW CALCULATIONS

There are two main types of gas law calculations.

1. A Single Set of Conditions: The Conditions Under Which a Gas Exists

A SINGLE set of conditions is given, describing the conditions to which a gas is subjected. There is no sense of time passing; that is, no "before" and "after".

EXAMPLE: How many moles of $O_2(g)$ are contained in a 500.0 mL bulb containing O_2 at 20.0 kPa and 60°C?

Assemble a "shopping list":
P = 20.0 kPa
V = 500.0 mL = 0.5000 L
n = ?
R = 8.31 kPa•L/mol•K
T = 60 + 273 = 333 K

Note that all the units used must agree with the units of R.

$$PV = nRT \quad \text{and} \quad n = \frac{PV}{RT} = \frac{20.0\,\text{kPa} \times 0.5000\,\text{L}}{8.31\,\text{kPa}\cdot\text{L/mol}\cdot\text{K} \times 333\,\text{K}} = \mathbf{0.00361\ mol}$$

EXAMPLE: If 16.0 g of an unknown gas occupy a volume of 2.50 L at 451 kPa and 100°C, what is the molar mass of the gas?

P = 451 kPa, V = 2.50 L, n = ?, R = 8.31 kPa•L/mol•K, T = 100 + 273 = 373 K

$$PV = nRT \quad \text{and} \quad n = \frac{PV}{RT} = \frac{451\,\text{kPa} \times 2.50\,\text{L}}{8.31\,\text{kPa}\cdot\text{L/mol}\cdot\text{K} \times 373\,\text{K}} = 0.364\ \text{mol}$$

$$\text{But} \quad \text{molar mass} = \frac{\text{mass}}{\text{moles}} = \frac{16.0\,\text{g}}{0.364\,\text{mol}} = \mathbf{44.0\ g/mol}$$

NOTE: Sometimes the following equation is used to solve the above problem.

$$\boxed{PV = \frac{m}{MW}RT}$$

where m = mass of gas
and MW = molar mass of gas

However, there is little advantage to memorizing a special equation for one type of problem.

EXERCISES:

7. If 2.00 mol of O_2(g) occupy 200.0 L at 0^oC, what is the pressure of the O_2?
8. How many moles of CH_4(g) are in a 3.50 L cylinder at 35^oC and 202.6 kPa?
9. A glass bulb with a volume of 2.75 L contains 1.54 g of N_2(g) at a pressure of 20.3 kPa. What is the temperature of the bulb?
10. When 0.640 g of O_2(g) is cooled to –40^oC, the pressure of the gas is 66.7 kPa. What is the volume of the container holding the gas?
11. A 0.500 g sample of a gas has a pressure of 23.3 kPa at 25^oC in a 0.750 L bulb. What is the molar mass of the gas?
12. What mass of gaseous ethane, C_2H_6, at 60.8 kPa pressure and –25^oC contains the same number of molecules as 9.20 g of NO_2(g) at STP?
13. The best vacuum that can be attained presently on earth is about 1.0 x 10^{-14} kPa at 0^oC. Under these conditions, how many molecules are contained in a volume of 1.00 mL?
14. Calculate the mass of one molecule of a gas if 20.4 g occupy 11.4 L at 507 kPa and 273^oC.
15. When 1.75 g of an unknown gas is put into a 1.25 L glass bulb at 39^oC, the pressure in the bulb is 86.4 kPa. What is the molar mass of the gas?
16. What is the pressure of a sample of helium gas having a density of 7.80 g/L at 273^oC?
17. A 1.25 g sample of oxygen gas at STP is found to contain the same number of molecules as 0.664 g of an unknown gas at 50.0 kPa and –75^oC. What is the molar mass of the unknown?
18. Calculate the density of a sample of nitrogen gas at –15^oC and 100.0 kPa.

2. Two Sets of Conditions: Before and After

Two sets of conditions are given. One set describes an initial or “before” set of conditions

$$P_1V_1 = n_1RT_1 \qquad \text{(R cannot change).}$$

A second set of values describes a final or “after” set of conditions

$$P_2V_2 = n_2RT_2 \text{ .}$$

Comparing the two sets of values in a ratio gives $\dfrac{P_1V_1}{P_2V_2} = \dfrac{n_1RT_1}{n_2RT_2}$

and canceling the constant R gives the final form $\boxed{\dfrac{P_1V_1}{P_2V_2} = \dfrac{n_1T_1}{n_2T_2}}$

IMPORTANT NOTE: Use the above equation if the unknown is “before”, so that the subscript “1” is in the numerator (above the division sign). If the unknown is “after”, invert the equation so that the subscript “2” is in the numerator. This makes it easier to rearrange the equation and less likely to have you make an error while rearranging. Also, always rearrange the equation and THEN place the values in the rearranged equation. This is more efficient and takes less writing.

