

Theory of ideal gas

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[Everything about ES 181](#)

Part of the book [Thermodynamics](#)

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A collection of molecules is called an ideal gas if their average distance is much larger than an individual molecule. They fly, collide, separate, and fly again. Between two collisions, a molecule flies as if all other molecules were absent.

This molecular motion picture is here turned into a quantitative theory.

We also describe experimental data. Ideal gases illustrate an enduring theme in science: division of labor between theory and experiment.

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Empirical laws and molecular theory

In lectures on [gas](#) and [energy](#), we have met two equations of equilibrium of ideal gases:

$$PV = Nk_B T$$

$$dU = Nc_V(T)dT$$

The thermal capacity $c_V(T)$ is measured experimentally.

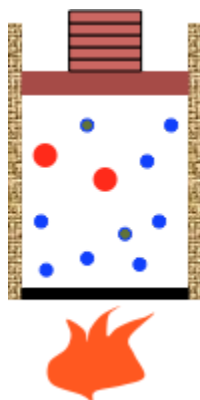
Historically, the two equations of equilibrium were discovered empirically over centuries. Today, they are deduced theoretically in a few lines, from a molecular picture.

The theory yields not only the two equations of equilibrium, but also other results. For example, when pure ideal gases are mixed at constant temperature and volume, the entropy of the mixture equals the sum of the entropies of the pure gases.

Exercise. Assume that an ideal gas of one species of molecules has a constant thermal capacity per molecule, c_v . Determine the function $s(u, v)$.

An ideal gas sealed in a cylinder by a piston

To a good approximation, air is an ideal gas, consisting mostly of two species of molecules, nitrogen and oxygen. We develop the theory using a mixture of two species. The theory readily reduces to one species, a pure gas, and generalizes to mixtures of three or more species.



Sealed in a cylinder by a piston, an ideal gas of two species of molecules is a [closed system](#). The gas interacts with the surroundings by thermal contact and moving the piston. The molecules neither leak nor react.

Two isolated systems collocate in the same volume, but have independent sample spaces

Because molecules neither leak nor react, each species has a fixed number of molecules, and forms a closed system. Let N_1 be the number of the molecules of species 1, and N_2 be the number of the molecules of species 2.

Because every molecule can fly anywhere in the cylinder as if all other molecules were absent, the two closed systems *collocate* in the volume of the cylinder, V . The volume changes when the piston moves.

The two closed systems exchange energy by thermal contact, mediated by molecular collision and separation. Let U_1 be the internal energy of species 1, and U_2 be the internal energy of species 2.

For now, we specify equilibria of the two collocating closed systems by *three* independent properties— U_1 , U_2 , V .

When U_1 , V , N_1 are fixed, species 1 forms an [isolated system](#), which has a certain number of states, $\Omega_1(U_1, V, N_1)$. For one molecule, the number of states is proportional to the volume V , because each molecule can fly anywhere in the container as if all other molecules were absent. In an ideal gas of N_1 molecules, molecules fly independently, so that the number of states scales with the volume as V^{N_1} . Write the number of states of the isolated system of species 1 as

$$\Omega_1(U_1, V, N_1) = V^{N_1} f_1(U_1, N_1)$$

The proportional factor f_1 depends on U_1 and N_1 , but not on V .

Recall the definition of [entropy](#):

$$S = k_B \log \Omega$$

The entropy of the isolated system of species 1 is

$$S_1(U_1, V, N_1) = N_1 k_B \log V + k_B \log f_1(U_1, N_1)$$

Similar expressions hold for species 2:

$$\begin{aligned} \Omega_2(U_2, V, N_2) &= V^{N_2} f_2(U_2, N_2) \\ S_2(U_2, V, N_2) &= N_2 k_B \log V + k_B \log f_2(U_2, N_2) \end{aligned}$$

The two isolated systems together constitute a composite isolated system. The two isolated systems collocate in the cylinder, but have *independent sample spaces*. Consequently, their numbers of states multiply to give the number of states for the composite isolated system:

$$\Omega = \Omega_1(U_1, V, N_1) \cdot \Omega_2(U_2, V, N_2)$$

The logarithmic function turns a product into a sum, so that the entropy of the composite isolated system is the sum of the entropies of the two component isolated systems:

$$S = S_1(U_1, V, N_1) + S_2(U_2, V, N_2)$$

Exercise. Run the basic algorithm of thermodynamics by constructing an isolated system with U_1, U_2, V as independent internal variables.

