THE ROLE OF ENTROPY IN THE AERO-SPACE SCIENCES

IT IS a great honour for me to deliver the second Daniel and Florence Guggenheim Memorial Lecture here in Zurich. We all know the profound insight of the Guggenheims into the value of a scientific treatment of the many important, and often only partially solved, questions of aeronautics and now also of astronautics. We are most thankful for the moral and financial help the research workers enjoy.

In our small country there always exists a remainder of "local-patriotsm" and so we are proud to remember that the Guggenheims stem from an old family which resided more than a hundred years ago at Lengnau, only twenty miles from here, or in American measure: "just around the corner". Meyer Guggenheim was born there in 1828 and emigrated to America in 1847. One of his seven sons was Daniel Guggenheim.

Our eminent master Professor von Kármán held the first Guggenheim lecture 1958 in Madrid. He gave one of his famous reviews of the state of the science of aerodynamics. For the poor people who suffer from the deluge of papers and reports, his lectures are an invaluable help as they treat the most recent developments with a really Latin clarity.

It is clear that other people (for instance the present speaker) should not simply imitate such a proceeding. I intend therefore to follow a somewhat different path. It is my hope that a "Spaziergang" across the wide field of aerothermodynamics in the light of the concept of entropy may not annoy you too much.

Nearly a hundred years have passed since Rudolf Clausius, then professor at this school, introduced entropy. Since then entropy has always been a favorite theme in Zurich, especially as engineering applications are concerned. I may mention the names of Gustav Zeuner and Aurel Stodola, the latter being my unforgettable teacher. Stodola was able to destroy the fear that befell so many students of this somewhat mystical concept, as he showed us how to use it in all sorts of thermodynamical calculations.

There are indeed some rather mysterious conclusions resulting from the entropy laws. Entropy is not conserved but is constantly growing.

The universe seems to run down to an end, the often cited "heat death". There are enigmas and it might be that in this connection cosmology has further surprises in store for the future. May space flight, one of our aims, help these scientists in their difficult task to find a way out!

But let us stay in the more homely regions of our science. With the realization of aeroplane and missile speeds equal to or even surpassing many times the speed of sound, thermodynamics has entered the scene and will never again leave our considerations. Re-entry at last has widened this fascinating field still more, as the tremendous temperatures involved produce chemical, and to a certain extent even electrical, changes in the composition of the air.

Entropy plays here quite an important part. But there are limits. On principle its classical definition applies only to the so-called equilibrium states, which are not present in extreme cases. A hundred years of development of equilibrium state physics finds its end, giving way to a much more sophisticated program: the amalgamation of micro- and macrophysics.

THE WORK OF CARNOT AND CLAUSIUS

Thermodynamics is a relatively young branch of the physical sciences. We may date the beginning back to 1824, when a young Frenchman Nicolaus Sadi Carnot theorized on the "puissance motrice du feu" [1] (Fig. 1).

FIG. 1. Nicolaus Léonard Sadi Carnot 1796–1832.

As did everybody at that time he adhered to the concept of a caloric, some kind of a very subtle, indestructible fluid. Notwithstanding that, he succeeded in finding very general laws by ingenious use of what we now-adays call "Gedanken-Experimente". First he remarked that the caloric
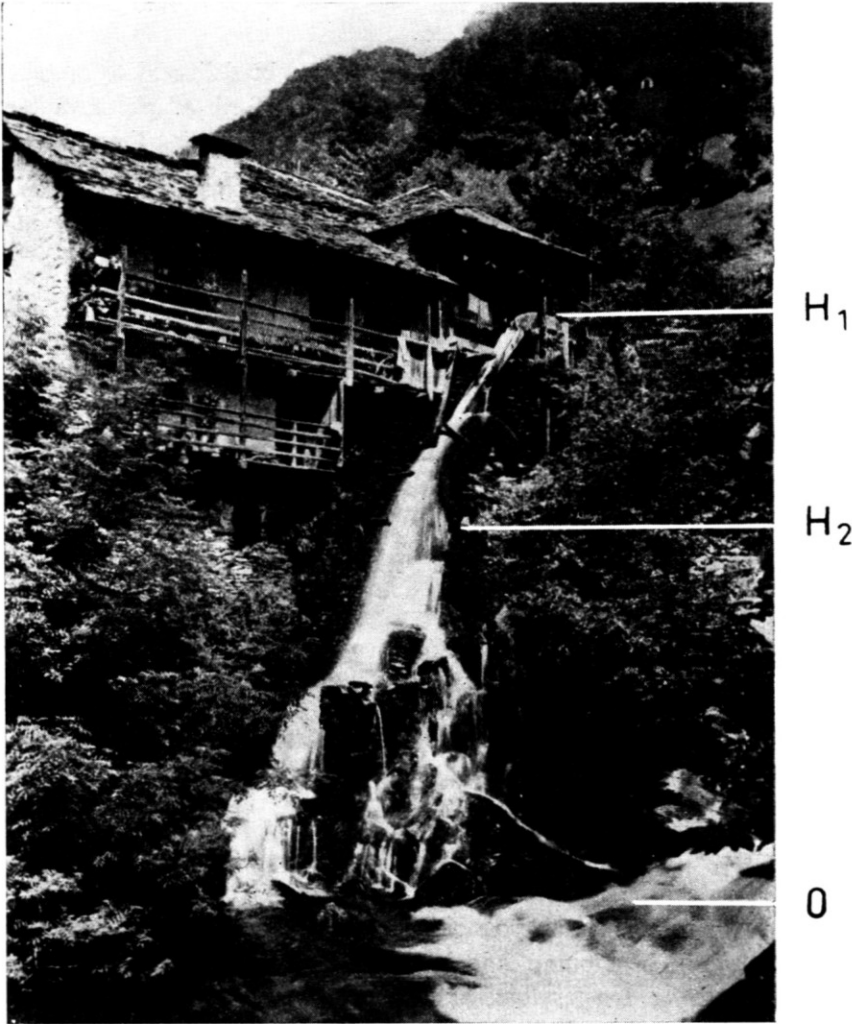

FIG. 2. Water-wheel analogy of a heat-engine. If we take the water-level as a measure of (absolute) temperature the "efficiency" $\eta = \dfrac{H_1 - H_2}{H_1}$ translates into $\eta_c = \dfrac{T_1 - T_2}{T_1}$, the Carnot-efficiency. But the analogy is only partially correct. Curiously enough, the obviously bad exploitation of the available power in this romantic plant is not worse than the thermodynamic efficiency of the steam process in a rather modern locomotive.

The lost head H_2 corresponds to the loss of energy in the steam-exhaust.

could do work only if there is a drop in temperature in the heat engine. To a certain extent he used an analogy with a hydraulic wheel, temperature taking the role of the water level.

Figure 2 immediately suggests some consequences of this analogy. For best efficiency: The whole of the water should enter the engine at the highest level and leave it at the lowest. No water should pass beside the wheel.

The caloric cannot do work direct but has to be delivered to or taken away from some material substance, preferably in form of gas or vapour, which show great changes in volume by heating or cooling them. In this
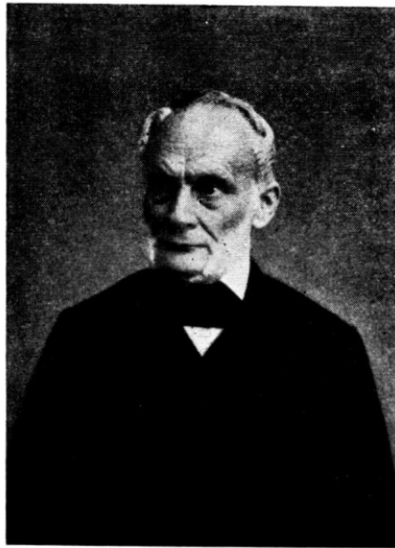

Fig. 3. Rudolph Clausius 1822–1888.

way he stated his famous Carnot-cycle consisting of two isothermal and two adiabatic processes working with a fluid of constant quantity. He realized the fundamental possibility of a reversed process, inventing, by the way, the heat pump, and he showed conclusively that with given upper and lower temperatures and a fixed amount of caloric his cycle gives maximum efficiency.

He could not make further progress, as the first, the energy law of thermodynamics, had still to be found, which states that heat and work can be transformed into each other in a fixed ratio. This step was made by Rudolf Clausius in 1850[2] (Fig. 3).

He combined the first law with Carnot's ideas. The heat quantity Q_1 enters at the high temperature T_1 and a smaller one Q_2 leaves the

system at T_2. The difference Q_1-Q_2 is equivalent to the work done and we have the simple relation:

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$$

or

$$\frac{Q_1}{T_1} - \frac{Q_2}{T_2} = 0 \tag{1}$$

The power is

$$L = Q_1 \cdot \left(1 - \frac{T_2}{T_1}\right) = Q_1 \cdot \eta_c \tag{2}$$
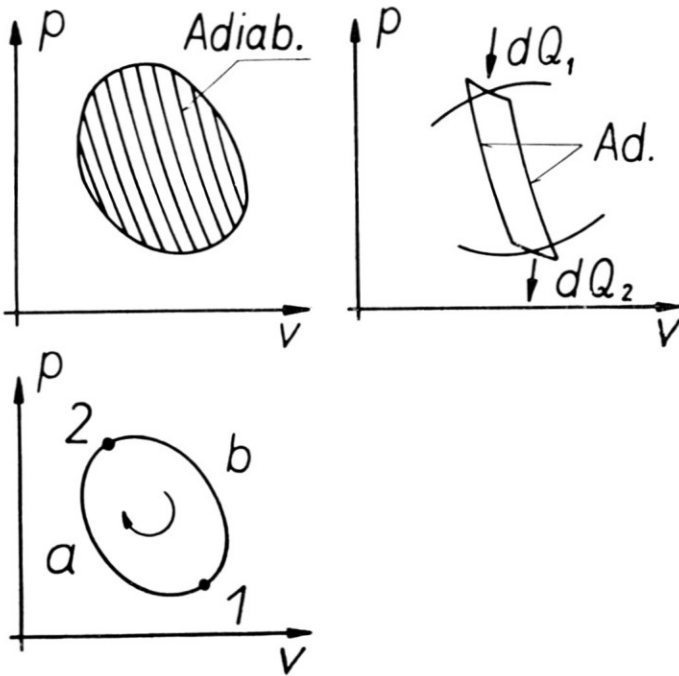
where η_c is the Carnot efficiency.

FIG. 4. Dissection of an arbitrary reversible cycle into elementary Carnot-cycles. As the integral $\oint \frac{dQ_{\text{rev}}}{T}$ equals zero, the entropy-difference $\int_1^2 \frac{dQ_{\text{rev}}}{T}$ is independent of the integration path and entropy appears as a state-function.

So, only a fraction of the heat supplied is transformed into mechanical work. We can see that low temperature of the environment is rather more important than high temperature on the supply side. Perhaps there

are lower temperated atmospheres on other planets which would allow higher efficiency, but that is perhaps not too encouraging considering other troubles coming from the diminished comfort for space men. The next step was a generalization of the Carnot-cycle by the introduction of arbitrary, but reversible, cycles.