EXAMPLE: A steel cylinder contains 2.00 L of $N_2(g)$ at $20^{o}C$ and 90.0 kPa. When a piston is pushed into the cylinder, the volume is compressed to 0.800 L and the pressure rises to 260.0 kPa. What is the final temperature?

$P_1 = 90.0$ kPa	$P_2 = 260.0$ kPa
$V_1 = 2.00$ L	$V_2 = 0.800$ L
$n_1 =$ ⟵ same ⟶	$n_2 =$
$T_1 = 20 + 273 = 293$ K	$T_2 = ?$

Rearranging $\frac{P_2V_2}{P_1V_1} = \frac{n_2T_2}{n_1T_1}$ and cancelling n

gives $T_2 = \frac{P_2V_2T_1}{P_1V_1} = \frac{260.0\text{ kPa x }0.800\text{ L x }293\text{ K}}{90.0\text{ kPa x }2.00\text{ L}} = \mathbf{339\ K\quad (66^{o}C)}$

EXAMPLE: A 600.0 mL container at $80^{o}C$ contains a gas at 45.0 kPa. A piston changes the volume to 400.0 mL, the temperature is raised to $160^{o}C$ and the mass of gas within the cylinder is doubled. What is the final pressure?

$P_1 = 45.0$ kPa	$P_2 = ?$
$V_1 = 600.0$ mL	$V_2 = 400.0$ mL
$n_1 = n$	$n_2 = 2\ n$
$T_1 = 80 + 273 = 353$ K	$T_2 = 160 + 273 = 433$ K

Rearranging $\frac{P_2V_2}{P_1V_1} = \frac{n_2T_2}{n_1T_1}$ gives $P_2 = \frac{n_2T_2P_1V_1}{V_2n_1T_1}$

and $P_2 = \frac{2n\text{ x }433\text{ K x }45.0\text{ kPa x }600.0\text{ mL}}{n\text{ x }353\text{ K x }400.0\text{ mL}} = \mathbf{166\ kPa}$

A final comment on Avogadro's Hypothesis

According to Avogadro's Hypothesis, "Equal volumes of gases at the same temperature and pressure contain the same numbers of moles". That is, when $V_1 = V_2$, $T_1 = T_2$ and $P_1 = P_2$, then $n_1 = n_2$.

This means $\frac{P_1V_1}{P_2V_2} = \frac{n_1T_1}{n_2T_2}$ reduces to $1 = \frac{n_1}{n_2}$ and therefore $n_1 = n_2$

So, if $V_1 = V_2$, $T_1 = T_2$ and $P_1 = P_2$, then $n_1 = n_2$ automatically, and therefore "Avogadro's Hypothesis" is just a special case derivable from the Ideal Gas Law. (But hey, let's give Avogadro due credit; he didn't have the advantage of knowing all the later discoveries about gases!)

EXERCISES:

19. A gas at 1621 kPa pressure occupies 11.0 L at $36^{o}C$. What is its new volume if the temperature is changed to $16^{o}C$ and the pressure to 3647 kPa?

20. A gas occupying 2.30 L at $-100^{o}C$ is allowed to warm up to $25^{o}C$. What is the new gas volume, if pressure is constant?

21. The reaction $2\ K(s) + 2\ H_2O(l) \longrightarrow 2\ KOH(aq) + H_2(g)$ produces 45.3 mL of $H_2(g)$ at $23^{o}C$ and 97.8 kPa. What mass of K(s) is used in the reaction?

22. The oxygen supply for a rocket engine on a satellite is contained in a steel sphere. The sphere has a volume of 10.0 L and delivers 1405 L of gas at SATP. What pressure must the sphere be able to withstand if the normal operating temperature of the sphere is $-10^{o}C$? What mass of $O_2(g)$ can be delivered from the sphere?