Energy

Recall the definition of temperature of a [closed system](#). Consider the closed system of species 1, taken to be in internal equilibrium, so that its temperature T is defined by

$$\frac{\partial S_1(U_1, V, N_1)}{\partial U_1} = \frac{1}{T}$$

Inserting the expression for the entropy, we obtain that

$$k_B \frac{\partial \log f_1(U_1, N_1)}{\partial U_1} = \frac{1}{T}$$

This equation indicates that the energy U_1 is independent of volume V , and is a function of two variables, $U_1(V, N_1)$.

Energy is extensive, and is therefore proportional to the number of molecules:

$$U_1 = N_1 u_1(T)$$

Here $u_1(T)$ is the average energy per molecule of species 1, defined by $u_1 = U_1/N_1$.

Recall the definition of thermal capacity under constant volume:

$$c_{V,1} = \frac{du_1(T)}{dT}$$

Thus,

$$du_1(T) = c_{V,1}(T)dT$$

Similar expressions hold for species 2.

Two closed systems in thermal equilibrium. When the two closed systems reach thermal equilibrium with each other, their temperatures equal:

$$\frac{\partial S_1(U_1, V, N_1)}{\partial U_1} = \frac{\partial S_2(U_2, V, N_2)}{\partial U_2}$$

In equilibrium, the two species have the same temperature T , so that U_1 and U_2 are dependent variables, both depend on the temperature: $U_1 = N_1 u_1(T)$ and $U_2 = N_2 u_2(T)$. The mixture is a closed system of two independent variables, for example, V and T . The internal energy of the mixture sums the energies of the two species:

$$U = N_1 u_1(T) + N_2 u_2(T)$$

Partial pressure

Recall the definition of pressure of a [closed system](#). Consider the closed system of species 1. In internal equilibrium, the pressure of the closed system is defined by

$$P_1 = T \frac{\partial S_1(U_1, V, N_1)}{\partial V}$$

We call P_1 the *partial pressure* in species 1. Inserting the expression for $S_1(U_1, V, N_1)$ into this definition, we obtain that

$$P_1 = \frac{N_1 k_B T}{V}$$

Similarly, the partial pressure in species 2 is

$$P_2 = \frac{N_2 k_B T}{V}$$

We can also regard the mixture as a single closed system. In internal equilibrium, this closed system has pressure P , defined by

$$P = T \frac{\partial S(U, V)}{\partial V}$$

Inserting the expression for entropy into this definition, we obtain that

$$P = \frac{(N_1 + N_2) k_B T}{V}$$

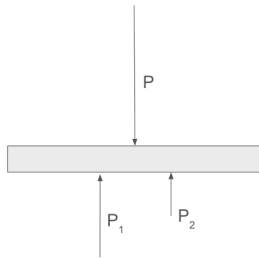
The pressure of the mixture sums the partial pressures in the two species.

$$P = P_1 + P_2$$

We have just deduced the ideal gas law!

As mentioned in the early chapters, the ideal gas temperature defined from empirical observations coincides with the temperature defined by energy and entropy.

Free body diagram of piston. To interpret the partial pressures, picture the mixture in a cylinder sealed by a piston. A constant weight placed above the piston exerts a downward pressure P . The mixture exerts on the piston two upward partial pressures, P_1 and P_2 . In equilibrium, the downward pressure due to the constant weight balances the sum of the upward partial pressures of the component gases.



Exercise. Dry air is composed mostly of nitrogen and oxygen. For every 100 molecules in dry air, assume that 79 are N_2 and 21 are O_2 . Consider dry air at 100 kPa, 25 Celsius. Calculate the volume divided by the number of molecules. Compare the volume to the volume per nitrogen molecule. Do your results support the statement that, to a good approximation, air is an ideal gas?

Wikipedia [Ideal gas law](#). Follow links in the entry to see centuries of experimental discoveries.

Volume

For an ideal gas mixture composed of two species of molecules, the equilibria are specified by three independent properties, which can be the three extensive properties, U_1, U_2, V , as we have mentioned. We next regard the three intensive properties, T, P_1, P_2 , as independent properties, and express other properties of the ideal gas mixture as their functions.

