

Thermodynamic Basics

Perfect Gas Laws

A perfect or ideal gas has the advantage that its properties can be described by simple equations with only one constant. Very little data is therefore required to describe the gas over a wide range of conditions and for many situations air and water vapour behave as an ideal gas^{†A.1}. The perfect gas equation was originally developed from experimental observation and is a combination of Boyle's law and Charles' law^{†A.2}.



The perfect gas law therefore states that in a closed system for a fixed mass of gas, its pressure times its volume is directly proportional to its absolute temperature.

$$p.V \propto T$$

However, for most engineering solutions the above 'equality' is not sufficient. What we need is an **equation** and this we can develop by introducing some 'constants of proportionality'.

Thus we can express the perfect gas law in the form:

$$p.V = m.R.T$$

where

p is the absolute pressure (kPa)^{†A.3}

V is the gas volume (m³)

m is the mass of gas (kg)

R is a constant for the gas – the specific gas constant (kJ/kg K)^{†A.4}

T is the absolute temperature (K).

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Variant Forms

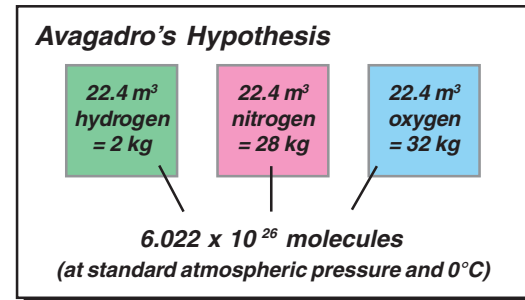
This ideal or perfect gas equation can be written in a number of forms. For example, the specific volume (v) is the volume of unit mass of dry air at a given temperature, normally expressed in m³/kg and is useful because the addition of water vapour actually has no effect on the volume (Dalton's Law). Thus the perfect gas equation can be changed from:

$$p.V = m.R.T \quad \text{to} \quad p.v = R.T$$

Apart from experimental measurements of p , V and T the specific gas constant (R) can also be found from the Universal Gas Constant (R_o), and the molecular mass (M) of the gas, where

$$R = \frac{R_o}{M} \quad \begin{matrix} \text{(kJ/kmol K)} \\ \text{(kg/kmol)} \end{matrix}$$

This relationship stems from Avagadro's important historic observation that 'equal volumes of gases under the same conditions of temperature and pressure contain the same number of molecules.'



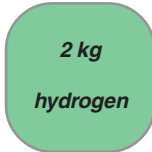


Note: Although the number of particles making up the volume is very large, each particle is very small, thus the volume of gas only depends upon the number of particles present, not the size of each.

Notes

Notes



The **mole** (or in this case the **kilogram mole** (kmol) is therefore a measure of the quantity of the material at the atomic or molecular level. The kilogram mole is defined as the amount of a substance which contains as many particles (eg electrons, atoms, ions, radicals or molecules, and these must be named) as there are atoms of carbon in 12kg of carbon-12 (an isotope of carbon) †A.5.

Mole		
		
1 kmol hydrogen molecules $= 6.022 \times 10^{26}$ molecules	1 kmol carbon atoms $= 6.022 \times 10^{26}$ atoms	1 kmol copper atoms $= 6.022 \times 10^{26}$ atoms

Thus we can also write the perfect or ideal gas equation as:

$$p \cdot V_o = R_o \cdot T$$

where V_o is the volume of 1 kmol of gas ($m^3/kmol$), and is the same for all gases at the same temperature and pressure - 22.4 (m^3) at 0°C and 101.325 kPa.

or
$$p \cdot V = n \cdot R_o \cdot T$$

where n is the number of kmoles of gas. For reference $R_o = 8.3144$ kJ/kmol K. Other useful constants are included here as an Extra.

Finally, in our variant forms for the perfect gas equation, we can write:

$$\frac{p_1 \cdot V_1}{T_1} = \frac{p_2 \cdot V_2}{T_2}$$

Gas Data



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Personal Feedback Question A.1

The table below indicates the proportion by volume, the molecular mass and the molecular mass fraction for the common atmospheric gases. Use the table to determine:

- (i) the molecular mass of dry air,
- (ii) the molecular mass of water vapour (H_2O)
- (iii) hence determine the specific gas constants for both dry air and water vapour.

