Thermodynamics and Ideal Gas Dynamics

by Alec Johnson

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1 Introduction.

All the thermodynamics that I have needed as an applied math fluids person follows from the basic 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).
$\rho :=$ 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
$\alpha :=$ number of degrees of freedom of a molecule
$c_v :=$ mass-specific heat capacity at constant volume
$c_p :=$ mass-specific heat capacity at constant pressure
$\gamma := c_p/c_v =$ 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 assumptions 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.

3. (Existence of reversible heat engines) Perfectly reversible heat engines exist. (That is, it is possible to approximate a perfectly reversible heat engine arbitrarily well.) A heat engine is a system which in one cycle begins and ends in the same state and in the cycle absorbs heat from a hotter system, surrenders some of this heat to a cooler system, and surrenders the rest of the heat energy it absorbed by doing work. When a heat engine is run in reverse the flows are reversed: it performs negative work (i.e. receives work), it absorbs heat from (i.e. surrenders negative heat to) the colder body, and it surrenders heat to the hotter body. When a (perfectly) reversible heat engine is run in reverse the quantities of heat and work exchanged are simply negated.

These assumptions lead to:

- The notion of an absolute temperature scale, unique up to rescaling. (The ratio of two temperatures is defined to be the ratio of the magnitudes of heat absorbed and surrendered by a perfectly reversible heat engine running between systems at these temperatures; this ratio must be the same for any two reversible heat engines, since otherwise the more efficient engine could be used to run the other engine in reverse with the only final result being that heat is transfered from the cold body to the warmer body.)

- The notion of entropy. Entropy is *additive*; that is, the total entropy of a system is the sum of the entropies of

its subsystems. The total entropy of a closed system remains constant for a reversible process and increases for an irreversible process. The entropy of a system in equilibrium only changes when it absorbs or surrenders heat energy. So entropy is an invariant of an adiabatic (non-heat-conducting) process. Seeking a definition of entropy that satisfies these requirements, we define the change in entropy to be $dS = \frac{dQ}{T}$. This ensures that running a reversible heat engine does not increase the entropy and that a less efficient heat engine does. For 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: $pv = RT$.

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

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
$= \frac{de}{dT}\frac{dT}{T} + \frac{p}{T}dv$	$e(T)$
$= c_v\frac{dT}{T} + R\frac{dv}{v}$	$e = c_v T,\ pv = RT$
$= c_v(d\ln T + \frac{R}{c_v}d\ln v)$	
$= c_v d(\ln T + (\gamma - 1)\ln v)$	
$= c_v d\ln(T v^{\gamma-1})$	
$= c_v d\ln(T \rho^{1-\gamma})$	$v = \rho^{-1}$
$= c_v d\ln(p\rho^{-\gamma})$	$T = p\rho^{-1}R^{-1}$
$= c_v d\ln(T^{\gamma} p^{1-\gamma})$	$\rho = pT^{-1}R^{-1}$
$= c_p d\ln(T p^{\frac{1-\gamma}{\gamma}})$	

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

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, $\boxed{\rho e = \frac{1}{\gamma-1}p}$

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.

$\frac{\text{energy}}{\text{degree of freedom}} = \frac{1}{2}kT$, 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 $\boxed{R = k/m}$. 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. $\rho e = (\frac{1}{2}kT)\alpha n = \frac{\alpha}{2}p$. Hence $\frac{e}{pv} = \frac{\rho e}{p} = \frac{\alpha}{2}$, i.e. $\boxed{\frac{1}{\gamma-1} = \frac{\alpha}{2}}$. To summarize:

ratio			$\alpha = 3$	$\alpha = 5$
$\left(\frac{c_v}{R}\right)$	$=\ \frac{1}{\gamma-1}$	$= \frac{\alpha}{2}$	$\frac{3}{2} = 1.5$	$\frac{5}{2} = 2.5$
$\left(\frac{R}{c_v}\right)$	$= \gamma - 1$	$= \frac{2}{\alpha}$	$\frac{2}{3} = 0.\overline{6}$	$\frac{2}{5} = 0.4$
$\left(\frac{c_p}{c_v}\right)$	$=\ \gamma$	$= \frac{2+\alpha}{\alpha}$	$\frac{5}{3} = 1.\overline{6}$	$\frac{7}{5} = 1.4$
$\left(\frac{R}{c_p}\right)$	$=\ \frac{\gamma-1}{\gamma}$	$= \frac{2}{2+\alpha}$	$\frac{2}{5} = 0.4$	$\frac{2}{7} = 0.\overline{285714}$

References

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[3] Herbert B. Callen, Thermodynamics and an Introduction to Thermostatistics, John Wiley & Sons, Inc., ©1985 (updated version of previous, adds section on statistical mechanics).

[4] Kerson Huang, Statistical Mechanics, John Wiley & Sons, Inc., ©1963.