

Thermodynamics and Ideal Gas Dynamics

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April 22, 2006

1 Introduction.

All the thermodynamics that I have needed as an applied math fluids person follows from the first two postulates of thermodynamics, the two postulates of an ideal gas, and two results of statistical mechanics. This paper attempts to derive and summarize all the thermodynamics that I have needed on a single sheet.

2 Definition of quantities.

T := temperature

p := pressure

Quantities per mass (mass-specific quantities).

v := volume per mass ($= 1/\rho$)

e := energy per mass

h := enthalpy per mass

s := entropy per mass

Quantities per volume (volume-specific quantities).

ρ := mass per volume ($= 1/v$)

n := number of molecules per volume

Total quantities of a system in equilibrium.

M := mass of system ($= Nm$)

V := total volume of the system

U := total heat energy of the system

Q := heat energy absorbed by the system in a process

L := work performed by the system in a process

S := entropy of the system

N := number of particles in the system

Thermodynamic parameters.

k := Boltzmann universal gas constant

$= 1.3806505 \times 10^{-23}$ joule/kelvin

$= 8.617343 \times 10^{-5}$ electron-volt/kelvin.

m := mass of each molecule

R := k/m = specific gas constant

α := number of degrees of freedom of a molecule

c_v := mass-specic heat capacity at constant volume

c_p := mass-specic heat capacity at constant pressure

γ := c_p/c_v = ratio of heat capacities

3 Laws of thermodynamics.

In applying these laws of equilibrium thermodynamics to gases that are not in equilibrium, we assume that the gas can be partitioned into small convected volume elements each of which contains a large number of particles that are approximately in equilibrium. It is helpful to think of “the system” as some such convected volume element in the following development.

Assume the following laws of thermodynamics.

1. (First Law) The first law of thermodynamics is the conservation of energy. It states that the change in heat energy of a system equals the work performed on the system plus the heat energy absorbed by the system:

$$\Delta U + L = Q.$$

Expressing this in differential form:

$$dU + pdV = dQ$$

To express this in mass-specific quantities, take the system to be a small convected fluid volume and let

$$e := \frac{U}{M}, v := \frac{V}{M}, dq := \frac{dQ}{M}.$$

Then we can write:

$$\boxed{de + pdv = dq}$$

2. (Second Law) It is impossible for the net effect of any process to be purely the transfer of heat from a colder to a warmer body. This assumption leads to:

- The notion of an absolute temperature scale, unique up to rescaling.
- The notion of entropy. Entropy is an invariant of an adiabatic (non-heat-conducting) process, and the change in entropy of a system generally satisfies $dS = \frac{dQ}{T}$. Considering a small convected fluid volume we get $\boxed{ds = \frac{dq}{T}}$.

4 Ideal gas law.

Three state variables (e.g. mass density, (energy density or temperature), and pressure) are sufficient to specify the state of the gas in the vicinity of a point.

We take the following as axioms of an ideal gas.

1. The product of pressure and volume is a simple (proportionality) function of temperature independent of density: $pv = RT$. For our purposes it will be enough to assume that $d(pv) = RdT$ over the relevant range of state variables. By redefining the zero of T if necessary, we can say that $\boxed{pv = RT}$. So for an ideal gas, two state variables are sufficient to specify the state.
2. Thermal energy is a simple (proportionality) function of temperature independent of density: $U(T) \iff e(T)$. For our purposes it will be enough to assume that $de = c_v dT$ over the relevant range of state variables. By redefining the zero of e if necessary, we can say that $\boxed{e = c_v T}$.

5 Enthalpy.

Adding the two assumptions of an ideal gas leads to the notion of the enthalpy h :

$$\underbrace{(e + pv)}_{\text{Call } h} = \underbrace{(R + c_v)}_{\text{Call } c_p} T.$$

6 Entropy of an ideal gas.

If we invoke the ideal gas law we can eliminate a state variable from the differential of entropy, giving us a formula for entropy in terms of two state variables.