Gas	Proportion (by volume)	Molecular Mass (M) (kg/kmol)	Molecular Mass Fraction (Proportion x M)
Nitrogen (N_2)	0.7803	28.02	21.86
Oxygen (O_2)	0.2099	32.00	6.72
Carbon Dioxide (CO_2)	0.0003	44.00	0.01
Hydrogen (H_2)	0.0001	2.02	0.00
Argon (Ar)	0.0094	39.91	0.36

Note: If you need to check your solution, or need a hint to get started then you will find a hint and worked solution at the back of this appendix.

Internal Energy (U)

This is a thermodynamic property and represents the molecular energy possessed by a substance. It includes the kinetic energy of translation (i.e. the transference of a body, or a form of energy, from one point to another), rotation and vibration of the molecules and their constituents, and the potential energy associated with the forces between them. The internal energy of a body is measured in Joules but not all the energy a body possesses is convertible to work. This energy is distributed over an immense number of molecules, each of which for example can have a vibrational energy in three orthogonal (x , y & z) axis, and it would therefore not be practical to produce a device which could extract all this energy from a body.

We can also measure the internal energy per unit mass of material. This is the **specific internal energy** (u) and is measured in kJ/kg.

Enthalpy (H)

Enthalpy (defined from the Greek meaning 'to heat') is also a measure of energy and although in psychrometry it is only the heat energy which is of interest, nevertheless this heat content is referred to as enthalpy. It has the units of energy (Joules) and is defined from $H = U + p.V$.

More usually however, it is defined in terms of its intensive or unit mass properties, in which case the **specific enthalpy** (h) is given by $h = u + p.v$.

In other words, the enthalpy of a body is the sum of its internal energy and the product of its volume and the pressure exerted upon it.

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Specific Heat

It is not possible to directly measure the specific internal energy or the specific enthalpy of a body. However for a closed system, it is possible and reasonable to measure a change in internal energy by a change in temperature at constant volume. Similarly, for a stream of air passing through an open system, the change in specific enthalpy at constant pressure can be determined by a change in temperature. Consider therefore heat being transferred to a system during which there is a temperature change. The specific heat is defined as the amount of heat required to change a unit mass by unit temperature. If the process occurs at constant volume, there will be no work, and the heat transfer equals the internal energy change. If the process occurs at constant pressure, then the heat transfer equals the enthalpy change. There are therefore two specific heats:

Specific heat at constant volume (c_v) given by:

$$c_v = \frac{u}{T} \quad (\text{kJ/kg K})$$

and the

Specific heat at constant pressure (c_p) given by:

$$c_p = \frac{h}{T} \quad (\text{kJ/kg K})$$

Hence the specific heat is a property that can be measured, or more precisely, can be calculated from quantities that can be measured, which can be used to calculate the internal energy or enthalpy changes for a material. In the case of a solid or a liquid, the energy and enthalpy depend primarily on temperature and only slightly on pressure or specific volume, but for a perfect or ideal gas, energy and enthalpy depend only on temperature which can be used to calculate changes in u or h .

$$u_2 - u_1 = c_v \cdot (T_2 - T_1) \quad \text{or} \quad h_2 - h_1 = c_p \cdot (T_2 - T_1)$$

For a perfect gas (or for practical gases over small changes in temperature) it is not necessary to know both values of specific heat since one can be defined in terms of the other, e.g.

$$h = u + p.v \quad \text{but since for a perfect gas} \quad p.v = R.T$$

$$\text{then} \quad h = (c_v + R).T \quad \text{i.e.} \quad c_p \text{ (defined as } \frac{h}{T} \text{)} = c_v + R$$

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Sensible and Latent Heat

When heat is added to a substance then there is usually an increase in temperature and hence the internal energy or the internal energy and the enthalpy will increase. This is referred to as sensible heat. However when heat is added to a substance sometimes a change of state will occur – such as melting or boiling – rather than a change of temperature. This is known as latent heat (from the Latin meaning hidden), and although during the process of change the temperature remains constant, there will still be a change in pressure or volume and so there will be a change in enthalpy.