By the well known artifice of dissecting these into elementary Carnot-cycles (Fig. 4) we find instead of (1) and taking Q algebraically

$$\oint \frac{dQ_{rev}}{T} = 0 \tag{3}$$

A simple proof shows that the integral along an arbitrary path from 1 to 2 is always:

$$S_2 - S_1 = \int_1^2 \frac{dQ_{rev}}{T} \tag{4}$$

provided that dQ is supplied in a reversible manner. S is therefore a function of the state, called by Clausius 1865 Entropy ($\dot{\eta}$ τροπή), "the change"[3].
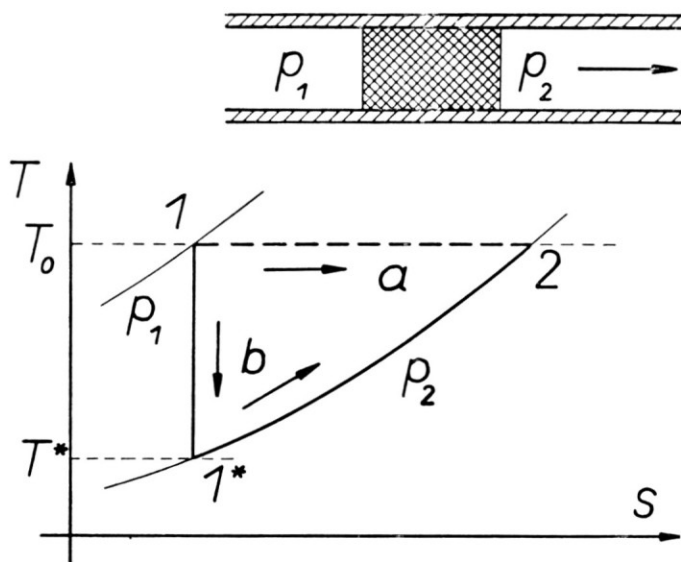

FIG. 5. Adiabatic, irreversible throttling of an ideal gas. No heat is exchanged, but entropy increases.

It is useful to remember that the suffix "reversible" in dQ_{rev} is necessary only for the calculation of entropy. If we have a non-reversible process going on some way from 1 to 2, the entropy difference is nevertheless determined. But then the heat exchange has no direct connection with entropy change.

A typical example may be mentioned here, the adiabatic throttling of an ideal gas (Fig. 5). From 1 to 2 the pressure falls, but the temperature is constant (as an energy check shows). Entropy increases, the process is completely irreversible. In order to calculate the entropy difference we choose a reversible path, first an isentrope from 1 to 1*, afterwards heating at constant pressure p_2 from 1* to 2. We get

$$\Delta S_{(T)} = R \cdot \ln \frac{p_2}{p_1} \tag{5}$$

For an irreversible process we have

$$\int_1^2 \frac{dQ_{irr}}{T} \leqq S_2 - S_1$$

in our previous example the integral is zero).

In the case of an irreversible cyclic process

$$\Phi \frac{dQ}{T} \leqq 0 \tag{6}$$

which seems to be the simplest statement of the so-called second law.

A process of this sort occurs in any closed wind tunnel, mechanically driven from outside. To secure a steady state inside the tunnel a cooler is needed. The entropy of the gas at a given position inside does, of course, not change. But the cooler draws heat away, equivalent to the mechanical work done from outside. So the entropy of the environment is rising steadily. The high rated mechanical energy is downgraded and can perform practically no work, being at nearly ambient temperature. As there always exists some irreversible friction, heat conduction, radiation, "the entropy of the universe" is growing to a maximum, where all high graded energy (which is conserved) has turned to heat. Clausius drew this dreary conclusion.

The late Robert Emden, a very ingenious scientist, used to stress that we on earth are not really living from solar-energy, as this, besides negligible amounts, is radiated back to the planetary space. Instead we are living from a deliberate increase of solar entropy[4]. In the words of Leon Brillouin[5] the sun delivers negative entropy or "negentropy" to earth, and organic life is catching and squandering this most useful present. But where did negentropy come from?—We simply do not know.

Formula (4) gives only entropy-differences. This is no drawback, if we consider one and the same element or compound. But if there are chemical changes, the so-called "absolute entropies" are needed. Before the advent of quantum statistics, which gives absolute entropies more

or less direct, a more indirect way was found by Nernst in 1906, when he introduced the so-called "third law of thermodynamics". In a somewhat simplified way it reads:

"The entropy of a substance disappears at absolute zero temperature."

As specific heat, heat of fusion and evaporation are known to a coniderable extent, absolute entropies can be calculated straightforward. Usually its value is given for one gram-mole in a standard state, the latter taken as especially convenient for the physical chemist (Pressure $p^* = 1$ atmosphere, Temperature $T = 298.1°K$).

Some figures show the order of magnitude:

C	(graphite)	$\dfrac{s^*}{R_m}$ = 0.684
Fe	(solid)	3.27
H_2	(gas)	15.71
O_2	(gas)	24.66
H_2O	(liquid)	8.43

R_m the molar gas constant $= 8.317 \cdot 10^7 \dfrac{\text{erg}}{°\text{K}}$.

Let me mention the well-known formula for the entropy of an ideal gas:

$$s_2 - s_1 = c_v \cdot \left\{ \ln \frac{p_2}{p_2^\gamma} - \ln \frac{p_1}{p_1^\gamma} \right\} \tag{7}$$

for constant specific heat.

$$\gamma = \frac{c_p}{c_v}$$

In most cases specific heat is dependent on temperature and not so much, on pressure. So we have

$$s_2 - s_1 = \int_1^2 c_p \frac{dT}{T} - R \cdot \ln \frac{p_2}{p_1} \tag{8}$$

The "real" gases have often a quite complicated equation of state $F (p, v, T) = 0$, if density grows to larger values. There are long equations for steam involving not less than 20 empirical constants.

As an example, and considering the importance in the aeronautical science, I shall mention the formula for the sound velocity a in a real gas.

Generally we have from mechanical considerations

$$a^2 = \left(\frac{\partial p}{\partial \varrho} \right)_{s = \text{const.}} \tag{9}$$

As entropy is a state function

$$ds = \left(\frac{\partial s}{\partial p}\right)_v \cdot dp + \left(\frac{\partial s}{\partial v}\right)_p \cdot dv$$

which can be transformed into

$$ds = \frac{c_v}{T} \cdot \left(\frac{\partial T}{\partial p}\right)_v \cdot dp + \frac{c_p}{T} \cdot \left(\frac{\partial T}{\partial v}\right)_p \cdot dv = 0 \qquad (10)$$

hence

$$a^2 = \gamma \cdot \frac{-\left(\dfrac{\partial T}{\partial \varrho}\right)_p}{\left(\dfrac{\partial T}{\partial p}\right)_\varrho}$$

and using a well known thermodynamical formula the simple result appears:

$$a^2 = \gamma \cdot \left(\frac{\partial p}{\partial \varrho}\right)_{T=\text{const.}} \qquad (11)$$

which for ideal gases gives the classical value:

$$a^2 = \gamma \cdot \frac{p}{\varrho} \qquad (12)$$

Real gases can be treated most practically with the help of entropy charts or diagrams. Often used are temperature-entropy (T, s) and enthalpy-entropy (H, s) (Mollier) diagrams.

ENTHALPY AND FREE ENTHALPY

The Ideal Heat Engine

In our motors, jets or rockets, chemical energy is transformed into mechanical energy. For instance in a turbo-jet the entering air is accelerated, the change in momentum producing the thrust.

But we know that the jet is also hot and thereby quite a considerable amount of energy is lost. The question is: how much mechanical (or electrical) work can we gain at best?

We imagine a hypothetical apparatus working continously and delivering mechanical or electrical power (Fig. 6). Within the "box" an unspecified type of chemical reaction is going on. On the left the fuel (air + hydrocarbon, oxygen + hydrogen etc.) is entering steadily, on the right the products leave, both at pressure p_0 and temperature T_0 of the surroundings. As we intend to have the best possible device, we naturally cannot afford a direct loss of heat at relatively high temperature.

If heat exchanges with the environment are necessary, they should take place reversibly at T_0. Mechanical work should be extracted through shaft and coupling and/or in the form of kinetic energy of the exhaust. Transformation to electrical energy is another alternative.
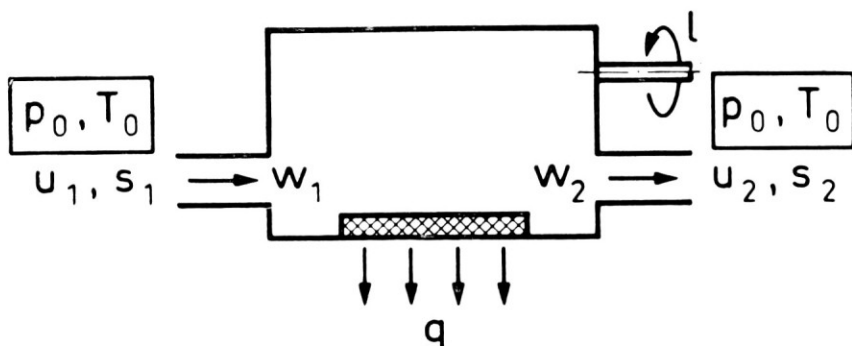

FIG. 6. Ideal, reversibly working propulsion mechanism using chemical propellents.

The first law gives immediately

$$l + \frac{w_2^2 - w_1^2}{2} = (u_1 + p_0 v_1) - q - (u_2 + p_0 v_2) \tag{13}$$

w is velocity, l mechanical or electrical work, u the (internal) energy, v volume, all taken for one gram.

The second law is used in the following way: To secure a maximum of efficiency we assume that the internal process works reversibly (combustion, expansions, compressions, etc.), and as mentioned before also the heat exchange q.

Then $q = -T_0(s_2 - s_1)$ and we have

$$l + \frac{w_2^2 - w_1^2}{2} = (u_1 + p_0 v_1 - T_0 s_1) - \\ (u_2 + p_0 v_2 - T_0 s_2) = g_0^1 - g_0^2 \tag{14}$$

where g is Gibbs' free enthalpy

$$g = (u + pv - Ts) = h - Ts, \tag{15}$$

specialized for $T_1 = T_2 = T_0$, $p_1 = p_2 = p_0$ ($h =$ enthalpy).

The part $h_1 - h_2$ is called heat of reaction at p_0, T_0; $(s_2 - s_1)$ is the change in absolute entropy as we have in general a change in chemical composition.

Gouy und Stodola (Fig. 7) were to my knowledge the first to apply free enthalpy to the evaluation of heat-engine-processes[6, 7]. When absolute

values of entropies were available, the maximum output for a given fuel input could be calculated.

For the reactions

$$C + O_2 = CO_2$$
$$CO + \tfrac{1}{2} O_2 = CO_2$$
$$H_2 + \tfrac{1}{2} O_2 = H_2O$$
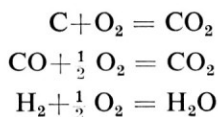
the output can reach nearly 100 per cent of the heat of reaction. There are even reactions, where more than 100 per cent can be gained. Here
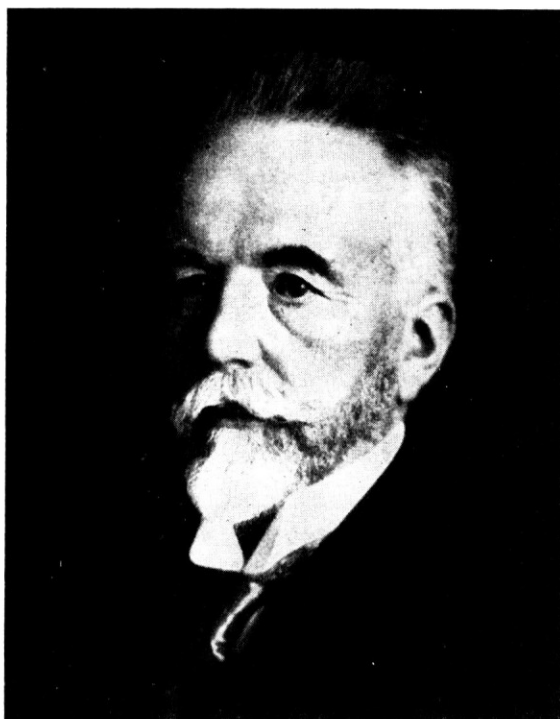

FIG. 7. Aurel Stodola 1859–1942.

heat is taken from the surroundings and transformed to work. There is no contradiction to the second law, as we have no cyclic process, but use up the fuel.

The crux is the assumed reversibility of the chemical changes. Normal fuel-air combustion is rather irreversible (look at a film, rolling backwards, of a gasoline-air explosion!).

Quantum chemistry has shown that a chemical reaction means a re-arrangement of the outermost electrons. Without further restraint the reaction products gain kinetic energy corresponding to the energy of the

order of one electron volt. But one electron volt corresponds to a "temperature" of 7740° K ($1.6 \cdot 10^{-12}$ erg $= \frac{3}{2} k T$). The next few collisions with inert molecules (N_2 etc.) lead to a degradation of this mechanical energy which is irreversible with a consequent rise in entropy.

