THERMODYNAMICS 2.

Gas Laws.

The gas laws are embodied in the equation pV=RT. Here it is supposed that we are dealing with 1 mole of gas.

p = pressure per unit area on the container of the gas.
V = volume of the gas.
T = absolute temperature.
R = a universal constant, the gas constant.

A mole of gas always contains the same number, N, of molecules. N is called Avogadro's constant; it is approximately 6×10^{23}.

An ideal gas would conform exactly to this equation. Many gases in actual practice approximate well to it, if they are at low pressure and high temperatures. It is possible to explain why this is so. We shall see in the following sections that the equation above can be deduced by assuming that the molecules of the gas have negligible volume and that there are no forces between molecules. A gas at low pressure fills a volume very large in comparison with the total volume of the molecules in it, so neglecting the volumes of the molecules does not cause any serious error. Also the forces between molecules are very small when the distance between them is large. On the other hand, with high pressures and low temperatures the gas is near the state in which it becomes a liquid; strong forces begin to act between the molecules and their volumes certainly cannot be neglected.

Statistical Mechanics.

Accordingly we consider a swarm of very small particles, with no forces between them, and moving in a very large space. A consequence of this is that encounters between molecules will be comparatively rare; for nearly all the time any molecule will be moving in free path. The molecules are supposed to be perfectly elastic; when they strike the walls of the container they rebound without loss of energy. This gives us a picture we can imagine, which is often very helpful.

Clausius in 1857 stated in mathematical form the kinetic theory of gases, i.e. the theory that gases can be imagined as consisting of moving masses obeying the laws of dynamics. However he did not allow for the fact that the velocities of the molecules must vary widely. In 1860 Maxwell removed this defect and produced a very satisfactory statistical theory of the movements of molecules in gases.

He began with the assumption of molecular chaos, the idea that so many millions of molecules were involved in such complicated processes that the eventual result was complete randomness.

Let f(u)du be the probability that the x-component of

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Calculating Pressure.

Force equals the rate of change of momentum, so we can find the pressure on a wall by seeing what change of momentum it produces on the particles hitting it per unit time.

We consider a rectangular block, with sides in the directions of the axes, with a wall of unit area in the plane x=constant, at the end where x is maximum. A particle with positive x-velocity, u, will hit the wall within a time $\triangle t$, if it lies within a distance $u\triangle t$ of the wall, that is to say in a region of volume $u\triangle t$. We suppose there are N particles in a volume V so the number of particles expected in this region is $Nu\triangle t/V$. The number of these expected to have x-velocity in u,u+du is $(Nu\triangle t/V)f(u)du$. If the particles have mass m, each will carry the momentum mu. This will be reversed on striking the wall, so the change in momentum is 2mu for each particle. Hence the change in momentum in time $\triangle t$ is

$$(2Nm/V)\ \triangle t\ \prod{}^{-1/2} a^{1/2} \int_0^{\infty} u^2 e^{-au^2}\ du \qquad (12)$$

Dividing this by $\triangle t$ gives the pressure. To evaluate the integral we apply the partial differentiation operator $\partial/\partial a$ to equation (10) above and change the sign. This gives

$$\int_{-\infty}^{\infty} u^2 e^{-au^2}\ du = (1/2)\ \prod{}^{1/2} a^{-3/2} \qquad (13)$$

In equation (12) we have the integral only from 0 to ∞, so we need 1/4 instead of 1/2 in the expression in (13). substituting this in (12) and removing the factor $\triangle t$, we find the pressure per unit area is

$$p = Nm/[2Va]. \qquad (14)$$

Identifying a.

The gas equation is pV = RT, so we identify Nm/[2a] with RT. This implies a = Nm/[2RT]. It is usual to represent the universal constant R/N by k. Thus a = (m/2)/(kT). It thus appears that the probability of the x-velocity being in u,u+du is proportional to

$$e^{-(1/2)mu^2/(kT)}\ du \qquad (15)$$

Note the appearance of the kinetic energy associated with the x-velocity in this formula.

Energy for an ideal gas.

The average value of $(1/2)mu^2$ is $(m/2)\int_{-\infty}^{\infty} u^2 f(u)du$. combining equations (11) and (13) we find this to be m/(4a). We have seen that a = m/(2kT), so m/(4a)=

on the path, for the integral in question is $\int y\,dx$, which arises when we calculate the area under a curve. For a closed path it is related to the area inside the curve.

On the other hand, if we take X=2x, Y=2y we have an exact differential, for $2x\,dx+2y\,dy = d(x^2+y^2)$ and the integral will give simply the difference in x^2+y^2 between the ends of the path. It can be checked that zero results if the integral is found around the path specified earlier.

