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Ideal gas law

The **ideal gas law**, also called the **general gas equation**, is the <u>equation of state</u> of a hypothetical <u>ideal gas</u>. It is a good approximation of the behavior of many <u>gases</u> under many conditions, although it has several limitations. It was first stated by <u>Émile Clapeyron</u> in 1834 as a combination of the empirical <u>Boyle's law</u>, <u>Charles's law</u>, <u>Avogadro's law</u>, and <u>Gay-Lussac's law</u>. [1] The ideal gas law is often written as

$$PV = nRT$$

where P, V and T are the pressure, volume and absolute temperature; n is the number of moles of gas; and R is the ideal gas constant. It is the same for all gases. It can also be derived from the microscopic kinetic theory, as was achieved (apparently independently) by August Krönig in $1856^{[2]}$ and Rudolf Clausius in 1857.

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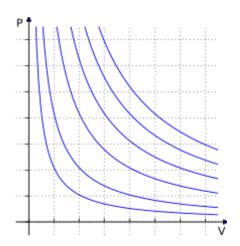
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Equation

The <u>state</u> of an amount of <u>gas</u> is determined by its pressure, volume, and temperature. The modern form of the equation relates these simply in two main forms. The temperature used in the equation of state is an absolute temperature: the appropriate SI unit is the kelvin.^[4]



Isotherms of an ideal gas. The curved lines represent the relationship between pressure (on the vertical axis) and volume (on the horizontal axis) for an ideal gas at different temperatures: lines that are farther away from the origin (that is, lines that are nearer to the top right-hand corner of the diagram) represent higher temperatures.

Common forms

The most frequently introduced form is

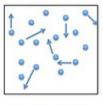
$$PV = nRT = Nk_{\rm B}T$$
,

where:

- *P* is the pressure of the gas,
- V is the volume of the gas,
- \bullet *n* is the amount of substance of gas (also known as number of moles).
- N is the number of gas molecules (or the Avogadro constant times the amount of substance $N_{\rm A} n$),
- R is the ideal, or universal, gas constant, equal to the product of the Boltzmann constant and the Avogadro constant,
- k_B is the Boltzmann constant
- *T* is the absolute temperature of the gas.

In <u>SI</u> units, *P* is measured in pascals, *V* is measured in <u>cubic metres</u>, *n* is measured in <u>moles</u>, and *T* in <u>kelvins</u> (the Kelvin scale is a shifted Celsius scale, where 0.00 K = -273.15 °C, the lowest possible temperature). *R* has the value $8.314 \text{ J/(K \cdot mol)} \approx 2 \text{ cal/(K \cdot mol)}$, or 0.08206 L·atm/(mol·K).





Propane Gas Tank

Molecules inside the gas tank

Molecular collisions within a closed container (the propane tank) are shown (right). The arrows represent the random motions and collisions of these molecules. The pressure and temperature of the gas are directly proportional: as the temperature is increased, the pressure of the propane increases by the same factor. A simple consequence of this proportionality is that on a hot summer day, the propane tank pressure will be elevated, and thus propane tanks must be rated to withstand such increases in pressure.

Molar form

How much gas is present could be specified by giving the mass instead of the chemical amount of gas. Therefore, an alternative form of the ideal gas law may be useful. The chemical amount (n) (in moles) is equal to total mass of the gas (m) (in grams) divided by the molar mass (M) (in grams per mole):

$$n = \frac{m}{M}$$
.

By replacing n with m/M and subsequently introducing density $\rho = m/V$, we get:

$$PV = rac{m}{M}RT$$
 $P = rac{m}{V}rac{RT}{M}$ $P =
horac{R}{M}T$

Defining the specific gas constant $R_{\text{specific(r)}}$ as the ratio R/M,

$$P = \rho R_{
m specific} T$$

This form of the ideal gas law is very useful because it links pressure, density, and temperature in a unique formula independent of the quantity of the considered gas. Alternatively, the law may be written in terms of the <u>specific volume</u> v, the reciprocal of density, as

$$Pv = R_{ ext{specific}}T.$$

It is common, especially in engineering applications, to represent the **specific** gas constant by the symbol R. In such cases, the **universal** gas constant is usually given a different symbol such as \bar{R} to distinguish it. In any case, the context and/or units of the gas constant should make it clear as to whether the universal or specific gas constant is being referred to.^[5]