Define $\gamma := \frac{c_p}{c_v}$. So $\gamma - 1 = \frac{R}{c_v}$. And $\frac{\gamma-1}{\gamma} = \frac{R}{c_p}$.

Statement/Expression	Reason
$dq = de + pdv$	First law
$ds = \frac{dq}{T}$	Definition of entropy
$= \frac{de}{dT} \frac{dT}{T} + \frac{p}{T} dv$	$e(T)$
$= c_v \frac{dT}{T} + R \frac{dv}{v}$	$e = c_v T, pv = RT$
$= c_v (d \ln T + \frac{R}{c_v} d \ln v)$	
$= c_v d(\ln T + (\gamma - 1) \ln v)$	
$= c_v d \ln(Tv^{\gamma-1})$	
$= c_v d \ln(T\rho^{1-\gamma})$	$v = \rho^{-1}$
$= c_v d \ln(pp^{-\gamma})$	$T = p\rho^{-1}R^{-1}$
$= c_v d \ln(T^\gamma p^{1-\gamma})$	$\rho = pT^{-1}R^{-1}$
$= c_p d \ln(Tp^{\frac{1-\gamma}{\gamma}})$	

So we can write, e.g., $s = c_v \ln(pp^{-\gamma}) + (\text{const})$

7 Relation between state variables of an ideal gas.

Since $dT = \frac{d(pv)}{R}$ and $de = c_v dT$, $de = \frac{c_v}{R} d(pv)$, i.e., defining the zero of e conveniently, $\rho e = \frac{1}{\gamma-1} p$

8 Results of statistical mechanics.

Statistical mechanics determines formulas for the parameters of an ideal gas based on the number of degrees of freedom α of each molecule and the mass per molecule m . These formulas are based on two basic results:

8.1 Equipartition theorem.

$$\frac{\text{energy}}{\text{degree of freedom}} = \frac{1}{2} kT, \text{ i.e. } \frac{\text{energy}}{\text{molecule}} = \frac{\alpha}{2} kT$$

This says that *the energy on average is equally distributed among all degrees of freedom* of the system:

8.2 Pressure versus energy density.

$$p = 2n \frac{\text{energy}}{\text{degree of freedom}} = nkT,$$

i.e. *pressure equals twice the density of translational kinetic energy in the direction perpendicular to some surface element.* (An elementary calculation of the rate of momentum transfer across a surface element establishes this relationship between pressure and kinetic energy.)

We infer the specific gas constant in $p = \rho RT$ to be $R = k/m$. To determine the ratio of heat capacities, we use that

$\left(\frac{\text{energy}}{\text{volume}}\right) = \left(\frac{\text{energy}}{\text{deg. of freedom}}\right) \left(\frac{\text{degs. of freedom}}{\text{molecule}}\right) \left(\frac{\text{molecules}}{\text{volume}}\right)$,
i.e. $\rho e = \left(\frac{1}{2} kT\right) \alpha n = \frac{\alpha}{2} p$. Hence $\frac{e}{pv} = \frac{\rho e}{p} = \frac{\alpha}{2}$, i.e. $\frac{1}{\gamma-1} = \frac{\alpha}{2}$. To summarize:

ratio	$\alpha = 3$	$\alpha = 5$
$\left(\frac{c_v}{R}\right) = \frac{1}{\gamma-1} = \frac{\alpha}{2}$	$\frac{3}{2} = 1.5$	$\frac{5}{2} = 2.5$
$\left(\frac{R}{c_v}\right) = \gamma - 1 = \frac{2}{\alpha}$	$\frac{2}{3} = 0.\bar{6}$	$\frac{2}{5} = 0.4$
$\left(\frac{c_p}{c_v}\right) = \gamma = \frac{2+\alpha}{\alpha}$	$\frac{5}{3} = 1.\bar{6}$	$\frac{7}{5} = 1.4$
$\left(\frac{R}{c_p}\right) = \frac{\gamma-1}{\gamma} = \frac{2}{2+\alpha}$	$\frac{2}{5} = 0.4$	$\frac{2}{7} = 0.285714$

References

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