The distinction between exact and inexact differentials is of great importance in thermodynamics. It was at one time believed that heat was a substance, that if heat came out of a body, there was less heat remaining inside the body. As the cannon boring experience suggested, there is no limit to the amount of heat that can come out of a body.

A quantity is said to be a **function of state** if its value can be determined by an object **as it is at this moment without any reference to its history.** Thus, for example, pressure, volume and temperature are functions of state, work done and heat entered are not.

Heat, Q, entering a body is usually regarded as positive, work, W, is regarded as positive when the body does work on the surroundings. We cannot regard either heat or work as something contained in a body, but during a certain period we can measure the heat transferred to the body and the work done by the body. The first Law of Thermodynamics, which is essentially the Conservation of Energy, can be stated as "The quantity Q-W depends only on the initial and final states of the system and is independent of the path followed." We define the change of energy of the body, $\triangle E$, by the equation

$$\triangle E = Q - W.$$

If we agree on the energy value to be associated with some specified state, then E is defined and is thus a function of state. For infinitesimal changes we may write

$$dE = \triangle Q - \triangle W.$$

The notation here is intended to indicate that dE is a true infinitesimal, related to the differentiation of a defined function, while $\triangle Q$ and $\triangle W$ represent observable changes, but are not exact differentials of anything.

In the case of an ideal gas we can think of E as the total kinetic energy of the molecules, as indeed we did when deriving the equation $E = (3/2)RT$.

Test for exact differential.

If X and Y have continuous partial derivatives, then $X\,dx+Y\,dy$ will be an exact differential if, and only if, $\partial X/\partial y = \partial Y/\partial x$. (See Piaggio, Differential Equations, appendix A.)

We can see that $\triangle W$ is not an exact differential, for $\triangle W = p\,dv$. This is $0\,dp + p\,dv$; $\partial 0/\partial v = 0$, $\partial p/\partial p =1$, not

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THERMODYNAMICS.

Historical Background.

Sadi Carnot (1796-1832), the founder of thermodynamics, was the son of L.N.M.Carnot, the "organizer of victory" in the French revolution. L.N.M.Carnot was an army engineer. He wrote on mathematics, military tactics and other topics. He played a very prominent part in the politics and wars of revolutionary France.

Sadi Carnot was a patriotic Frenchman. He was interested in the application of science to industry. Britain had derived great benefits from its possession of the steam engine, years before other countries. Carnot hoped that scientific understanding of how the engine worked would help France in its rivalry with Britain.

In Britain, the condensing of steam to raise water from mines had been used as early as 1698. Round about 1770 there were in use steam engines in the modern sense - for producing movement.

"Science since 1500" comments that Britain used steam engines for decades and never bothered to study them scientifically. On the other hand theoretical studies were produced in France almost immediately after the arrival of engines there. This of course is typical. Britain, advancing into the unknown, used empiricism, pioneering by trial and error. On the continent, the industrial classes were continually frustrated by working under the control of aristocratic regimes; this indeed was one of the great driving forces of the French Revolution. Unable to do what they wanted, they spent their time dreaming and thinking about the potential of the new developments.

Many useful concepts were already available to Carnot. In 1738 D.Bernouilli had considered gas as a swarm of moving particles, and had shown that an increase in temperature would lead to an increase in pressure. He also had the idea of Conservation of Mechanical Energy (in frictionless processes).

Outline of Carnot's argument.

Carnot raised a fundamental question. He accepted the idea of the conservation of energy, but realized that heat energy, although existing, might be unavailable. (Pledge, Science Since 1500, p.143.) He thought of heat being like water, which drives a watermill by falling from a height (high temperature to low temperature). You cannot get any more mechanical work from the water once it has reached the lowest position available, - similarly for heat.

Carnot, like many physicists at that time, accepted the caloric theory, the belief that heat is an enduring substance. Count Rumford, in 1798, from the experience of boring cannon, had come to believe that you could make as much heat as you wanted by performing work. Conversely heat can be destroyed when work is being done. Carnot did not realize "that heat is lost as work is gained".(Pledge, p.143.) This however did not prevent him from arriving at correct and very important conclusions.