Statistical mechanics

In statistical mechanics the following molecular equation is derived from first principles

$$P = nk_{\rm B}T$$

where *P* is the absolute <u>pressure</u> of the gas, *n* is the number of molecules in the given volume *V* (the <u>number density</u> is given by the ratio n = N/V, in contrasts to the previous formulation in which *n* is the *number of moles*), *T* is the <u>absolute</u> temperature, and k_B is the Boltzmann constant relating temperature and energy, given by:

$$k_{
m B}=rac{R}{N_{
m A}}$$

where N_A is the Avogadro constant.

From this we notice that for a gas of mass m, with an average particle mass of μ times the <u>atomic mass constant</u>, $m_{\rm u}$, (i.e., the mass is μ u) the number of molecules will be given by

$$N=rac{m}{\mu m_{
m u}},$$

and since $\rho = m/V = n\mu m_u$, we find that the ideal gas law can be rewritten as

$$P=rac{1}{V}rac{m}{\mu m_{
m u}}k_{
m B}T=rac{k_{
m B}}{\mu m_{
m u}}
ho T.$$

In SI units, P is measured in pascals, V in cubic metres, and T in measured kelvins. $k_{\rm B}$ has the value 1.38·10⁻²³ J/K in SI units.

Combined gas law

Combining the laws of Charles, Boyle and Gay-Lussac gives the **combined gas law**, which takes the same functional form as the ideal gas law save that the number of moles is unspecified, and the ratio of PV to T is simply taken as a constant:^[6]

$$\frac{PV}{T} = k,$$

where P is the <u>pressure</u> of the gas, V is the <u>volume</u> of the gas, T is the <u>absolute temperature</u> of the gas, and k is a constant (for a fixed amount of gas). When comparing the same substance under two different sets of conditions, the law can be written as

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

Energy associated with a gas

According to the assumptions of the kinetic theory of gases, we assumed that there are no intermolecular attractions between the molecules of an ideal gas. In other words, its <u>potential energy</u> is zero. Hence, all the energy possessed by the gas is kinetic energy.

$$E=rac{3}{2}RT$$

This is the kinetic energy of one mole of a gas.

Energy of gas	Mathematical formula	
energy associated with one mole of a gas	$E=rac{3}{2}RT$	
energy associated with one gram of a gas	$E=rac{3}{2}rT$	
energy associated with one molecule of a gas	$E=rac{3}{2}k_{B}T$	

Applications to thermodynamic processes

The table below essentially simplifies the ideal gas equation for a particular processes, thus making this equation easier to solve using numerical methods.

A <u>thermodynamic process</u> is defined as a system that moves from state 1 to state 2, where the state number is denoted by subscript. As shown in the first column of the table, basic thermodynamic processes are defined such that one of the gas properties (P, V, T, S, or H) is constant throughout the process.

For a given thermodynamics process, in order to specify the extent of a particular process, one of the properties ratios (which are listed under the column labeled "known ratio") must be specified (either directly or indirectly). Also, the property for which the ratio is known must be distinct from the property held constant in the previous column (otherwise the ratio would be unity, and not enough information would be available to simplify the gas law equation).

In the final three columns, the properties (P, V, or T) at state 2 can be calculated from the properties at state 1 using the equations listed.