We should be able to hold firmly the reaction products and divert their energy slowly outwards. This is the process in the ordinary galvanic cell, where an electric field holds the charged particles back. Their efficiency (at low current density) is quite high, very near to the maximum. No high temperatures are involved.

You know that there is some sort of renaissance of this process in the form of the modern fuel cells. Maybe one day their output density will be high enough for practical applications even in the field of space flight. At the moment there is no other way to reach high power output but by irreversible burning.

We can approach reversibility by using pure fuels (LOX + hydrocarbon or hydrogen) and very high temperatures (2000°–3000°K). Then we are nearing an equilibrium between association and dissociation, where burning is reversible. To a certain extent this is realized in the rocket combustion chambers. But there we have an input of relatively cold material (even with regenerative cooling) and a corresponding entropy increase during the heating to equilibrium temperature. On principle we should use isentropic precompression up to this temperature, but the practical difficulties are obvious and need no further comment.

PROPULSION IN THE VOID

In the planetary space the environment is different in several respects. Pressure is practically zero and temperature is not defined.

Problems appear, if there is a need for dissipation of heat. Several new propulsion systems as ionic drive or plasma jets include thermal machinery, steam or gas turbines both working with closed cycles, more or less along Carnot's cycle. The high temperature T_1 is limited as usual by material properties but the lower temperature is not fixed. We would naturally strive for a low T_2. But as there is no convention, radiation takes its place and the energy radiated (per cm² and second) goes up with its fourth power of T_2 (Stefan-Boltzmann's law). Low T_2 means a big radiation surface and better efficiency, high T_2 the contrary. A simple calculation shows that for an ideal Carnot process the smallest radiating surface demands the temperature ratio:

$$\frac{T_2}{T_1} = \frac{3}{4}$$

The corresponding Carnot-efficiency would be 0.25, a relatively low figure. But it is supposed in all the projects that there is plenty of heat available, the heat source being a nuclear reactor.
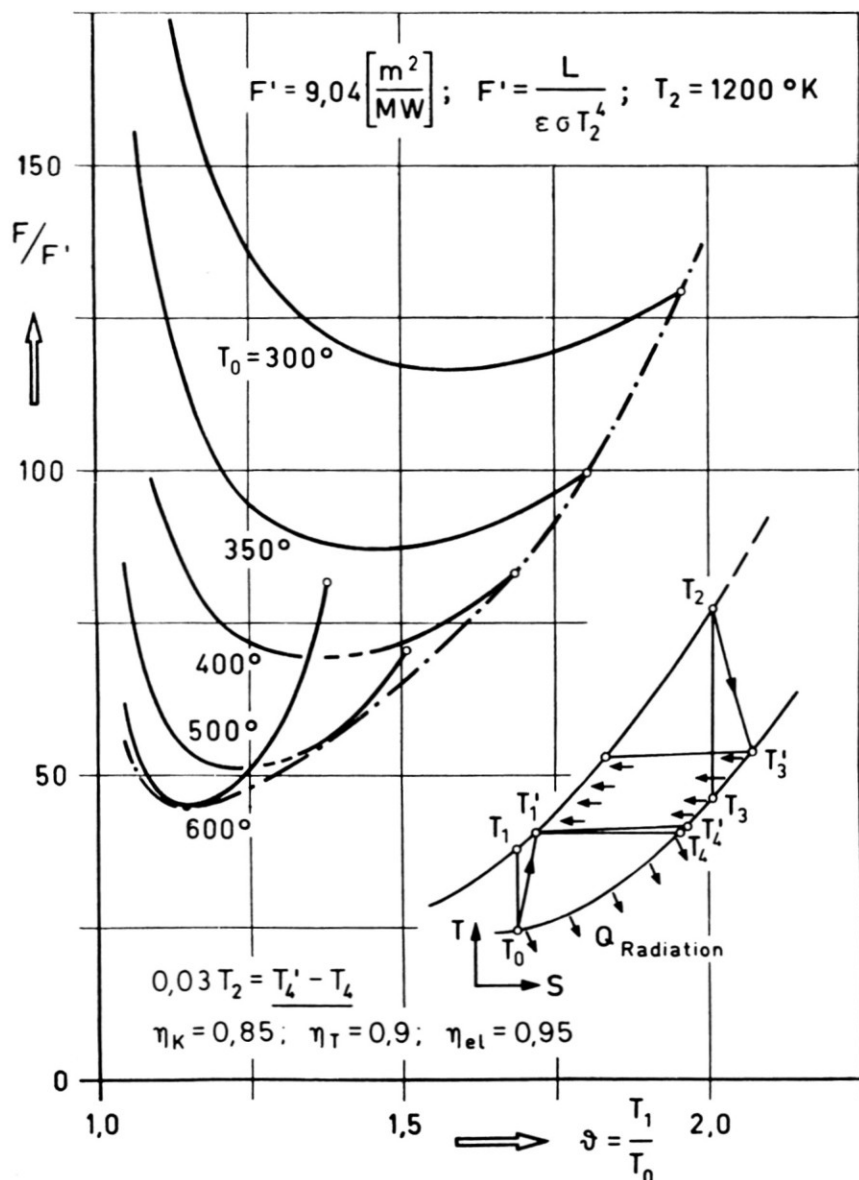

FIG. 8. Closed-cycle gas turbine generator working with nuclear reactor heat. Radiator area in function of radiator temperature T_0 and ideal temperature ratio in the compressor. η_K = isentropic compressor efficiency, η_T turbine efficiency, η_{el} efficiency of electric generator.

Similar results can be seen in Fig. 8. Here a closed cycle gas turbine with regenerator is considered. Some allowance was made for losses in turbine, compressor and heat exchanger. The hatched line gives the minimum specific radiation surface for different pressure ratios. T_{max} is fixed at 1200° K. The smallest radiation surface per megawatt of power is connected with $T_2 = \frac{1}{2} T_1$. Even then the absolute area is rather large and construction may be quite a problem.

In rockets the diminishing counterpressure gives a useful contribution to the specific impulse. But the theoretical limit is well known. An isentropic expansion from a chamber temperature T_1 to $T_2 = 0$, gives an exhaust speed of

$$w_{max} = \sqrt{2c_p T_1} \qquad (16)$$

(constant specific heat assumed for simplicity). w_{max} is independent the chamber pressure, in fact the theoretical pressure ratio would anyway be infinite. It is well known that this limit cannot be reached practically, because of finite nozzle dimensions, wall friction, energy losses by incomplete combustion etc.

With the introduction of nuclear heating and use of isentropic expansion of hydrogen very high exhaust velocities are possible. But the reactor temperatures have to be extremely high, at least by present standards (some 1600–2000° K or even more). It is therefore interesting to remember that, considering the nearly unlimited supply of heat and the infinite pressure ratio, an isothermal expansion could give any specific impulse you wish[8].

Indeed the formula writes

$$w_{isoth} = \sqrt{2RT \cdot \ln \frac{p_1}{p_2}} \qquad (17)$$

tending to ∞ if $p_2 \to 0$.

The simplest scheme would be a system of long nozzles surrounded by a nuclear reactor. Heat would be exchanged through the walls. Contrary to expectation, friction would not alter the exhaust speed, only a change in dimension would be necessary. But there is another limit which destroys all hopes[9]. Wall friction is intimately connected with heat production in the boundary layer. If the so-called recovery factor is equal to one (which is nearly the case in turbulent boundary layers), we find by a simple calculation that the maximum velocity is exactly the same as with isentropic expansion. The reason is that at a certain velocity in the center of the nozzle the boundary layer temperature, caused by friction, reaches the wall temperature and heat exchange stops (see Note 1).
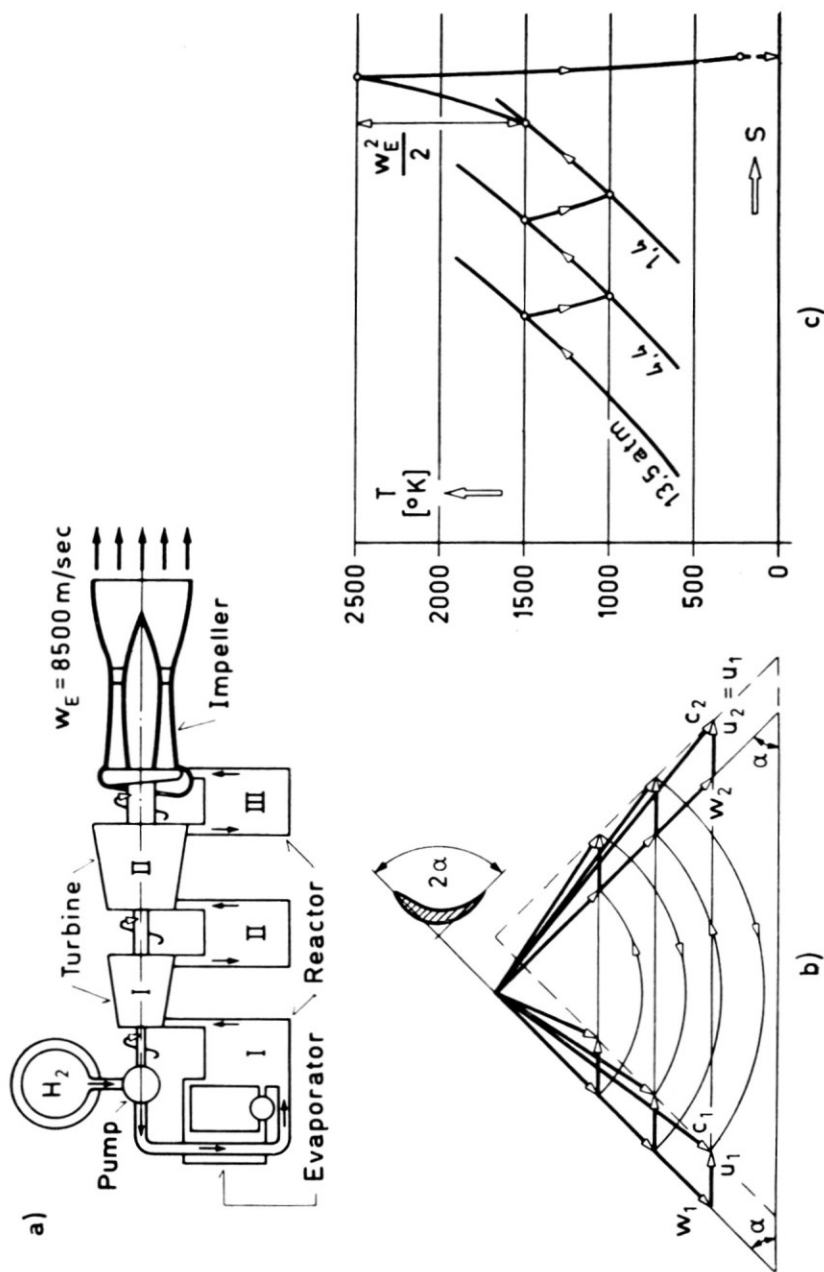
FIG. 9. Scheme of a turbine driven rocket. Liquid hydrogen is evaporated at relatively high pressure, heated and reheated by nuclear reactors. Work is drawn out by turbines during the expansion and delivered to a mechanical impeller in form of a multi-stage compressor. As compressor efficiency is not critical, the blade arrangement can be made for acceleration rather than for pressure rise. Alternatively the mechanical work could be transformed into electrical power for further use in a hydrogen plasma device. This gives an approximation to isothermal expansion.