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For adiabatic expansion we have insulation that ensures no heat enters of leaves. The external pressure is lowered gradually, so the gas expands and therefore does work. This work can only come from a reduction in the internal energy of the gas. Thus $dE = -p\,dV$. Now $dE = C\,dT$, so we have

$$C\,dT + p\,dV = 0. \qquad (1)$$

For a mole of ideal gas we have $pV = RT$, so $CT = (C/R)pV$. Hence

$$(C/R)(p\,dV + V\,dp) + p\,dV = 0.$$

This gives, on multiplying by R and collecting terms involving dV and dp

$$p(C+R)dV + CVdp = 0$$

Let $\qquad (C+R)/C = g. \qquad (2)$

(In printed work this is always called "gamma". As I do not have Greek letters on my printer, "g" is the best I can do.) The equation becomes

$$g\,dV/V + dp/p = 0$$

from which it follows that $\ln p + g \ln V$ is constant. Hence, for an adiabatic change

$$pV^g = \text{constant} \qquad (3)$$

Adiabatic changes are reversible; the same equation holds for an adiabatic contraction.

Work in an adiabatic change.

Let pressure and volume change from p_1, V_1 to p_2, V_2 adiabatically. Then, during the change $p = Kv^{-g}$, where

$$K = p_1 V_1{}^g = p_2 V_2{}^g. \qquad (4)$$

Integrating $p\,dV$ we find the work done is

$$[K/(1-g)] \cdot [V_2{}^{1-g} - V_1{}^{1-g}].$$

By using equation (4) we can show that this equals

$(p_2 V_2 - p_1 V_1)/(1-g)$. From equation (2) we see that

$1-g = -R/C$. Using the equation $pV=RT$ for the initial and final stages, we eventually reach the simple formula for W, the work done

$$W = C(T_1 - T_2) \qquad (5)$$

In an adiabatic expansion the temperature falls, and, as expected, W will be positive. In a contraction the work will be negative, that is to say, work will have to be done on the gas to make it happen.

It is useful to derive equation ((5) by considering the details of what happend during an adiabatic process. It can be derived directly from the principle of conservation of energy. At the start, the internal energy of the gas is $E_1 = C_1$; at the end it is $E_2 = CT_2$; the work done comes

CT_1

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contributions of BD and CA to the work done cancel out.

From equation (6) we see that the work done in AB is $RT_1(\ln V_2 - \ln V_1)$, where V_1 and V_2 are the volume at A and the volume at B. Now in the graph we are using, the x-co-ordinate is $\ln V$, **so $\ln V_2 - \ln V_1$ is simply the length of the line AB.** As ABDC is clearly a parallelogram, the length of CD is the same as that of AB. The expression for the work in DC will differ from that for AB only in having T_2 instead of T_1, and having a minus sign in front, as in DC the gas is being compressed and work is being done against the desire of the pressure.

Thus the work done in the whole cycle is
$$W = R(T_1 - T_2)(\ln V_2 - \ln V_1) \qquad (7)$$

Now the efficiency of the machine is measured by W/Q, where **Q is the amount of heat put into the machine in stage AB.** This determines how much coal has to be burnt. Heat comes out of the machine at the lower temperature T_2, but this is of no interest to the machine operator. As stage AB is at constant temperature and as internal energy depends only on temperature, the heat absorbed is numerically equal to the work done in AB, which we calculated above. Hence
$$Q = RT_1(\ln V_2 - \ln V_1) \qquad (8)$$
Thus the efficiency
$$W/Q = (T_1 - T_2)/T_1 \qquad (9)$$
This efficiency is a function of the temperatures alone, and no machine operating between the temperatures T_1 and T_2 can ever do better.

Calculating Pressure.

Force equals the rate of change of momentum, so we can find the pressure on a wall by seeing what change of momentum it produces on the particles hitting it per unit time.

We consider a rectangular block, with sides in the directions of the axes, with a wall of unit area in the plane x=constant, at the end where x is maximum. A particle with positive x-velocity, u, will hit the wall within a time $\triangle t$, if it lies within a distance $u\triangle t$ of the wall, that is to say in a region of volume $u\triangle t$. We suppose there are N particles in a volume V so the number of particles expected in this region is $Nu\triangle t/V$. The number of these expected to have x-velocity in u,u+du is $(Nu\triangle t/V)f(u)du$. If the particles have mass m, each will carry the momentum mu. This will be reversed on striking the wall, so the change in momentum is 2mu for each particle. Hence the change in momentum in time $\triangle t$ is

$$(2Nm/V)\ \triangle t\ \pi^{-1/2}\ a^{1/2} \int_0^\infty u^2 e^{-au^2}\ du \qquad (12)$$

Dividing this by $\triangle t$ gives the pressure. To evaluate the integral we apply the partial differentiation operator $\partial/\partial a$ to equation (10) above and change the sign. This gives

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$$e^{-(1/2)mu^2/(kT)}\ du\ . \qquad (15)$$

THERMODYNAMICS 3.
Note. Some theorems, that in a systematic treatise would
have to be proved, are here quoted without proof.