		l			
Process	Constant	Known ratio or delta	P ₂	V ₂	T ₂
Isobaric process	Pressure	V ₂ /V ₁	$P_2 = P_1$	$V_2 = V_1(V_2/V_1)$	$T_2 = T_1(V_2/V_1)$
		T ₂ /T ₁	$P_2 = P_1$	$V_2 = V_1(T_2/T_1)$	$T_2 = T_1(T_2/T_1)$
Isochoric process (Isovolumetric process) (Isometric process)	Volume	P ₂ /P ₁	$P_2 = P_1(P_2/P_1)$	$V_2 = V_1$	$T_2 = T_1(P_2/P_1)$
		T ₂ /T ₁	$P_2 = P_1(T_2/T_1)$	$V_2 = V_1$	$T_2 = T_1(T_2/T_1)$
Isothermal process	Temperature	P ₂ /P ₁	$P_2 = P_1(P_2/P_1)$	$V_2 = V_1/(P_2/P_1)$	$T_2 = T_1$
		V ₂ /V ₁	$P_2 = P_1/(V_2/V_1)$	$V_2 = V_1(V_2/V_1)$	$T_2 = T_1$
Isentropic process (Reversible adiabatic process)	Entropy ^[a]	P ₂ /P ₁	$P_2 = P_1(P_2/P_1)$	$V_2 = V_1(P_2/P_1)$ (-1/y)	$T_2 = T_1(P_2/P_1)^{(\gamma)}$ - 1)/\gamma
		V ₂ /V ₁	$P_2 = P_1(V_2/V_1)^{-Y}$	$V_2 = V_1(V_2/V_1)$	$T_2 = T_1(V_2/V_1)^{(1)}$
		T ₂ /T ₁	$P_2 = P_1(T_2/T_1)^{\gamma/(\gamma - 1)}$	$V_2 = V_1(T_2/T_1)^{1/(1 - Y)}$	$T_2 = T_1(T_2/T_1)$
Polytropic process	P V ⁿ	P ₂ /P ₁	$P_2 = P_1(P_2/P_1)$	$V_2 = V_1(P_2/P_1)$	$T_2 = T_1(P_2/P_1)^{(n)}$
		V ₂ /V ₁	$P_2 = P_1(V_2/V_1)^{-n}$	$V_2 = V_1(V_2/V_1)$	$T_2 = T_1(V_2/V_1)^{(1)}$
		T ₂ /T ₁	$P_2 = P_1(T_2/T_1)^{n/(n-1)}$	$V_2 = V_1(T_2/T_1)^{1/(1-n)}$	$T_2 = T_1(T_2/T_1)$
Isenthalpic process (Irreversible adiabatic process)	Enthalpy ^[b]	P ₂ – P ₁	$P_2 = P_1 + (P_2 - P_1)$		$T_2 = T_1 + \mu_{JT}(P_2 - P_1)$
		T ₂ – T ₁	$P_2 = P_1 + (T_2 - T_1)/\mu_{JT}$		$T_2 = T_1 + (T_2 - T_1)$

 $[\]hat{}$ **a.** In an isentropic process, system entropy (*S*) is constant. Under these conditions, $P_1 V_1^{\gamma} = P_2 V_2^{\gamma}$, where γ is defined as the <u>heat capacity ratio</u>, which is constant for a calorifically <u>perfect gas</u>. The value used for γ is typically 1.4 for diatomic gases like <u>nitrogen</u> (N₂) and <u>oxygen</u> (O₂), (and air, which is 99% diatomic). Also γ is typically 1.6 for mono atomic gases like <u>noble gases helium</u> (He), and <u>argon</u> (Ar). In internal combustion engines γ varies between 1.35 and 1.15, depending on constitution gases and temperature.

Deviations from ideal behavior of real gases

The equation of state given here (PV=nRT) applies only to an ideal gas, or as an approximation to a real gas that behaves sufficiently like an ideal gas. There are in fact many different forms of the equation of state. Since the ideal gas law neglects both <u>molecular size</u> and inter molecular attractions, it is most accurate for <u>monatomic</u> gases at high temperatures and low pressures. The neglect of molecular size becomes less important for lower densities, i.e. for larger volumes at lower

 $[\]hat{\ }$ **b.** In an isenthalpic process, system enthalpy (H) is constant. In the case of <u>free expansion</u> for an ideal gas, there are no molecular interactions, and the temperature remains constant. For real gasses, the molecules do interact via attraction or repulsion depending on temperature and pressure, and heating or cooling does occur. This is known as the <u>Joule–Thomson effect</u>. For reference, the Joule–Thomson coefficient μ_{JT} for air at room temperature and sea level is $0.22 \, ^{\circ}\text{C/bar}.^{[7]}$

pressures, because the average distance between adjacent molecules becomes much larger than the molecular size. The relative importance of intermolecular attractions diminishes with increasing thermal kinetic energy, i.e., with increasing temperatures. More detailed <u>equations of state</u>, such as the <u>van der Waals equation</u>, account for deviations from ideality caused by molecular size and intermolecular forces.