Consider for example a substance at its saturation temperature such as water boiling in a kettle open to the atmosphere. The liquid water remains at 100°C until all the liquid boils away. Thus the change in specific internal heat is zero ($\Delta u = 0$). However boiling will result in a very large increase in volume and so a large increase in enthalpy.

We shall also see during the unit, that it is not necessary for water to be at 100 °C to evaporate. Water can be converted to water vapour at much lower temperatures and the higher the air temperature for example, the greater the amount of water vapour it can contain. Thus when we supply heat to water for example, not all of the heat supplied will be ‘sensible, i.e. will result in an increase in temperature. The ‘latent’ heat portion will be used to supply energy to molecules of water so that then can escape the surface of the liquid and become a vapour (evaporate). Thus enthalpy is a much more convenient measure of energy content than internal energy, as it takes into account both sensible and latent heat. In fact the change of enthalpy which occurs as water is evaporating is used to define and represent this energy change and is termed the latent heat of evaporation (h_{fg}),

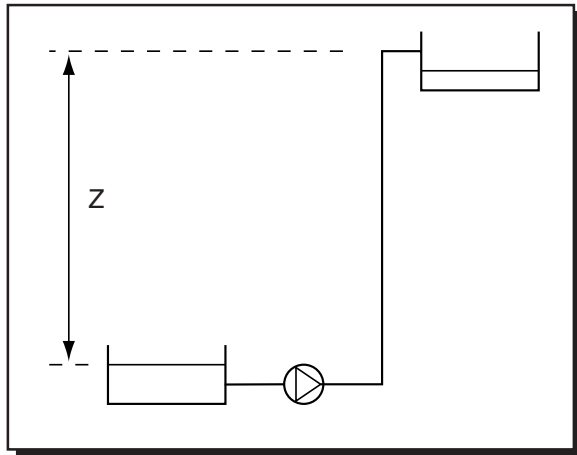
$$\text{where: } h_{fg} = h_g - h_f^{\dagger A6}.$$



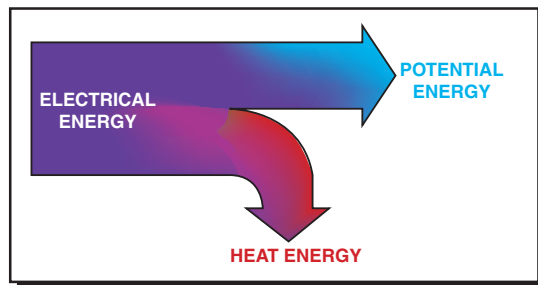
1st Law of Thermodynamics - (Conservation of Energy)

The first law of thermodynamics is that the total amount of energy never changes; so that energy cannot be created or destroyed, it can only be transformed from one form to another.

An example of this is where an electric pump is used to raise water from one water tank to a higher one.



All the electrical energy input to the electric motor of the pump is converted to energy of another form. i.e. the total amount of energy is constant.



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Thus the electrical energy is converted to:

- (1) potential (or stored) energy - the water in the higher tank has increased potential energy given by:
 $mass \times gravitational \ constant \times height \ (m.g.z)$ (Joules)
- (2) thermal energy -
 - (i) an increase in the internal energy of the water due to a rise in temperature caused by friction.
 - (ii) and increase in internal energy of the ambient air due to a rise in temperature caused by heating of the motor (iron, copper and friction losses within the motor).

The sum of (1) and (2) will add up to the electrical energy input, but of course only the energy in form (1) is 'useful' and desired, although the other effects are a necessary by-product of the action. Hence we can get a measure of the overall usefulness or efficiency of the system from: **efficiency** = $\frac{\text{useful energy}}{\text{input energy}}$

Steady-state Flow Energy Equation

Regardless of what happens within the above system, provided the energy flow is steady we can, using the first law of thermodynamics, define the process by the following equation:

$$Q - W = m \cdot \left(h + \frac{c^2}{2} + g \cdot z \right)_2 - m \cdot \left(h + \frac{c^2}{2} + g \cdot z \right)_1$$

where

Q is the rate of heat transfer to the system,

W is the rate of work done by the system,

m is the mass flow rate of the fluid through the system,

h is the enthalpy of the fluid (h_2 at exit, h_1 at entry),

c is the velocity of the fluid at entry and exit

(assumed to be the same),

z is the height difference the fluid is raised through,

g is the acceleration due to gravity.