23. The average breath that a 16 year old male takes when resting is about 300 mL in volume at $20^{o}C$ and 105 kPa. His respiratory rate is about 20 breaths per minute. What volume of air at STP does he breathe in one minute?

24. The density of oxygen gas is 1.29 g/L at $20.0^{o}C$ and 100.0 kPa. What is the volume occupied by 1.00 mol of oxygen under these conditions?

25. A steel cylinder holds 1.00 mol of a gaseous hydrocarbon and 4.00 mol of oxygen. The temperature and pressure of the container is $25^{o}C$ and 202.6 kPa. A spark ignites and completely reacts the gases. If the final pressure is 709.1 kPa and combustion produces 3.00 mol of $CO_2(g)$ and 4.00 mol of $H_2O(g)$, what is the temperature after the ignition occurs?

26. A rocket probe to the surface of Mars collected a sample of gas from a surface crack in the soil. When compressed and warmed to STP (only a wisp of gas was collected), a 5.07 mL sample of the compressed gas had a mass of 6.26 mg. The scientists in charge of the Martian Probe project hoped that the gas was CO_2, in support of an important theory of the Martian atmosphere. They were also aware of the fact that the combustion of hydrazine, N_2H_4, was used to propel the descent rocket of the landing module:

$$N_2H_4 + O_2 \longrightarrow 2\ H_2O + N_2.$$

Was the gas CO_2, or did rocket exhaust contaminate the experiment?

27. Calculate the density of $NH_3(g)$ at STP.

28. A cylinder contains 3.00 mol of $N_2(g)$ at a temperature of $100^{o}C$ and a pressure of 405.2 kPa in a volume of 23.0 L. If the cylinder is heated to $400^{o}C$ and the volume expands to 50.0 L by moving out a piston, what mass of N_2 must be removed to lower the pressure to 100.0 kPa?

29. Calculate the volume of oxygen gas at $150^{o}C$ and 95.0 kPa required to react completely with 15.0 g of NH_3 gas at $250^{o}C$ and 115 kPa if the reaction is:

$$4\ NH_3 + 7\ O_2 \longrightarrow 4\ NO_2 + 6\ H_2O.$$

30. A cylinder having a volume of 883.0 L contains 200.0 g of $CH_4(g)$ at 33.3 kPa and $10^{o}C$. If the total volume is compressed to 500.0 L, the temperature is kept constant and another 480.0 g of CH_4 are added, what is the final pressure?

31. What volume of HCl(g) at $50^{o}C$ and 120.0 kPa can be formed by reacting 15.0 L of $H_2(g)$ at $150^{o}C$ and 85.0 kPa with 12.0 L of $Cl_2(g)$ at $100^{o}C$ and 125.0 kPa?

32. A glassblower uses an oxygen tank having a volume of 15.0 L. The tank remains at a temperature of $21^{o}C$ at all times. If the tank pressure decreases from 1.930×10^4 kPa to 1.896×10^4 kPa, what mass of oxygen is delivered from the tank?

33. In order to make 125 kg of $(NH_4)_2SO_4$, what volume of 9.00 M H_2SO_4 and what volume of NH_3 gas at 2.53×10^3 kPa and $5^{o}C$ is required for the reaction?

34. A 700.0 mL bulb contains 0.00100 mol of $N_2(g)$ at 3.60 kPa. If the temperature is unchanged, how many moles of N_2 have to be added to bring the pressure up to 20.00 kPa?

35. A sample bulb contains 0.712 g of $H_2(g)$ at a certain temperature and pressure. Under the same temperature and pressure conditions, the bulb can hold 13.0 g of an unknown gas. What is the molar mass of the unknown gas?

36. A 2.00 L storage tank contains $F_2(g)$ at 126 kPa and $30^{o}C$. A 1.00 L reaction vessel contains Xe(g) at 50.4 kPa and $30^{o}C$. The $F_2(g)$ is pumped into the reaction vessel containing the Xe(g) and the reaction mixture is heated for a few hours, allowing the reaction

$$Xe(g) + 2\ F_2(g) \longrightarrow XeF_4(s)$$

to occur. After all the Xe(g) is used up, the reaction vessel is cooled to $-10^{o}C$. Assuming all the XeF_4 remains in the solid phase, what pressure of $F_2(g)$ remains in the reaction vessel?