The two closed systems collocate in the same volume, V . For species 1, write the ideal gas law as

$$V = \frac{N_1 k_B T}{P_1}$$

For species 1, define the volume per molecule by $v_1 = V/N_1$, so that

$$v_1 = \frac{k_B T}{P_1}$$

Similar expressions hold for species 2:

$$V = \frac{N_2 k_B T}{P_2}$$

$$v_2 = \frac{k_B T}{P_2}$$

Because the two species collocate in the same volume V , the rule of mixture does not apply to volume:

$$V \neq N_1 v_1 + N_2 v_2$$

Rather,

$$V = N_1 v_1 = N_2 v_2$$

Enthalpy

For the closed system of species 1, define the enthalpy per molecule by $h_1 = H_1/N_1$. Recall the definition of enthalpy:

$$h_1 = u_1 + P_1 v$$

For pure gas 1, the enthalpy per molecule is

$$h_1(T) = u_1(T) + k_B T$$

Recall the definition of thermal capacity under constant pressure:

$$c_{P,1} = \frac{dh_1(T)}{dT}$$

Thus,

$$c_{P,1}(T) = c_{V,1}(T) + k_B$$

$$dh_1 = c_{p,1}(T)dT$$

Similar expressions hold for species 2. The enthalpy of the mixture sums the enthalpies of the two species:

$$H = N_1 h_1(T) + N_2 h_2(T)$$

Entropy

For the closed system of species 1, define the entropy per molecule by $s_1 = S_1/N_1$. Recall an identity for any [closed system](#):

$$ds_1 = \frac{1}{T}dh_1 - \frac{v_1}{T}dP_1$$

Further recall that

$$dh_1 = c_{p,1}(T)dT$$

$$v_1 = \frac{k_B T}{P_1}$$

A combination of the above equation gives that

$$ds_1 = \frac{c_{p,1}(T)}{T}dT - \frac{k_B}{P_1}dP_1$$

Let T_0 be a fixed temperature and P_0 be a fixed pressure. Assume that we know the absolute entropy per molecule in one equilibrium, $s_1(T_0, P_0)$. Integrating the above equation, we obtain that

$$s_1(T, P_1) = s_1(T_0, P_0) + \int_{T_0}^T \frac{c_{p,1}(T)}{T}dT - k_B \log \frac{P_1}{P_0}$$

This equation is commonly written as two equations:

$$s_1(T, P_1) = s_1(T, P_0) - k_B \log \left(\frac{P_1}{P_0} \right)$$

$$s_1(T, P_0) = s_1(T_0, P_0) + \int_{T_0}^T \frac{c_{p,1}(T)}{T}dT$$

Similar expressions hold for the molecules of species 2.

When ideal gases of different molecular species are mixed at constant temperature and volume, in equilibrium, the entropy of the mixture sums the entropies of the pure gases.

$$S = N_1 s_1(T, P_1) + N_2 s_2(T, P_2)$$

Gibbs function

For the closed system of species 1, define the Gibbs function per molecule by $g_1 = G_1/N_1$.

Recall the definition of [Gibbs function](#):

$$g_1 = u_1 + P_1 v_1 - T s_1$$

Thus,

$$g_1(T, P_1) = h_1(T) - T s_1(T, P_0) + k_B T \log \frac{P_1}{P_0}$$

A similar expression holds for the molecules of species 2. The Gibbs function for the mixture is

$$G(T, P) = N_1 g_1(T, P_1) + N_2 g_2(T, P_2)$$

Free energy

For the closed system of species 1, define the free per molecule by $f_1 = F_1/N_1$. Recall the definition of [free energy](#):

$$f_1 = u_1 - T s_1$$

Thus,

$$f_1(T, v_1) = u_1(T) - T s_1(T, v_0) - k_B T \log \frac{v_1}{v_0}$$

where

$$s(T, v_0) = s(T_0, v_0) + \int_{T_0}^T \frac{c_v(T)}{T} dT$$

$$v_0 = \frac{k_B T_0}{P_0}$$

$$c_{V,1}(T) = c_{P,1}(T) - k_B$$

Exercise. Let us continue the discussion of [a gas bubble in a liquid](#). The bubble contains a fixed number of gas molecules, N . The liquid is under atmospheric pressure P_{air} . The surface energy γ and the atmospheric pressure P_{air} drives the bubble to shrink, while the entropy of the gas inside the bubble drives the bubble to expand.