A <u>residual property</u> is defined as the difference between a <u>real gas</u> property and an ideal gas property, both considered at the same pressure, temperature, and composition.

Derivations

Empirical

The empirical laws that led to the derivation of the ideal gas law were discovered with experiments that changed only 2 state variables of the gas and kept every other one constant.

All the possible gas laws that could have been discovered with this kind of setup are:

$$PV=C_1$$
 or $P_1V_1=P_2V_2$ (1) known as Boyle's law

$$rac{V}{T}=C_2 ext{ or } rac{V_1}{T_1}=rac{V_2}{T_2}$$
 (2) known as Charles's law

$$rac{V}{N}=C_3 ext{ or } rac{V_1}{N_1}=rac{V_2}{N_2} ext{ (3) known as } rac{ ext{Avogadro's law}}{ ext{}}$$

$$rac{P}{T}=C_4 ext{or} \; rac{P_1}{T_1}=rac{P_2}{T_2}$$
 (4) known as Gay-Lussac's law

$$NT = C_5 \text{ or } N_1 T_1 = N_2 T_2$$
 (5)

$$\frac{P}{N} = C_6 \text{ or } \frac{P_1}{N_1} = \frac{P_2}{N_2}$$
 (6)

Where "P" stands for <u>pressure</u>, "V" for <u>volume</u>, "N" for number of particles in the gas and "T" for <u>temperature</u>; Where $C_1, C_2, C_3, C_4, C_5, C_6$ are not actual constants but are in this context because of each equation requiring only the parameters explicitly noted in it changing.

To derive the ideal gas law one does not need to know all 6 formulas, one can just know 3 and with those derive the rest or just one more to be able to get the ideal gas law, which needs 4.

Since each formula only holds when only the state variables involved in said formula change while the others remain constant, we cannot simply use algebra and directly combine them all. I.e. Boyle did his experiments while keeping N and T constant and this must be taken into account.

Keeping this in mind, to carry the derivation on correctly, one must imagine the gas being altered by one process at a time. The derivation using 4 formulas can look like this:

GayLussac
Boyle PV = kCharles Avogadro

Relationships between Boyle's, Charles's, Gay-Lussac's, Avogadro's, combined and ideal gas laws, with kN = nR. In each law, properties circled are variable and properties not circled are constant.

at first the gas has parameters P_1, V_1, N_1, T_1

Say, starting to change only pressure and volume, according to Boyle's law, then:

$$P_1V_1=P_2V_2$$
 (7) After this process, the gas has parameters P_2,V_2,N_1,T_1

Using then Eq. (5) to change the number of particles in the gas and the temperature,

$$N_1T_1=N_2T_2$$
 (8) After this process, the gas has parameters P_2,V_2,N_2,T_2

Using then Eq. (6) to change the pressure and the number of particles,

$$rac{P_2}{N_2}=rac{P_3}{N_3}$$
 (9) After this process, the gas has parameters P_3,V_2,N_3,T_2

Using then Charles's law to change the volume and temperature of the gas,

$$rac{V_2}{T_2}=rac{V_3}{T_3}$$
 (10) After this process, the gas has parameters P_3,V_3,N_3,T_3

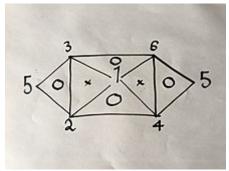
Using simple algebra on equations (7), (8), (9) and (10) yields the result:

$$\frac{P_1V_1}{N_1T_1} = \frac{P_3V_3}{N_3T_3}$$
 or $\frac{PV}{NT} = K_B$, Where K_B stands for Boltzmann's constant.

Another equivalent result, using the fact that $nR = NK_B$, where "n" is the number of <u>moles</u> in the gas and "R" is the universal gas constant, is:

PV = nRT, which is known as the ideal gas law.

If you know or have found with an experiment 3 of the 6 formulas, you can easily derive the rest using the same method explained above; but due to the properties of said equations, namely that they only have 2 variables in them, they cant be any 3 formulas. For example if you were to have Eqs. (1), (2) and (4) you would not be able to get any more because combining any two of them will give you the third; But if you had Eqs. (1), (2) and (3) you would be able to get all 6 Equations without having to do the rest of the experiments because combining (1) and (2) will yield (4), then (1) and (3) will yield (6), then (4) and (6) will yield (5), as well as would the combination of (2) and (3) as is visually explained in the following visual relation:



Relationship between the 6 gas laws

Where the numbers represent the gas laws numbered above.