Equation using entropy.
We suppose we have a system, such as a gas, the energy
of which can change only by heat being added or work being
done. If E is the energy of the system, $/\backslash Q$ heat added and
pdV work done, the conservation of energy shows that
$$dE = /\backslash Q - pdV.$$
We have seen that $/\backslash q/T$ is a perfect differential dS, with S
the entropy. Thus our equation becomes
$$dE = TdS - pdV \qquad (16)$$
An important difference is that here all the variables are
functions of the state, unlike heat and work.
Thermodynamics can be applied to the study of
radiation, as radiation acts in many ways like a gas.
It is rather surprising that an exact formula for the
relation between temperature and the density of radiation
can be obtained by such general arguments.

Pressure of Radiation.
Radiation can be localized in space. If a beam of
radiation falls normally on a region of unit area for s
seconds and is completely absorbed, the heat generated
comes from the region of volume cs, occupied by the part of
the beam that has just been absorbed, c being the velocity
of light. By measuring that heat we can calculate the
energy per unit volume in the beam. This is known as the
"spatial energy density" (Planck,Theory of Heat,p.177). We
follow Planck by using $\underline{u}$ for this quantity.
That radiation exerts pressure can be deduced from the
conservation of energy. Suppose a beam of radiation falls
on a black body (i.e. one that absorbs all the radiation)
of unit area, and we move the body a distance $\underline{h}$ towards
the source of the radiation. The effect of this is that the
body absorbs $\underline{hu}$ more units of energy in the given time
than if it had been left alone. If we could move it
without effort, we would have gained this energy for
nothing. Therefore it must require a force $\underline{p}$ to make it
move, and the work done will be $\underline{hp}$. Hence $\underline{hu} = \underline{hp}$, We have
the very simple law
$$p = u. \qquad (17)$$
If the body was a perfect reflector, this would have to be
doubled, p=2u.

Pressure on the wall of a container.
The radiation inside a container is directed randomly in
all directions. By detailed calculations using
electromagnetic theory , Planck reaches the generally
accepted conclusion that the pressure on a perfectly
reflecting surface of the container is u/3. Other
arguments can be used to arrive at this conclusion.
Planck points out that it is immaterial whether the

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external pressure on the piston is gradually reduced, and the piston moves under the pressure of the radiation until B is reached with volume V_2. The temperature and pressure are still T and p_1. The radiation density throughout is u, and so the pressure is $p_1 = u/3$.

In this stage, heat is drawn in, since the system is doing work and there is no other source of energy.

The work done in pushing the piston out is $(V_2-V_1)u/3$.

There is also another demand for energy. The volume has increased and the new space is to be filled with radiation having density u. This requires $(V_2-V_1)u$.

Altogether in the first stage work $(4/3)(V_2-V_1)u$ is done, and so this amount of heat energy, H, must be supplied.

$$H = (4/3)(V_2-V_1)u \qquad (18)$$

Stage 2. In the second stage, B to C, the cylinder is insulated and allowed to expand further. It does more work, which must come out of the heat contained, so the temperature drops, and reaches the value T_2 at C. The change is taken to be infinitesimal. The radiation intensity, being a function of temperature, will decrease; if we call the amount of decrease du, the intensity falls by du. As $p=u/3$, p decreases by $dp=du/3$.

Stage 3. In this stage, C to D, the cylinder is compressed with the small aperture again open, and held opposite the opening of a black body maintained at temperature T_2. Work is done on the system, and heat leaves it to keep the temperature constant.

Stage 4. D to A. The aperture is closed again, and the system insulated. Work is done on it and the temperature returns to T.

All of this is supposed to be done very slowly and reversibly.

Now Carnot showed that no engine can be more efficient than a reversible one. It follows that any two reversible engines must have the same efficiency, namely $(T_1-T_2)/T_1$. Here $T_1=T$ and $T_2=T-dT$; here again we are writing differentials for decreases. Thus the efficiency must be dT/T.

The work done in the cycle is the area in the p,V diagram of the quadrilateral ABCD. The sides AD and BC are not truly parallel, but the divergences are such as to be negligible in the limit, and we may treat ABCD as a parallelogram. Hence this area may be taken to be $(V_2-V_1)dp = (V_2-V_1)du/3$.

The heat, H, taken in during stage AB, was given in equation (18).

The efficiency = work done/H, and so is

$$\frac{(V_2-V_1)du/3}{(4/3)(V_2-V_1)u} \quad \text{which simplifies to} \quad \frac{du}{4u} .$$

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