Something like an isothermal expansion can nevertheless be realized by a more complicated arrangement[10]. The scheme is seen in Fig. 9. A light substance (helium or hydrogen) in liquid state is vaporized and passes through a first reactor. After heating, an expansion in a turbine follows which delivers mechanical work. The process can be repeated and after a last passage through the reactor the effective temperature of the gas is increased by transmitting the work of the turbines in electrical or even mechanical form to the gas. In Fig. 9 the second way is illustrated. It is interesting to remark that the efficiency of the mechanical accelerator need not be high, so we could use quite uncommon blade shapes, turning angles and velocities, and most important some high melting ceramic material. For very high temperatures electric transmission would be more promising, but that requires the successful development of ultra-light electric machinery.
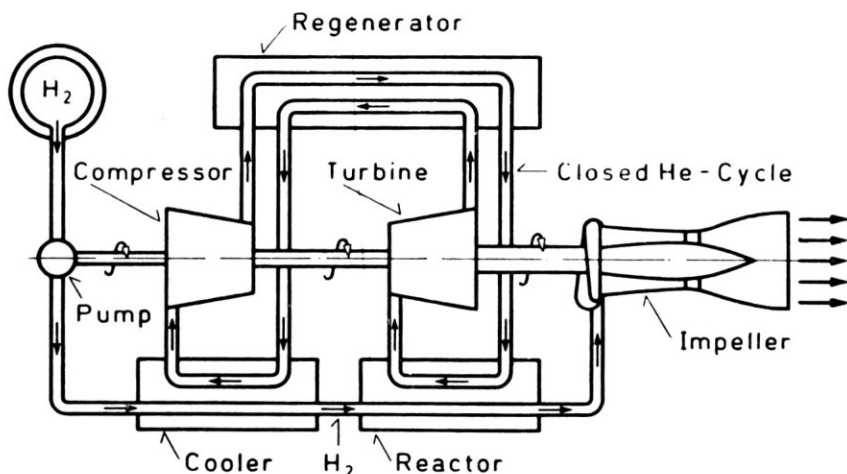

Fig. 10. A turbine-rocket drive after the proposal of N. Rott and E. L. Resler. Helium is used in a closed-cycle process with very low inlet temperature. The power is transformed into electrical or mechanical work to accelerate a hydrogen jet.

A highly interesting alternative was proposed by Resler and Rott[11] (Fig. 10). They also use a turbine and an electrical (or mechanical) drive. But they intend to use a regenerative helium cycle inserted in the process, with a heat sink at liquid hydrogen temperature. This closed-cycle machine would truly give the utmost of Carnot-efficiency, the temperature ratio being something like 50 to 1.

With both arrangements some 700–8000 m/sec may be produced at reactor (gas-) temperatures in the region of 1200° to 1500°K. If reactor gas-temperatures of 2000° or even 2500°K are possible, the direct heating will of course be more practical.

ENTROPY IN GAS - FLOW

Non-viscous Flow Vortex Theorems

In non-viscous flow the well-known theorem of Helmholtz-Kelvin applies:

$$\frac{d\Gamma}{dt} = -\oint \frac{dp}{\varrho} \qquad (18)$$

Γ is the circulation along a line moving with the gas. This theorem can be written in terms of entropy and enthalpy.

With

$$dS = \frac{du + p\,dv}{T} = \frac{dq}{T}$$

and

$$h = u + pv$$

the integral transforms to

$$\frac{d\Gamma}{dt} = \oint \{T\,ds - dh\}$$

As h is a single valued function of state, the second term drops and we have

$$\frac{d\Gamma}{dt} = \oint T\,ds \qquad (19)$$

a formula which is much used in meteorology after Bjerknes had introduced it.
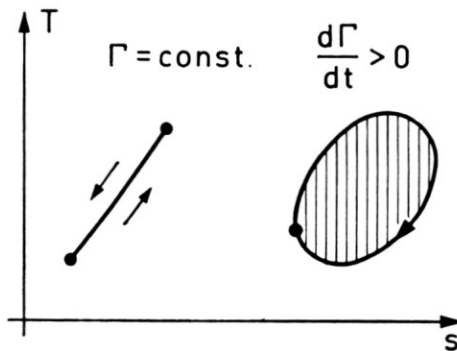

FIG. 11. The circulation-theorem in the T, s-diagram. The area circumscribed by the process line is proportional to the rate of change of circulation along a closed fluid line.

In the T, s-diagram the integral is given by the area circumscribed. If p and ϱ are in a single valued relation, this area disappears and there is no change in circulation (Fig. 11).

2

Another interesting theorem was found by Luigi Crocco[12]. He started with Euler's equation for inviscid compressible gases

$$\frac{\partial \vec{w}}{\partial t} - \vec{w} \times \text{rot} \vec{w} + \text{grad} \frac{w^2}{2} = -\text{grad}\, h + T \cdot \text{grad}\, s \qquad (20)$$

If now the flow is assumed to be stationary and of constant energy in the whole field,

$$h + \frac{u^2}{2} = \text{const.}$$

a condition which is fulfilled even if shock waves are present:

$$\text{grad} \frac{w^2}{2} + \text{grad}\, h = 0$$

and therefore

$$\vec{w} \times \text{rot}\, \vec{w} = -T \cdot \text{grad}\, s \qquad (21)$$

The following conclusions can be drawn:

(α)   A stationary gas flow irrotational and with constant energy is an isentropic flow,

(β)   If there are entropy changes within the field, vortices (vortex sheets) will generally appear.

The last consequence is of importance for instance in the case of shock waves in front of a blunt body. Vortex sheets will be formed whose strength will decrease at greater distances from the body.

ENTROPY IN BOUNDARY LAYERS

Oswatitsch's theorem

Entropy is produced in boundary layers at a relatively high rate, as dissipation is mostly concentrated in these layers. Let us consider
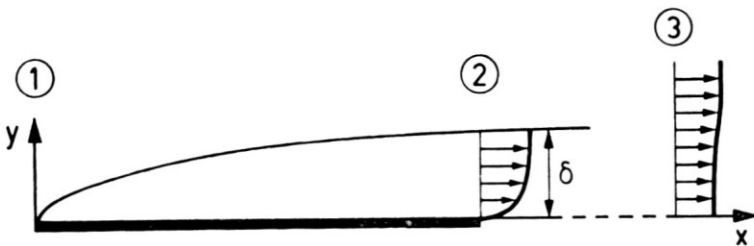

FIG. 12. Boundary-layer along a flat plate in uniform stream of gas. According to the theorem of Oswatitsch drag is connected with the entropy flux.

a simple case: a plate parallel to a stream of constant velocity (Fig. 12). We further assume that the Prandtl-number

$$Pr = \frac{\mu c_p}{\lambda} \qquad (\lambda = \text{heat conductivity})$$

equals one, if the boundary layer is laminar. In the turbulent case the equivalent ratio Pr^* of "apparent" coefficients has also this value, even if Pr is not exactly one. Busemann has shown that for Pr or $Pr^* = 1$ the simple relation applies:

$$h + \frac{w^2}{2} = c_p \cdot T + \frac{w^2}{2} = \text{const.} \tag{22}$$

$$w = \text{velocity parallel to plate}$$

The flux of entropy can now be calculated for a section (3) relatively far downstream. Index 1 applies to the undisturbed flow, index 2 to the profile at the end of the plate. As the pressure is constant, the specific entropy in section 3 is given by (s_1 taken as zero)

$$s_3 \cdot c_p \cdot \ln \frac{T_3}{T_1} = c_p \cdot \ln \left(1 + \frac{w_1^2 - w_3^2}{2 c_p T_1} \right) \tag{23}$$

As w_3 is quite near to w_1, we get for the entropy-flux:

$$S_3 = c_p \int_0^\infty \varrho_3 w_3 \cdot \frac{w_1 + w_3}{2} \cdot \frac{w_1 - w_3}{c_p T_1} \cdot dy = \frac{1}{T_1} \int_0^\infty \varrho_3 w_3 w_1 \cdot (w_1 - w_3) \cdot dy$$

We now compare this formula with the momentum equation which gives us the frictional drag D of the plate

$$D = \int_0^\infty \varrho_3 w_3 (w_1 - w_3) \cdot dy$$

So we see that

$$D \cdot w_1 = T_1 \cdot S_3 \tag{24}$$

This is a special case of the important theorem of Oswatitsch[13].

An interesting question arises, if we carry out our flux calculation in section (2). S_2 is different from S_3 ($S_2 < S_3$). What does $T_1 \cdot S_2$ mean? Nothing else but the minimum power that is needed for propulsion. We can think of a sophisticated propulsion mechanism that leaves a wake behind the plate which possesses (in an absolute system) no visible kinetic energy, the undisturbed temperature and undisturbed entropy. To obtain this effect we have to apply two mechanisms:

(a) a Carnot-cycle heat engine which utilizes the temperature difference T_2 to T_1 and transforms it into power. The entropy of the environment is consequently growing.

(b) an isentropic compressor which accelerates the air from w_2 to $w_3 = w_1$.

(a) is sensibly smaller than (b)—(see Note 2).

Such equipment would have to be installed in great numbers, namely for every fluid filament. The gain in power is considerable, but such a complicated machinery is of course an absurdity. In certain applications of boundary layer suction, however, the second part of this effect may well be present.

In the last instance it is the sticking of molecules to solid surfaces that initiates boundary layers. Sticking is physically quite different from the mechanism of internal friction. Maybe one day an ingenious inventor will find an anti-sticking device; at the moment nothing of this kind is in sight. The next progress on the way to the reduction of frictional resistance will be laminarization. The latest results of Pfenninger seems to be encouraging[14].

ENTROPY IN SHOCK WAVES

When Riemann discovered the shock waves by theoretical reasoning, he assumed an isentropic change of state. This is nearly true for weak shocks, but not for strong ones.

The Hugoniot-Rankine equation

$$\frac{\gamma}{\gamma-1}\left(\frac{p_2}{\varrho_2} - \frac{p^1}{\varrho^1}\right) = \frac{\varrho_2+\varrho_1}{2\varrho_1\varrho_2}(p_2-p_1) \tag{25}$$

(suffix 1 in front of, 2 behind the shock)
can be transformed into the simple Kármán relation:

$$\frac{p_2-p_1}{\varrho_2-\varrho_1} = \gamma \cdot \frac{p_2+p_1}{\varrho_2+\varrho_1} \tag{26}$$

which, by the way, is equal to the square of the so-called critical velocity a^*.

For extremely weak shocks this becomes in the limit

$$\frac{dp}{d\varrho} = \gamma \cdot \frac{p}{\varrho} \tag{27}$$

the common isentropic equation.

In stronger shocks the entropy increases. We find

$$\frac{s_2-s_1}{R} = \frac{1}{\gamma-1} \cdot \ln\left[1 + \frac{2\gamma}{\gamma+1}(M_1^2-1)\right] + \frac{\gamma}{\gamma-1} \cdot \ln\left[1 - \frac{2}{\gamma+1}\left(1 - \frac{1}{M_1^2}\right)\right]$$

$$M_1 = \frac{w}{a_1} \tag{28}$$

where w is the gas velocity in front of the shock relative to the shock front; a_1 is the speed of sound in this region.

Stagnation pressure is reduced, stagnation temperature (as a consequence of the first law) remains constant.

We have

$$\frac{p_{0_2}}{p_{0_1}} = e^{-\frac{S_2-S_1}{R}} \tag{29}$$

For weak shocks an approximation gives

$$\frac{S_2-S_1}{R} \rightarrow \frac{\gamma-1}{12\gamma^2} \cdot \left(\frac{p_2-p_1}{p_1}\right)^3 = \frac{2}{3} \cdot \frac{\gamma}{(\gamma+1)^2} \cdot (M_1^2-1)^3 \tag{30}$$

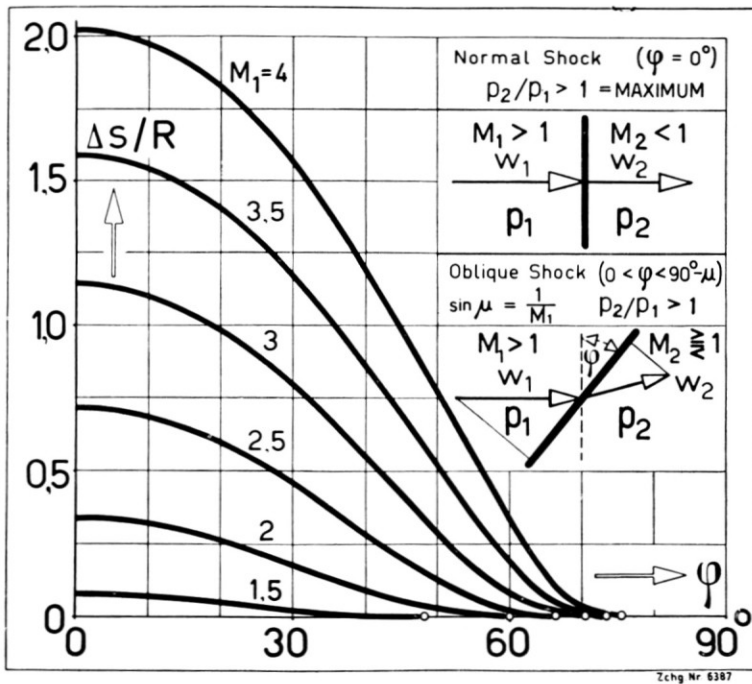From this formula it is evident that the irreversibility is quite small near $M_1 \approx 1$.