If you were to use the same method used above on 2 of the 3 laws on the vertices of one triangle that has a "O" inside it, you would get the third.

For example:

Change only pressure and volume first: $P_1V_1 = P_2V_2$ (1')

then only <u>volume</u> and <u>temperature</u>: $rac{V_2}{T_1}=rac{V_3}{T_2}$ (2´)

then as we can choose any value for V_3 , if we set $V_1=V_3$, Eq. (2´) becomes: $\frac{V_2}{T_1}=\frac{V_1}{T_2}$ (3´)

combining equations (1') and (3') yields $\frac{P_1}{T_1} = \frac{P_2}{T_2}$, which is Eq. (4), of which we had no prior knowledge until this derivation.

Theoretical

Kinetic theory

The ideal gas law can also be derived from <u>first principles</u> using the <u>kinetic theory of gases</u>, in which several simplifying assumptions are made, chief among which are that the molecules, or atoms, of the gas are point masses, possessing mass but no significant volume, and undergo only elastic collisions with each other and the sides of the container in which both linear momentum and kinetic energy are conserved.

Statistical mechanics

Let $\mathbf{q} = (q_x, q_y, q_z)$ and $\mathbf{p} = (p_x, p_y, p_z)$ denote the position vector and momentum vector of a particle of an ideal gas, respectively. Let \mathbf{F} denote the net force on that particle. Then the time-averaged kinetic energy of the particle is:

$$egin{aligned} \left\langle \mathbf{q}\cdot\mathbf{F}
ight
angle &=\left\langle q_{x}rac{dp_{x}}{dt}
ight
angle +\left\langle q_{y}rac{dp_{y}}{dt}
ight
angle +\left\langle q_{z}rac{dp_{z}}{dt}
ight
angle \ &=-\left\langle q_{x}rac{\partial H}{\partial q_{x}}
ight
angle -\left\langle q_{y}rac{\partial H}{\partial q_{y}}
ight
angle -\left\langle q_{z}rac{\partial H}{\partial q_{z}}
ight
angle =-3k_{B}T, \end{aligned}$$

where the first equality is <u>Newton's second law</u>, and the second line uses <u>Hamilton's equations</u> and the <u>equipartition</u> theorem. Summing over a system of *N* particles yields

$$3Nk_BT = -igg\langle \sum_{k=1}^N \mathbf{q}_k \cdot \mathbf{F}_k igg
angle.$$

By <u>Newton's third law</u> and the ideal gas assumption, the net force of the system is the force applied by the walls of the container, and this force is given by the pressure *P* of the gas. Hence

$$-iggl(\sum_{k=1}^{N}\mathbf{q}_{k}\cdot\mathbf{F}_{k}iggr)=Piggl(\int_{\mathrm{surface}}\mathbf{q}\cdot d\mathbf{S},$$

where d**S** is the infinitesimal area element along the walls of the container. Since the divergence of the position vector \mathbf{q} is

$$abla \cdot \mathbf{q} = rac{\partial q_x}{\partial q_x} + rac{\partial q_y}{\partial q_y} + rac{\partial q_z}{\partial q_z} = 3,$$

the divergence theorem implies that

$$P\oint_{
m surface} {f q}\cdot d{f S} = P\int_{
m volume} \left(
abla\cdot{f q}
ight) dV = 3PV,$$

where dV is an infinitesimal volume within the container and V is the total volume of the container.

Putting these equalities together yields

$$3Nk_BT = -igg\langle \sum_{k=1}^N \mathbf{q}_k \cdot \mathbf{F}_k igg
angle = 3PV,$$

which immediately implies the ideal gas law for N particles:

$$PV = Nk_BT = nRT$$
,

where $n = N/N_A$ is the number of moles of gas and $R = N_A k_B$ is the gas constant.

See also

- Van der Waals equation Gas equation of state based on plausible reasons why real gases do not follow the ideal gas law.
- Boltzmann constant Physical constant relating particle kinetic energy with temperature
- Configuration integral Function in thermodynamics and statistical physics
- Dynamic pressure
- Internal energy

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