- Construct a thermal system with an internal variable.
- Find the free energy as a function of the radius of the bubble. Sketch this function.
- Determine the equilibrium radius.

Pure ideal gas

The theory developed for an ideal gas mixture is readily reduced to a pure ideal gas. Specify equilibria of a pure ideal gas by values of two intensive properties: temperature T and pressure P . Each of the other properties is a function of T and P .

$$\begin{aligned} v &= \frac{k_B T}{P} \\ du &= c_V(T) dT \\ dh &= c_P(T) dT \\ c_P(T) &= c_V(T) + k_B \\ s(T, P) &= s(T, P_0) - k_B \log \frac{P}{P_0} \\ s(T, P_0) &= s(T_0, P_0) + \int_{T_0}^T \frac{c_P(T)}{T} dT \\ g(T, P) &= h(T) - Ts(T, P_0) + k_B T \log \frac{P}{P_0} \\ f(T, v) &= u(T) - Ts(T, v_0) - k_B T \log \frac{v}{v_0} \end{aligned}$$

Each relation is an equation of equilibrium. So far we have normalized extensive properties by the number of molecules. If we normalize extensive properties by the number of moles, the above equations still hold, provided we replace k_B by $R = k_B N_A$, where N_A is the number of molecules per mole (i.e., the Avogadro number).

For many species of molecules, the enthalpy $h(T)$ and the absolute entropy $s(T, P_0)$ are listed in [ideal gas tables](#). The reference pressure is set as $P_0 = 100$ kPa. These tables of data, along with the above equations of equilibrium, fully define the model of ideal gases.

TABLE A.8

Ideal Gas Properties of Various Substances, Entropies at 0.1-MPa (1-Bar) Pressure, Mass Basis

T (K)	Nitrogen, Diatomic (N ₂) $R = 0.2968 \text{ kJ/kg-K}$ $M = 28.013 \text{ kg/kmol}$			Oxygen, Diatomic (O ₂) $R = 0.2598 \text{ kJ/kg-K}$ $M = 31.999 \text{ kg/kmol}$		
	u (kJ/kg)	h (kJ/kg)	s_T^0 (kJ/kg-K)	u (kJ/kg)	h (kJ/kg)	s_T^0 (kJ/kg-K)
200	148.39	207.75	6.4250	129.84	181.81	6.0466
250	185.50	259.70	6.6568	162.41	227.37	6.2499
300	222.63	311.67	6.8463	195.20	273.15	6.4168
350	259.80	363.68	7.0067	228.37	319.31	6.5590
400	297.09	415.81	7.1459	262.10	366.03	6.6838
450	334.57	468.13	7.2692	296.52	413.45	6.7954

[Image credit](#)

Division of labor between theory and experiment

Ideal gases illustrate an enduring theme—division of labor between theory and experiment.

Each pure ideal gas is characterized by a single number, $s(T_0, P_0)$, and a single curve, $c_p(T)$, measured experimentally by combining calorimetry and thermometry. Once pure ideal gases are characterized, all equations of equilibrium of any ideal gas mixture are determined by theory.

Exercise. Mix 0.6 kg of O₂ and 1.4 kg of CO₂ at 150 kPa and 300 K.

- Find the volume of the mixture.
- Find the partial pressure of each species of molecules.
- Find the enthalpy of the mixture.
- Find the internal energy of the mixture.
- Find the entropy of the mixture.

Exercise. A mixture of 2 kg oxygen and 2 kg argon is in a thermally insulated piston-cylinder setup at 100 kPa, 300 K. The piston now compresses the mixture to half of its initial volume. Find the final pressure, temperature, and the change in the potential energy of the weight placed above the piston. Adopt the approximation that thermal capacity is independent of temperature.

Exercise. In a helium gas, each molecule consists of a single helium atom. For such a gas of single-atom molecules, the thermal capacity per molecule is $c_v = 1.5k_B$, and is independent of temperature. Calculate the thermal capacity per mole of helium. Calculate the thermal capacity per unit mass of helium. The molar mass of helium is 4 kg/kmol.

Exercise. Use the ideal gas tables to find the energy, enthalpy, and entropy of O₂ at 1000 K, 1 MPa.