FIG. 13. Entropy rise in normal and oblique shocks.

Oblique shocks can be treated in much the same way. Here only the velocity component normal to the shock front undergoes a change.

The formula is

$$\frac{S_2-S_1}{R} = \frac{1}{\gamma-1} \cdot \ln\left[1+\frac{2\gamma}{\gamma+1}(M_1^2 \cdot \cos^2\varphi-1)\right]$$

$$+ \frac{\gamma}{\gamma-1} \cdot \ln\left[1-\frac{2}{\gamma+1} \cdot \left(1-\frac{1}{M_1 \cdot \cos^2\varphi}\right)\right] \tag{31}$$

Figure 13 shows the substantial reduction of entropy increase. According to Oswatitsch's theorem drag can be reduced by sweeping back the shock front. The same principle explains the advantage of Oswatitsch's multi-
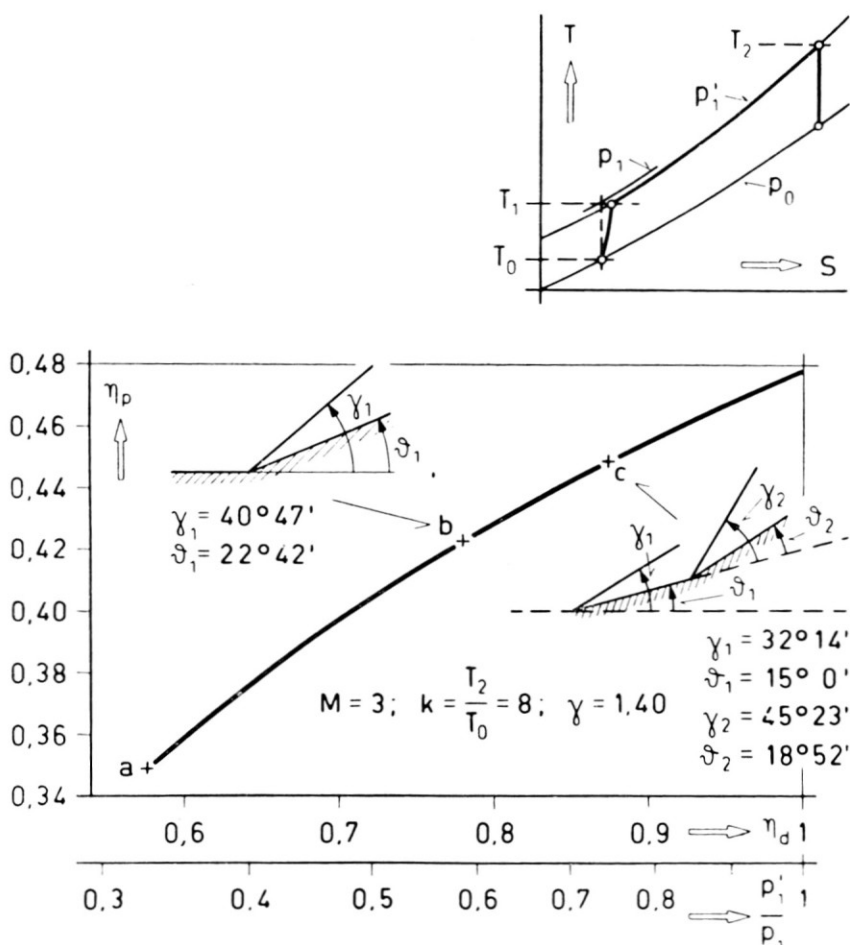

FIG. 14. Two-dimensional ramjet with shock diffusors: (a) is normal shock; (b) (c) oblique shock compression; η_p = propulsion efficiency;

$$\eta_d = \frac{\dfrac{T_1}{T_0} \cdot \left(\dfrac{p_1'}{p_1}\right)^{\frac{\gamma-1}{\gamma}} - 1}{\dfrac{T_1}{T_0} - 1}$$

= diffusor efficiency.

shock diffusor inlet. An infinite number of shocks with vanishing strength gives as a limit isentropic compression, but even a very limited multiplicity shows a considerable gain, as exemplified in the case of a (plane)

ramjet where the propulsive efficiency is improved (Fig. 14). Well designed intake diffusors are of great importance for the realization of economic supersonic airliners.

The structure of shock waves

Shock waves are not real discontinuities, though they are sometimes very thin. An attempt can be made to apply the one-dimensional Navier-Stokes equation, combined with the energy and continuity equations. Besides the heat conduction $\lambda \dfrac{\mathrm{d}T}{\mathrm{d}x}$, the compressional viscous stress enters the equation:

$$\pi_{xx} = -2\mu \frac{\partial w_x}{\partial x} + \frac{2}{3}\mu \cdot \operatorname{div} \vec{w} - \frac{2}{3}\mu' \cdot \operatorname{div} \vec{w} \tag{32}$$

with μ as normal, μ' as bulk viscosity.

For the one-dimensional case:

$$\pi_{xx} = -\left(\frac{4}{3}\mu + \frac{2}{3}\mu'\right) \cdot \frac{\partial w_x}{\partial x} \tag{33}$$

If there is no bulk viscosity: $\pi_{xx} = -\dfrac{4}{3}\mu \cdot \dfrac{\partial w_x}{\partial x}$

A very crude order of magnitude argument shows immediately that the thickness of the shock turns out to be really small in normal cases. We can assume that π_{xx} must be comparable to the total pressure difference, say $\frac{1}{2}(p_2 - p_1)$. Then we find for the thickness d

$$d = \frac{8}{3} \cdot \frac{\nu}{a_1} \cdot \frac{1}{M_1} \qquad (M_1 > 1) \tag{34}$$

that gives for atmospheric air and for medium Mach-numbers something of the order of 10^{-5} cm, quite comparable with the free path length.

Many people have given exact solutions on the basis of the Navier-Stokes equation. One of the first was R. Becker[15]. He neglected the change of viscosity, and heat conduction coefficients with temperature, and assumed a gas with Prandtl-number 3/4 to simplify the calculations. Figure 15 shows the transition in the shock. Entropy is first rising and afterwards there is a small reduction. M. Roy has shown that the entropy maximum corresponds to the abszissa where the velocity curve is steepest[16]. The different terms of the energy equation are drawn separately. This equation can be transformed by introduction entropy into the simple form:

$$(\varrho w) \cdot T \cdot \frac{\mathrm{d}s}{\mathrm{d}x} = \mu \cdot \left(\frac{\mathrm{d}w}{\mathrm{d}x}\right)^2 + \lambda \cdot \frac{\mathrm{d}^2 T}{\mathrm{d}x^2} \tag{35}$$

If we call $(\varrho w) \cdot s = S$ an entropy flux, the left hand side means $T \cdot \operatorname{div} S$, the right hand side contains the entropy sources. Both concepts play an important role in the new science of irreversible thermodynamics.
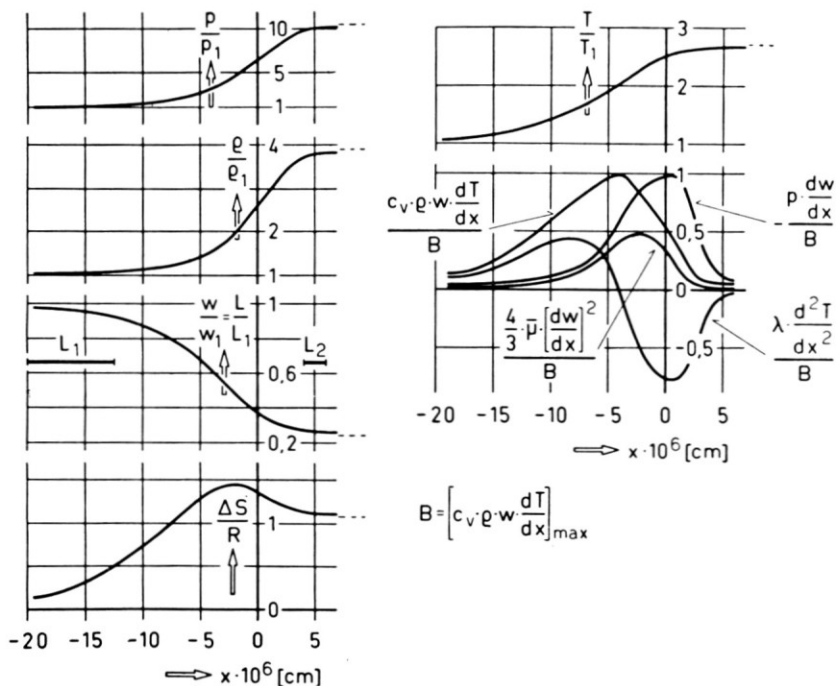

FIG. 15. Values of the state variables inside a normal shock after R. Becker. L is free path length. The different terms of the energy-equation are drawn separately in the last diagram. $M_1 = 3$, $T_1 = 295°K$, $p_1 = 10^6 \ \dfrac{\text{dyn}}{\text{cm}^2}$, $\bar{\mu} = 2.85 \cdot 10^{-4} \ \dfrac{\text{g}}{\text{cm sec}}$.   Energy equation: $c_v \cdot \varrho \cdot w \cdot \dfrac{dT}{dx} = -\left(p - \dfrac{4}{3} \mu \cdot \dfrac{dw}{dx}\right) \cdot \dfrac{dw}{dx} + \lambda \cdot \dfrac{d^2 T}{dx^2}$

Thomas has included the variability of the coefficients of heat conduction and viscosity $(\mu \sim \sqrt{T})$ and he found values for the thickness little differing from Becker's[17]. For air $(T_1 = 300°K, \ \gamma = 1,4)$ and different Mach numbers:

$$M = \ \begin{array}{cl} 2 & 173.8 \cdot 10^{-7} \ \text{cm} \\ 3 & 106.6 \\ 4 & 87.6 \\ 5 & 79.5 \\ \infty & 65.8 \end{array}$$

The finite limit comes from the indefinite growing of viscosity and heat conductivity with shock strength. Green, Cowan and Hornig were

able to measure the thickness with an interesting light reflection method [18, 19], and Sherman did the same using a temperature probe in a relatively weak shock at reduced density[20]. In Fig. 16 (after Patterson) some results are shown compared with different theories, especially with different laws of temperature dependence of viscosity ($\mu \sim T^N$)[21].
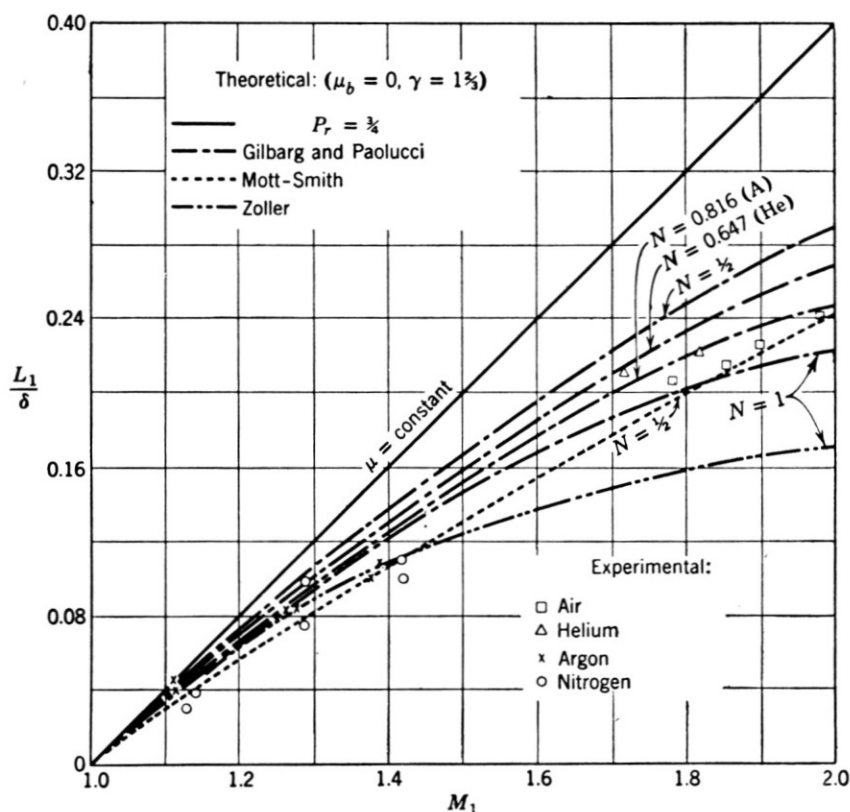

FIG. 16. Shock thickness (after Patterson). μ = constant applies to Becker's solution. The other curves are obtained by variation of the exponent N for the viscosity-temperature dependence. Experimental points confirm the order of magnitude.