In the previous example

$\frac{c^2}{2}$ represents the unit mass kinetic energy

and

$g \cdot z$ represents the unit mass potential energy.

However for many processes (especially air conditioning), changes in kinetic and potential energy are negligible and there is no work done, which leads to a greatly simplified equation:

$$Q = m \cdot (h_2 - h_1)$$

This is a very useful expression which can be repeatedly applied to psychrometric processes in air conditioning.

Appendix Notes

†C-1: Perfect gases;
most gases do deviate from a 'perfect' gas except at high pressures and low temperatures. In fact at very low pressures all gases and vapours behave as almost perfect gases.

†C.2: Boyle's Law;
for a fixed mass of gas at constant temperature, the pressure times volume is a constant; e.g., if you double the pressure you halve the volume, or conversely, if you halve the pressure you double the volume.

Charles' Law;
for a fixed mass of gas maintained at constant pressure, the volume is directly proportional to the absolute temperature.

†C.3: Pressure;
force per unit area, i.e. the force spread over a particular area, is measured in newtons and area in square metres. So pressure is measured in newtons per square metre but it can also be measured in pascal (symbol Pa, where $1 \text{ Pa} = 1 \text{ N/m}^2$).

Traditionally, it has also been common to express atmospheric pressure in units of bar (from the Greek meaning weight, thus a 'barometer' [a word agains derived from the Greek meaning weight + measure] is an instrument to measure the weight or pressure of the) or millibar (mbar), where $1 \text{ bar} = 10^5 \text{ Pa}$.

†C-4: Units;
these units may seem a little strange, but the specific gas constant is usually evaluated experimentally for a gas by measuring p , V , T and m . Hence re-arranging the equation gives:

$$R = \frac{p.V}{T.m}$$

In terms of units, $p.V$ yields units of $(\text{kPa} \times \text{m}^3)$, but as we saw in note †C.1, $(\text{Pa} = \text{N/m}^2)$ hence we may also write $P.V$ as units of $(\text{kPa} \times \text{m}^3/\text{m}^2)$ which reduces to units of $(\text{kN} \times \text{m})$.

Now the Joule is the unit of work and is measured as force times distance, i.e. $1\text{J} = 1\text{N} \times 1\text{m}$.

Hence $p.V$ can have units of (kJ) and $\frac{p.V}{T.m}$ units of (kJ/kg K) .

†C.5: Avagadro's Number;
the number of particles in 1 kilogram mole (kmol) is known as **Avagadro's Number** and equals 6.022×10^{26}

†C.6: Subscripts;
any state where a liquid exists in equilibrium* with its vapour is known as a saturation state. The subscripts noted are therefore standard subscripts used to identify:

f - property of saturated liquid,
 g - property of dry saturated vapour,
 fg - liquid - vapour saturation property difference.

*When a substance is present in both its liquid and vapour phase (e.g. water and water vapour), an equilibrium will be set up between its rate of evaporation and rate of condensation.

Solution to Personal Feedback Question A.1

Hint

- (i) The molecular mass of dry air is the total of column 3 (the molecular mass fraction).
- (ii) The molecular mass for water vapour (H_2O) is determined from the molecular masses of its components.
- (iii) The specific gas constants can be found from $R = \frac{R_o}{M}$

Solution

- (i) The molecular mass for dry air is the sum of the molecular mass fraction i.e. $21.86 + 6.72 + 0.01 + 0.36 = 28.97$ kg/kmol.
- (ii) Water vapour has a composition of H_2O , thus its molecular mass is given by:
- $$(2 \times 1.01) + (1 \times 16) = 18.02 \text{ kg/kmol.}$$

- (iii) Specific Gas Constants.

Using $R_o = 8.3144$ kJ/kmol K we get:

$$R_a (\text{Dry air}) = \frac{8.3144}{28.97} = 0.287 \text{ kJ/kg K}$$

$$R_s (\text{Steam}^*) = \frac{8.3144}{18.02} = 0.461 \text{ kJ/kg K}$$

* Steam here refers to water vapour and in this context does not imply boiling water.