Exercise. Use the ideal gas tables to find the energy, enthalpy, and entropy of H₂O at 1000 K, 100 kPa.

Semipermeable boxes

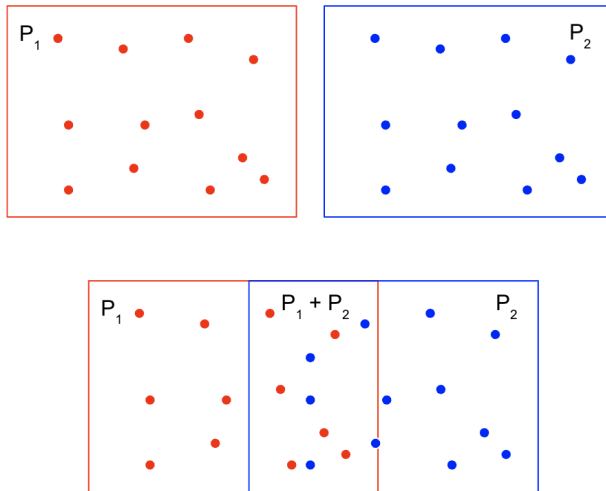
Consider a process of mixing the two species of molecules. Two boxes have the same volume, V . Each box is *semipermeable*. Box 1 is impermeable to species 1, but permeable to species 2. Box 2 is impermeable to species 2, but permeable to species 1.

In the initial equilibrium, each box contains a pure ideal gas of the same temperature T . Box 1 contains N_1 molecules of species 1 and pressure

$$P_1 = \frac{N_1 k_B T}{V}$$

Box 2 contains N_2 molecules of species 2 and pressure

$$P_2 = \frac{N_2 k_B T}{V}$$



When we slide the two boxes relative to each other, species 1 permeates into box 2, and species 2 permeates into box 1. Because box 1 is impermeable to species 1, and box 2 is impermeable to species 2, each species remains to be a closed system of volume V and temperature T . In equilibrium, the pressure of the closed system of species 1 remains to be P_1 , and the pressure of the closed system of species 2 remains to be P_2 . In the overlapping volume of the two boxes, the two species mix, and the pressure is $P_1 + P_2$.

In the final equilibrium, the volumes of the two boxes coincide, and the two species are mixed. Assume that the boxes slide without friction, and slide slowly so that molecules have enough time to permeate and equalize the (partial) pressure of each species. Under these assumptions, sliding requires no external force. The two boxes of molecules together constitute an isolated system. Sliding connects the initial and final constrained equilibria of the isolated system by a reversible process.

The mixture contains N_1 molecules of species 1 and N_2 molecules of species 2, and has volume V , temperature T , and pressure

$$P = (N_1 + N_2) \frac{k_B T}{V}$$

The isolated system conserves energy, so that the energy of the mixture in the final equilibrium equals the sum of the energies of the pure gases in the initial equilibrium:

$$U = N_1 u_1(T) + N_2 u_2(T)$$

The isolated system undergoing a reversible process keeps its energy stationary, so that the entropy of the mixture in the final equilibrium equals the sum of the entropies of the two pure gases in the initial equilibrium:

$$S = N_1 s_1(T, P_1) + N_2 s_2(T, P_2)$$

Exercise. Consider another process of mixing. In the initial equilibrium, two pure gases have different species of molecules, but have the same temperature T and the same pressure P . In the final equilibrium, the mixture also has the temperature T and pressure P . Calculate the change in entropy of the process. Is this a reversible process?

Summary

For two species of molecules sealed in a cylinder by a piston, each species exerts on the piston a partial pressure:

$$P_1 = \frac{N_1 k_B T}{V}$$

$$P_2 = \frac{N_2 k_B T}{V}$$

The enthalpy of the gas is

$$H = N_1 h_1(T) + N_2 h_2(T)$$

The entropy of the gas is

$$S = N_1 s_1(T, P_1) + N_2 s_2(T, P_2)$$

The entropy per molecule of species 1 is

$$s_1(T, P_1) = s_1(T, P_0) - k_B \log\left(\frac{P_1}{P_0}\right)$$

A similar expression holds for molecules of species 2.

For many species of molecules, the enthalpy $h(T)$ and the absolute entropy $s(T, P_0)$ are listed in [ideal gas tables](#).