Mott-Smith's theory is different as he uses a mixture of two Maxwellian distributions[22]. The most astonishing conclusion is that the macroscopic treatment by Navier-Stokes does not apply too badly, and that other theories do not seem to show much improvement.

The application of shock tubes for the study of supersonic and hypersonic gas flow is well known. Here I shall consider only a simple case of shock reflexion, the so-called resonance tube[23]. A cylindrical tube completely or nearly closed at one end and open at the other end is used. A super-

sonic air jet is directed towards the open end. Long ago Hartmann found that this device produces a periodic in-and-out flow of gas and outside intense ultrasonic waves[21]. He was chiefly interested in these, but the phenomena inside the tube are not less interesting. The part of the tube near the closed end is heated to a considerable temperature. An elementary
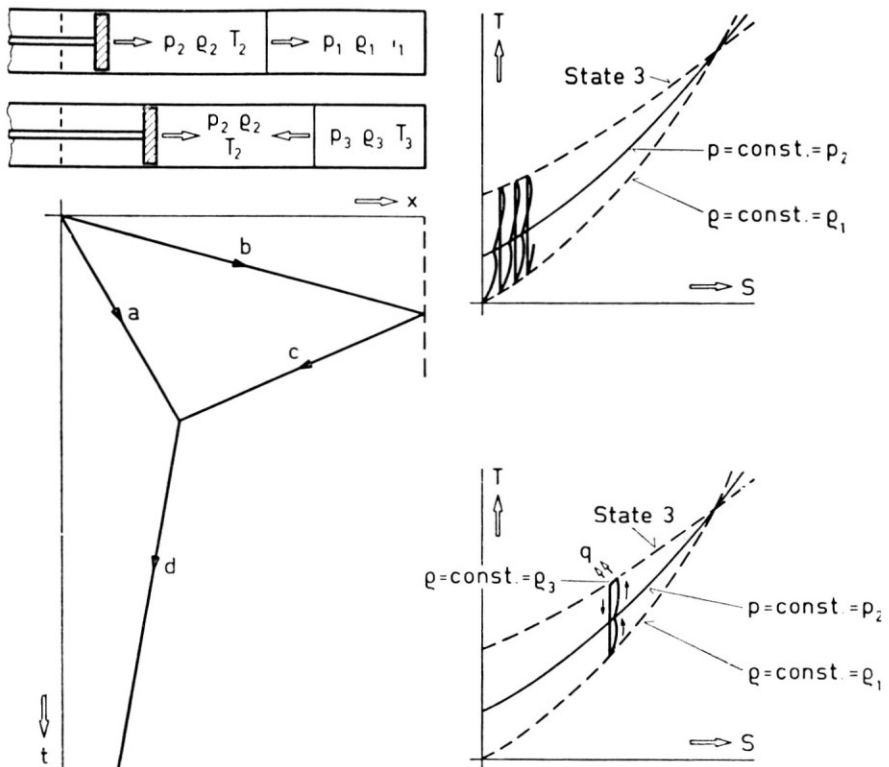

FIG. 17. Shock wave propagation in the tube. Schematic entropy-diagrams for the assumed thermal processes. Above without energy removal; Lower diagram with radiation resulting in a stationary process. Entropy increase per cycle:

$$\frac{\Delta S}{R} = \frac{1}{\gamma-1} \cdot \ln \frac{p_3}{p_1} - \frac{\gamma}{\gamma-1} \cdot \ln \frac{\varrho_3}{\varrho_1}$$

explanation may be given by considering the movement of shock waves inside the tube (Fig. 17). The influence of the impinging jet may be represented by a mass-less piston which is driven by a constant pressure from outside. A shock wave b is built up, which is reflected at the closed end (c). After a certain time the reflected wave reaches the piston. From that time on a relatively slow expansion takes place untill the original volume is regained. Then a new cycle starts. The entropy as well as the tempera-
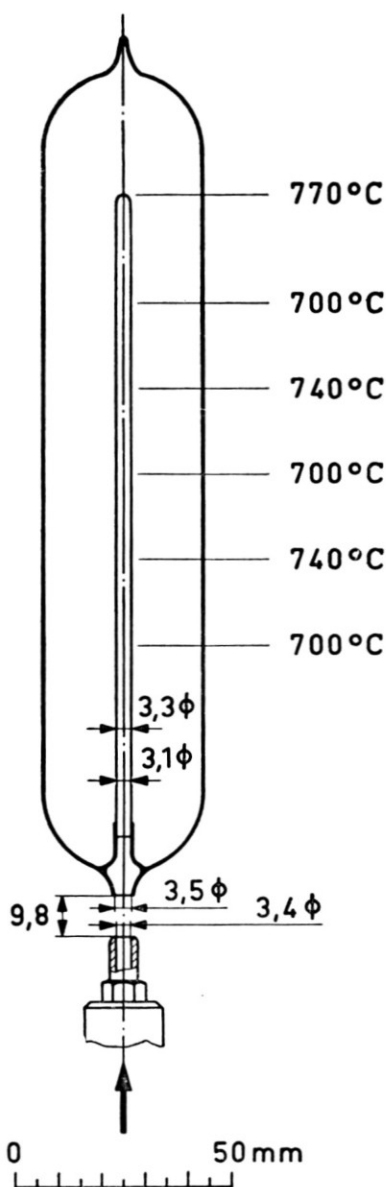
FIG. 18. Resonance tube. Air with a pressure of about 4.1 atmospheres absolute and with a stagnation temperature of 20°C flows as a small jet against the opening of a straight circular platinum tube closed at the other end. Shock waves are running into the tube and are reflected at the closed end. Depending on pressure several shocks may be simultaneously in the tube. The tube is thermally insulated by an evacuated bulb and glows. Surface temperatures are about 1000°K, and the light emitted is quite appreciable.

ture have increased as the shocks were irreversible. If there were no heat extraction, the temperature would rise to:

$$\frac{T_{max}}{T_1} = \frac{p_2}{p_1} \quad \text{independent of } \gamma.$$

With heat extraction the process will be stationary at some intermediate temperature. We can demonstrate the effect quite simply. A thin tube of platinum is fixed in an evacuated lamp bulb (Fig. 18). Air of about 4 atmospheres absolute at room temperature leaves a cylindrical nozzle as a free jet. The tube heats up and is glowing at about 700°C. There is some indication that accidents with high pressure valves might have been caused by similar phenomena.

CONNECTIONS BETWEEN ENTROPY AND MOLECULAR THEORY

Up to here we have used the classical definition of entropy which is sufficient for most of the practical problems. But very early phenomena not explicable by macroscopic theory were observed. For instance there was the riddle of specific heat of two-atomic gases, where one degree of
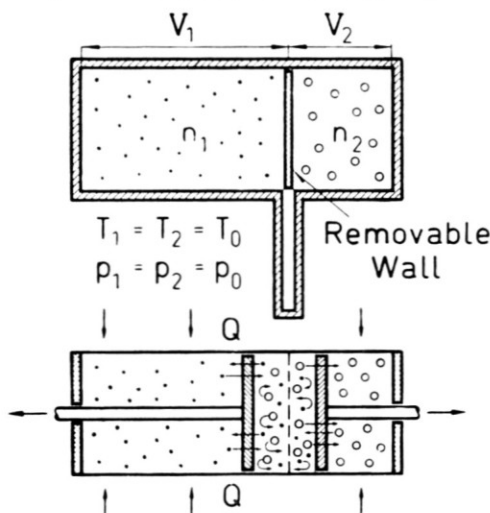

FIG. 19. Above: Irreversible mixing of gases. Below: Reversible mixing by the use of semi-permeable pistons. Work is done and heat has to be added.

freedom is evidently not in action, contrary to the otherwise well established equi-partition theorem. This "cloud over the mechanical theory of heat" in the words of Lord Kelvin was dispersed much later by the quantum theory.

A very curious conclusion was drawn quite early by Gibbs[25]. He considered the mixing of different gases (Fig. 19). If we have two

volumina of gases at the same pressure and temperature and let them mix, the process is clearly irreversible and total entropy increases. For its calculation in the classical way we have to perform the mixing in a reversible way which can be done, at least on principle, by the application of semi-permeable pistons. Heat has to be added and work is done. If we use one mole of each gas for example, entropy is increased by

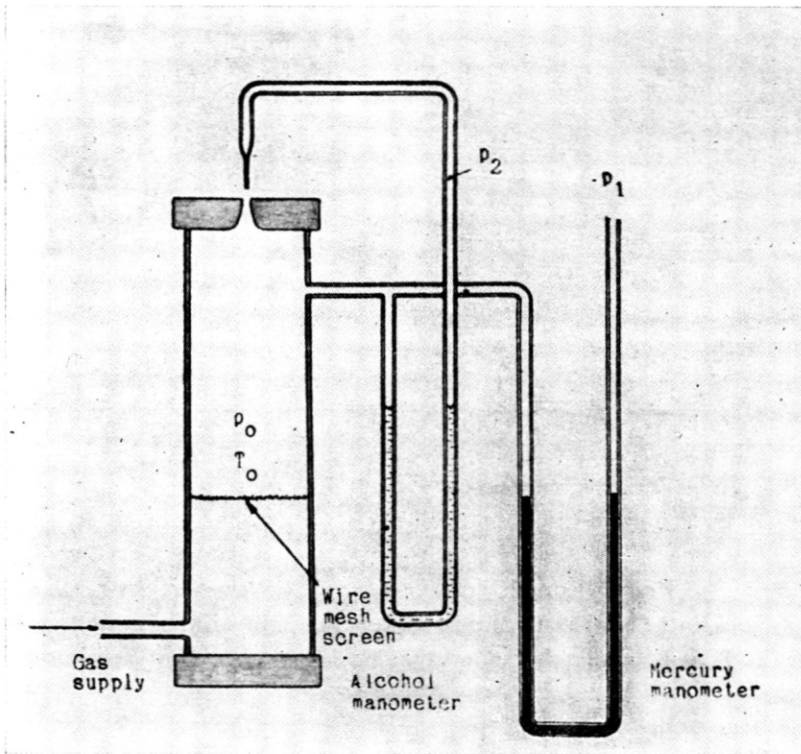$$\Delta s = R \cdot 2 \cdot \ln 2$$

as a simple calculation shows.

FIG. 20. Experiment of Kantrowitz, showing loss of stagnation pressure in consequence of an entropy increase by relaxation.

But the formula contains an astonishing paradox, as there is no influence of the nature of the gases. So two gases of identical nature would show the same increase, contrary to experience where nothing happens if a separating wall in a mass of gas is drawn out.

The paradox is that the slightest difference gives an effect, but complete identity gives none. This suggests that the calculation of entropy must in reality be a counting process. As an illustration let us imagine two

specimens of coins from different countries but of equal monetary value. They may both have the same weight. In normal times, for a control of your fortune, you may simply weigh the whole lot. This is a "macroscopic" method. But if monetary perturbations occur it might be wiser to make a closer inspection and to count the coins "microscopically", in our case: to look at the molecules.

First I would like to mention an experiment by Kantrowitz, equally simple as interesting[26]. Carbon dioxide is a gas consisting of linear three-atomic molecules. In normal equilibrium the molecules have translational, rotational and, to a certain extent also, vibrational energy. Kantrowitz let the gas flow under some pressure from a receiver through a nozzle and impinge on a very small pitot head (Fig. 20). One would expect that the pitot shows exactly the pressure of the gas in the receiver. But with CO_2 it was visibly smaller. The explanation is the following: As the compression before the pitot occurs in a very short time, the oscillation does not follow immediately, some 30,000 impacts are needed to excite vibration. For a short time the gas behaves as if it possessed a smaller number of degrees of freedom and during this time it reaches a higher temperature. But immediately afterwards the vibration gets continuously excited to the equilibrium level. This means an irreversible temperature drop and consequently an entropy rise. But we know that greater entropy at the same equilibrium temperature means lower stagnation pressure and this corresponds to the observation.

This "relaxation"-phenomenon is well known also from experiments on the "dispersion" of the sound velocity in CO_2, a change of sound velocity with frequency. A fine confirmation of the relaxation was given by Bleakney[27]. He measured interferometrically the density variation in a shock in CO_2. The total entropy change is invariably given by equation (28), but immediately behind the shock there is a clearly visible zone, of relaxation (Fig. 21).

It is plausible to assume that a similar entropy increase will occur at any object put into a stream of CO_2. According to Oswatitsch's theorem an additional drag will result[28]. It would be interesting to obtain an experimental verification.

There seems to be a connection with the aforementioned bulk viscosity μ'. Busemann[29] taking into consideration that a change of specific volume first changes the translational degrees of freedom, the other following after a certain small relaxation time, gave an approximate formula:

$$\mu' = \frac{5-3\gamma}{2} \cdot \mu \tag{36}$$

It follows that we should have no bulk viscosity in mono-atomic gases ($\gamma = 5/3$) and it seems that the experiment confirms this conclusion. Multi-atomic gases ($\gamma \to 1$) would show, according to the formula, a bulk viscosity equal to the normal viscosity, $\mu' = \mu$. But it seems that the
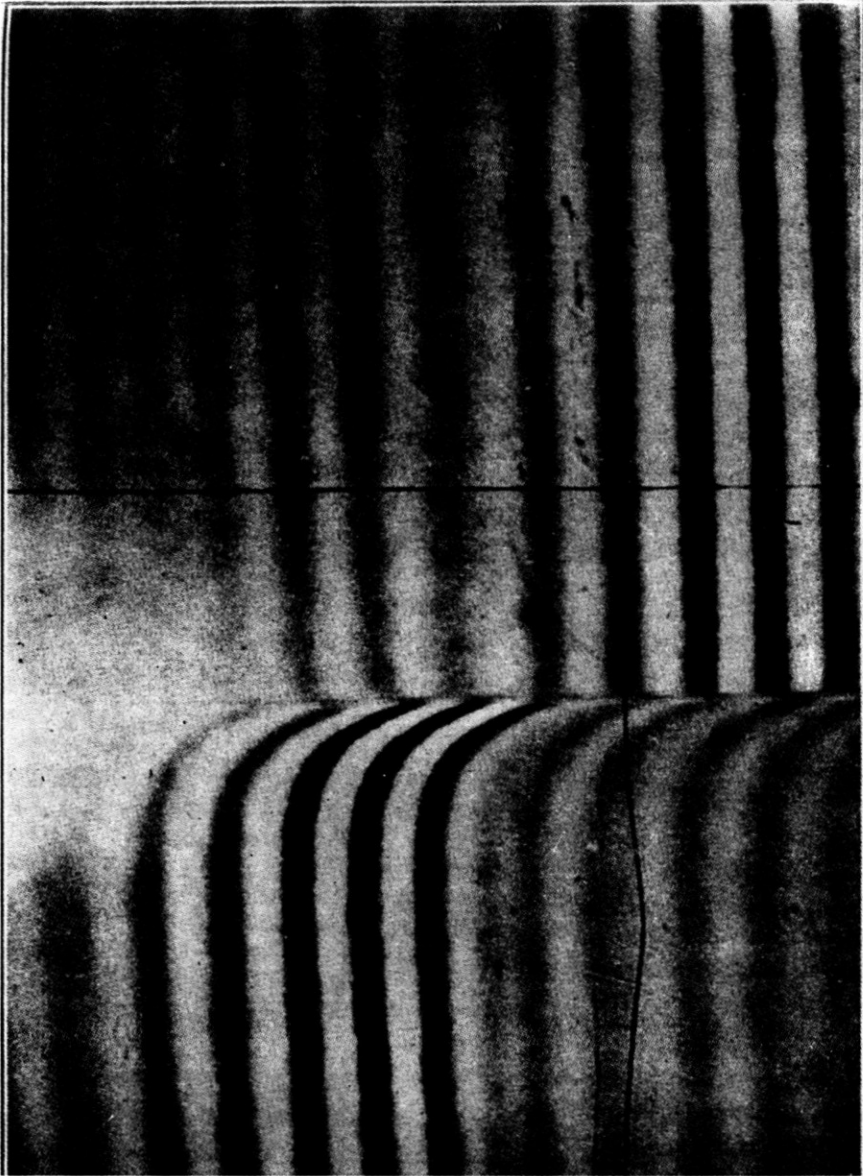

FIG. 21. Relaxation in a plane shock in CO_2 after Bleakney. The adjustment of vibrational energy takes a certain time and the corresponding length for transition is clearly visible. Flow direction from right to left.

whole question of bulk viscosity is not yet settled. There are indications that for CO_2 μ' is in reality much bigger than μ. In this case the relaxation time is much greater for vibration than for rotation, and Busemann's formula does not apply without change.

CHEMICAL EQUILIBRIUM

In rocket combustion chambers temperatures are so high that dissociation occurs. In the chambers where flow-velocities are relatively low the state of the gas mixture approaches equilibrium. Here at least entropy is well defined and if its standard values for the different components are known, the whole state is theoretically determined. As we strive for simplicity, the example of dissociating hydrogen

$$H_2 \rightleftarrows H_1 + H_1$$

shall be discussed.

We consider a mixture of H_2 and H_1 with a total mass of 1 mole H_2 ($= 2g$) and at a pressure of p_{tot}. The composition is given by the value of α which designates the proportion of H_2 molecules which are dissociated, so that we have in moles:

H_2	H_1	mixture
$1-\alpha$	2α	$1+\alpha$

α depends on p_{tot} and on the temperature T.

The free enthalpies of the different constituents are

$$g_i = u_i + p_i v - T s_i$$

p_i is the partial pressure of the component i.

The total free enthalpy is given by

$$g = \sum_i g_i$$

Now the equilibrium composition is determined by the condition that in this state entropy should be a maximum, in other words that the variation δg of g disappears for small changes of α.

Then the equilibrium formula is found:

$$\ln K_p = \ln\left(\frac{p_{H_1}^2}{p_{H_2}}\right) = -\frac{Q_p}{RT} + \frac{(2S_{H_1} - S_{H_2})_{abs}}{R} \tag{37}$$

Here Q_p is the heat of reaction at constant pressure and at the temperature T. It can be taken from calorimetric measurements and the known values of specific heats. S_{H_1} and S_{H_2} are the absolute entropies. α is connected with K_p by

$$\alpha = \sqrt{\frac{K_p}{K_p + p_{tot}}} \tag{38}$$

For example at $p_{tot} = 1$ and at $T = 4000°K$:

$$K_p = 2.768, \quad \alpha = 0.64.$$

Figure 22 shows a temperature-entropy chart for hydrogen in equilibrium state. α and the enthalpy are included.

In an analogous way much more complicated reactions have been treated and there are charts for air and combustion products up to $15,000°K$ available.

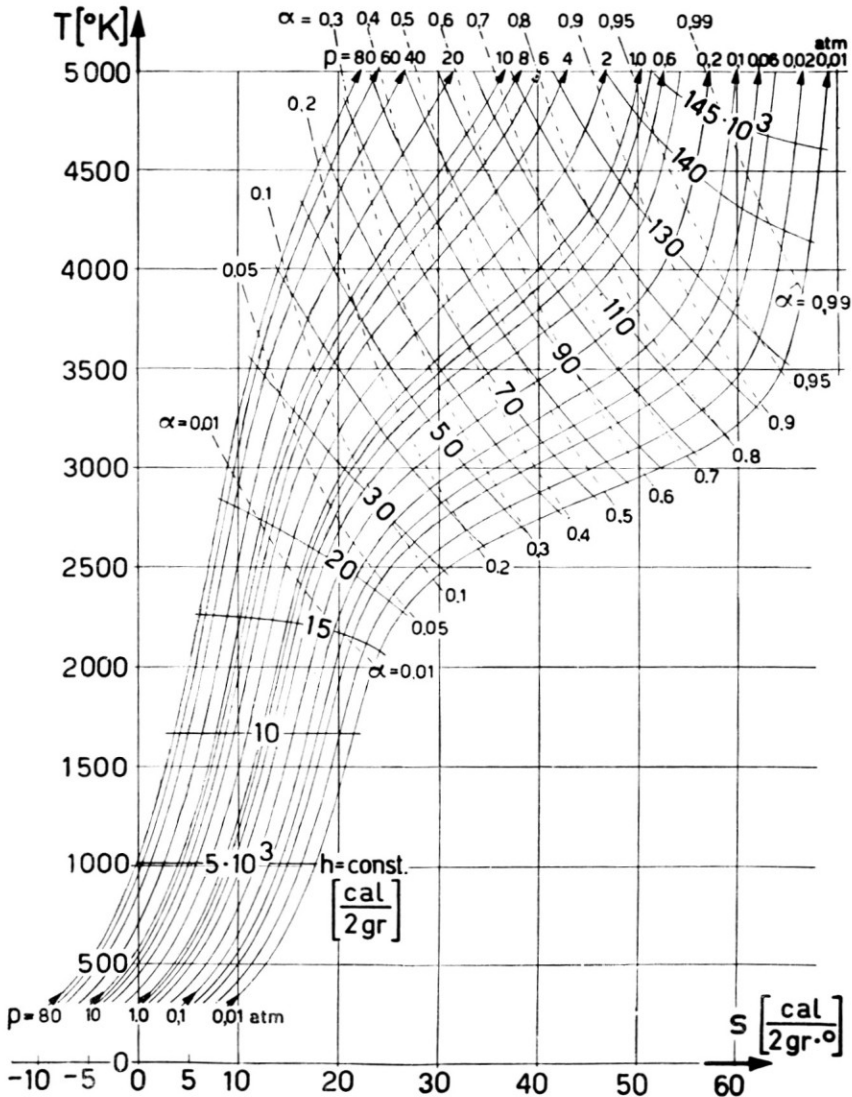FIG. 22. Entropy chart for hydrogen gas taking dissociation into account. α is the degree of dissociation, h the enthalpy for one gram-mole of H_2 (2 g).

A most interesting consequence of quantum theory is the possibility of calculating the entropy of the gaseous state of an element or compound without using details of fusion or vaporization or even specific heats.

For a mono-atomic gas (also for an electron gas) the absolute entropy for the aforementioned standard state (T^*, p^*) is

$$\frac{S^*}{R_m} = \frac{2}{5} + \frac{3}{2}\ln M + \frac{5}{2}\ln T^* - \ln p^* + \ln\left\{\left(\frac{2\pi}{N}\right)^{3/2} \cdot \frac{k^{5/2}}{h^3}\right\} \qquad (39)$$

Here R_m is the gas constant for one mole,

    M the molecular weight,
    N Avogadro number,
    k Boltzmann constant,
    h Planck constant.   (See Note 3).

For more complicated molecules further terms including moments of inertia, vibration frequencies etc are to be added; spectroscopy is generally able to deliver the necessary data.

NON-EQUILIBRIUM STATES

Up to now we have mostly considered equilibrium states. Chemical thermodynamics does not go any further. But non-equilibrium states are of growing importance; strictly speaking exact equilibrium is relatively seldom in gas-dynamics. But a rational theory of non-equilibrium states has necessarily to be extremely complicated. There are two ways for further progress being followed now with great impetus.

First a theory of steady irreversible thermodynamics was developed (Baumann, Onsager, de Groot[31], Prigogine and others), a partially phenomenological approach which has been very successful in the treating of phenomena where different effects are operating simultaneously, for instance heat conduction plus diffusion. For a simple gas flow at high speed there is not much progress to be mentioned to date, as equations of the type of formula (35) result, where entropy flux and sources of entropy can be calculated directly. But we may expect that important developments will come along with time.

The other way is more fundamental. It goes back to the kinetic theory of non-uniform gases, using Maxwell-Boltzmann's equation. There, entropy has a new definition which, in the limit, leads to the classical equilibrium relations.

So we see that a new era begins for thermodynamics rather more adapted to practical phenomena, if viscosity, heat conduction, diffusion and chemical reactions all act at the same time. It may be that the old generation will be disappointed at the growing complications, but then we have

the young scientists well aquainted with abstract thinking and with the tre-
mendous possibilities of electronic calculations. The rate of theoretical
development may be slow at times, but there is always some way out of
the difficulties. Let us only remember that at the beginning of this century
viscous flow at high Reynolds numbers was practically intractable with
the old methods, especially if turbulence occurred, but owing to the work
of Prandtl, Kármán, Taylor, Dryden, and many others these problems
are now solved to quite a considerable extent. So there never is room
for despair.

ACKNOWLEDGMENTS

Note 1

Isothermal Expansion

Taking the recovery factor equal to one for simplicity the temperature
T_{g_w} of the gas near the wall is higher than the gas temperature T_{g_c} in
the nearly undisturbed center by the amount $\dfrac{w_c^2}{2c_p}$(Fig. 23). Heat transfer
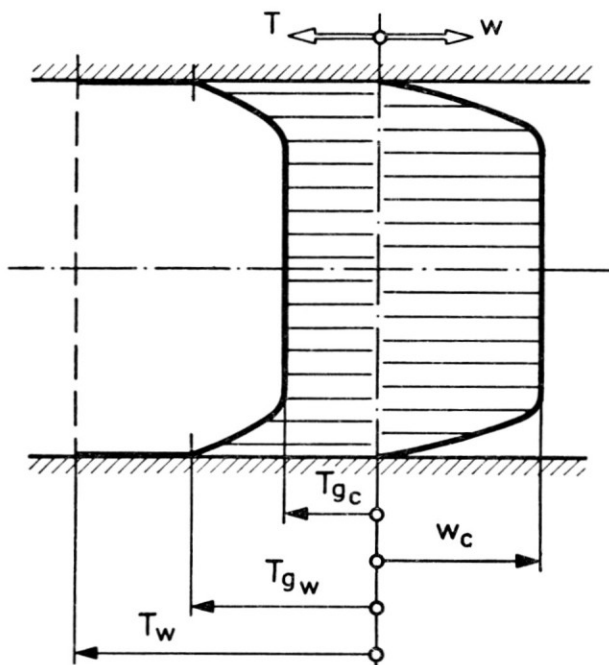

FIG. 23. (belongs to Note 1).

from the wall stops, if $T_{g_c} + \dfrac{w_c^2}{2c_p} = T_w$. From this point on an adiabatic expansion to zero pressure gives

$$\frac{w_{max}^2 - w_c^2}{2c_p} = T_{g_c}$$

so that

$$\frac{w_{max}^2}{2c_p} = T_{g_c} + \frac{w_c^2}{2c_p} = T_w$$

This means that there is no gain over the simple isentropic expansion (equation (16) of the text).

Note 2

Minimum Propulsive Power

Step a: Power is produced by using the temperature-difference between T_2 and T_1 in a Carnot-cycle, the pressure and velocity of the gas remaining constant.

We have to take away continuously the heat (per unit mass):

$$dq = -c_p \, dT$$

The Carnot-efficiency is equal to

$$\eta_c = 1 - \frac{T_1}{T}$$

Integrated between the limits T_2 and T_1 the work comes out as:

$$\varDelta A = c_p \cdot \left\{ (T_2 - T_1) - T_1 \cdot \ln \frac{T_2}{T_1} \right\}$$

Summed up across the whole boundary layer the power gained is:

$$L_a = \int_0^{\delta_2} \varrho_2 w_2 c_p \cdot \left\{ (T_2 - T_1) - T_1 \cdot \ln \frac{T_2}{T_1} \right\} \cdot dy$$

Step b: The gas at uniform temperature T_1 and variable velocity w_2 is now accelerated to w_1 by isentropically working fans. The power needed is simply:

$$L_b = \int_0^{\delta_2} \varrho_2 w_2 \cdot \left(\frac{w_1^2 - w_2^2}{2} \right) \cdot dy = \int_0^{\delta_2} \varrho_2 w_2 c_p \cdot (T_2 - T_1) \cdot dy$$

The total propulsive power is the difference of L_b and L_a:

$$L_p = L_b - L_a = c_p T_1 \cdot \int_0^{\delta_2} \varrho_2 w_2 \cdot \ln \left(\frac{T_2}{T_1} \right) \cdot dy$$

$$= c_p \cdot T_1 \cdot \int_0^{\delta_2} \varrho_2 \cdot w_2 \cdot \ln \left(1 + \frac{w_1^2 - w_2^2}{2c_p T_1} \right) \cdot dy$$

On the other hand the entropy flux S_2 is given by the following integral

$$S_2 = c_p \cdot \int_0^{\delta_2} \varrho_2 \cdot w_2 \cdot \ln\left(\frac{T_2}{T_1}\right) \cdot dy$$

Hence we have:

$$L_p = T_1 \cdot S_2$$

We can introduce an equivalent drag $D' = \dfrac{T_1 S_2}{w_1}$ which is smaller than D by the factor $\dfrac{S_2}{S_3}$.

As a simplified example we may take a laminar boundary layer with $Pr = 1$, $\gamma = 1.40$, at Mach-number 2 where the velocity profile is approximately linear. The ratio $\dfrac{D'}{D}$ equals 0.62 and the ratio $\dfrac{L_a}{L_b}$ is 0.18.

Note 3

Absolute Entropy of a Mono-atomic Gas

A relatively simple method for the calculation of the entropy from first principles due to H. A. Lorentz[30] can be modified to include quantum effects. For simplicity we take one gram-atom of a mono-atomic gas. Its volume v contains then N atoms ($N = 6.025 \cdot 10^{23}$ Avogadro's number).

For a detailed description of the state of this complicated mechanical system we should know $3N$ positional coordinates ($q_1\ q_2 \cdots q_{3N}$) and $3N$ momentum components ($p_1\ p_2 \cdots p_{3N}$).

We shall imagine a $6N$-dimensional "phase-space" (q, p). The microscopic state of the gas is then represented by one single point in this space. If v and T are fixed, this point can move only in a limited region, the so-called phase-volume. It is given by the integral:

$$\Phi' = \dots \int \int \int dq_1 \cdot dq_2 \cdot \dots \cdot dq_{3N} \cdot dp_1 \cdot dp_2 \cdot \dots \cdot dp_{3N}$$

which can be divided into a spatial factor

$$\Phi'_{sp} = \dots \int \int \int dq_1 \cdot dq_2 \cdot \dots \cdot dq_{3N}$$

and a momentum factor

$$\Phi'_{mom} = \dots \int \int \int dp_1 \cdot dp_2 \cdot \dots \cdot dp_{3N}$$

as coordinates and momenta are independent.

Φ'_{sp} is simply equal to v^N, as every molecule has the full spatial range v. Φ'_{mom} requires a special consideration. The total energy E of the gas

is kinetic, as we exclude interaction of the atoms besides the impacts in collisions. Therefore the momenta have to fulfil the condition:

$$\frac{p_1^2}{2m} + \frac{p_1^2}{2m} + \cdots + \frac{p_{3N}^2}{2m} = E = \frac{3}{2} R_m \cdot T$$

m being the mass of one atom.

In other words: the representative point moves on a spherical surface in the momentum space (p) with radius:

$$P = \sqrt{p_1^2 + p_2^2 + \cdots + p_{3N}^2} = \sqrt{2mE}$$

Now it is important to remark that the volume enclosed by a many-dimensional sphere is practically concentrated in an extremely thin surface shell. Indeed if we write for the total volume

$$J = \text{const.} \cdot r^N$$

a surface layer of small thickness Δr has the partial volume

$$\Delta J = \text{const.} \cdot n \cdot r^{n-1} \cdot \Delta r$$

the ratio being

$$\frac{\Delta J}{J} = n \cdot \frac{\Delta r}{r}$$

As n is of the order 10^{24}, ΔJ is comparable to J even if the thickness Δr is only the 10^{24}th part of r. Therefore we can take the whole volume of the p-sphere instead of a very thin surface layer.

According to a well known calculation the volume of such a hypersphere turns out as

$$\Phi'_{\text{mom}} = \frac{\pi^{\frac{3N}{2}}}{\left(\dfrac{3N}{2}\right)!} \cdot P^{3N}$$

The total phase volume is now:

$$\Phi' = \Phi'_{sp} \cdot \Phi'_{\text{mom}} = v^N \cdot \Phi'_{\text{mom}}$$

If we take classical mechanics to the last consequence, there is no sense in substituting an infinitesimally thin sheet for a volume. But with Heisenberg's famous principle of indeterminacy quantum mechanics has brought a certain latitude $(\Delta p, \Delta q)$ in the fixation of momenta and coordinates. For one degree of freedom we have for instance

$$\Delta x \cdot \Delta p_x = h = \text{Planck's constant}$$

For $3N$ degrees of freedom the elementary volume of phase space is therefore not infinitesimal but equals h^{3N}.

We have to measure the phase volume in this unit (Sackur-Tetrode), and the surface layer has a small but finite thickness.

So we find:

$$\Phi'' = \frac{\Phi'}{h^{3N}}$$

as a natural measure of phase volume. This is not the end. Another quantum phenomenon enters: the *indistinguishability* of the atoms. If we interchange the nth and the mth atom, the representative point changes place in the surface layer if the atoms are considered as distinct. But if they are indistinguishable, both points represent the same physical reality and the accessible phase volume consequently is reduced. We can exchange every atom with every other in $N!$ ways and the phase volume that really counts, is:

$$\Phi = \frac{\Phi''}{N!}$$

Entropy is now defined as being proportional to the logarithmic measure of the accessible phase volume, the constant factor being Boltzmann's

$$k = \frac{R_m}{N}$$

So we obtain the following formula for the absolute entropy:

$$s = k \cdot \ln \Phi = k \cdot \ln \left\{ \frac{v^N \cdot \pi^{\frac{3N}{2}} \cdot p^{3N}}{\left(\frac{3N}{2}\right)! \cdot h^{3N} \cdot N!} \right\}$$

As N is an extremely great number we can use Stirling's formula with good approximation:

$$\ln n! = n \cdot \ln n - n$$

and after some simple algebraic manipulation we find:

$$\frac{s}{R_m} = \ln v + \ln \pi^{3/2} + \ln \left(\frac{2mE}{h^2}\right)^{3/2} + \frac{5}{2} - \frac{5}{2} \cdot \ln N - \frac{3}{2} \cdot \ln \frac{3}{2}$$

Substituting p (pressure) and T for v and $E = \frac{3}{2} R_m \cdot T$ we gain equation (39) of the text.

<div align="right">J. ACKERET</div>

<div align="center">LITERATURE</div>

As entropy is treated in many books on physics, physical chemistry and gas-dynamics, there is no need for a general survey of literature. Therefore only a few books and papers immediately connected with the substance of this lecture are cited.

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