

A Sketch for a History of EARLY THERMODYNAMICS

By *E. Mendoza*

ACCOUNTS of the origins of the first and second laws of thermodynamics follow a fairly standard pattern. The caloric theory of heat, we are told, assumed that heat was a fluid endowed with a number of properties, among them indestructibility. The cannon-boring experiments of Rumford (1798) and the ice-rubbing experiment of Davy (1799) destroyed the basis of the caloric theory because they showed that heat could be created by the expenditure of work. A full half-century elapsed, however, before Joule repeated and extended Rumford's experiments and measured the conversion factor J accurately with his paddle wheels. In the meantime (in 1824) Carnot formulated the second law of thermodynamics and drew many valid conclusions about the efficiency of heat engines though his ideas were based on the caloric theory. Kelvin came across Carnot's work, as rewritten by Clapeyron; he became convinced of its truth and because it was based on the caloric theory he found it difficult to accept Joule's results. However, by 1850 both Kelvin and Clausius had formulated the first and second laws as we know them now. In retrospect, the caloric theory of heat seemed to have been slightly ridiculous.

It seems to me that the pattern just sketched out is incorrect in many ways. It is particularly unfortunate that it should be so, for the discovery of the first law is an episode in the history of physics which can be studied by students as an example of the way that the great ideas of science have evolved.

The facts seem to be that the caloric theory did not reach its highest state of development till *after* the work of Rumford and Davy had (in our modern view) destroyed its very basis—indeed these same experiments were regarded by the physicists of the time as enrich-

ing the caloric theory, as filling in some of the missing details. Further, at its highest point, the caloric theory was sophisticatedly mathematical; the properties of the caloric fluid—the model behind the abstract mathematics—were rarely stressed and were indeed usually regarded as irrelevant. The mathematics predicted most of the correct results, and where the equations differed in essential ways from our own correct ones, there were reputable experimental results to support them. Finally, when the modern two laws of thermodynamics were formulated, the whole of the mathematical apparatus of the caloric theory was taken over. The attitudes of modern thermodynamics, with its jargon of perfect differentials and of partial differential coefficients, were inherited from the previous epoch. Perhaps this account implies that science does not progress tidily, but I think it is worthwhile giving.

The Two Theories of Heat

THE two hypotheses—that heat was a mode of motion of the particles of bodies, and that heat was a substance—had their origins in two quite different sets of observations. The obvious production of heat by friction gave rise to the one; indeed the mechanical theory of heat is by far the more ancient of the two. On the other hand, the idea of the conservation of heat in calorimetric experiments was only conceived in the eighteenth century. Joseph Black had defined several interlocking quantities—temperature, specific heat, latent heat, and quantity of heat—and had at the same time postulated the conservation in a thermal mixing process. Then with the rise of the atomic theory and the discovery of oxygen, many quantitative things could be explained by the idea that heat was a gas of indestructible atoms. The conservation of heat was assured on this model; further, the atoms of caloric could enter into chemical combination with the atoms of a sub-

E. Mendoza is senior lecturer in physics at the Physical Laboratories of Manchester University in England.

stance (when the heat was latent) or be free (when the heat could affect a thermometer). In Lavoisier's view, the caloric atoms were an essential constituent of oxygen and their release gave rise to the heat of combustion. Thus, in contrast to the old-fashioned dynamical theory, the caloric theory of heat used a few basic ideas of the up-to-date atomic theory and could explain beautifully the facts of combustion and calorimetry.

Yet the French physicists and chemists always kept it firmly in mind that there were two hypotheses which at the time were equally valid. Every statement of the theory of heat invariably placed the two theories side by side, usually with a statement that the two, though seemingly quite different, must be only varied aspects of the same underlying cause. There was no obvious contradiction between the two hypotheses. One of the earliest statements of this kind comes from the *Memoir on Heat* written by Laplace and Lavoisier in 1786. They state:

We will not decide at all between the two foregoing hypotheses. Several phenomena seem favourable to the one, such as the heat produced by the friction of two solid bodies, for example; but there are others which are explained more simply by the other—perhaps they both hold at the same time. . . . In general, one can change the first hypothesis into the second by changing the words "free heat, combined heat and heat released" into "*vis viva*, loss of *vis viva* and increase of *vis viva*".

Here we may note that the words "heat" and "caloric" were always regarded as interchangeable and that the *vis viva*—the living force—of a system of particles was twice the kinetic energy. The identity of the two theories is therefore explicitly stated. This statement, though an early one, is typical of all those written by French scientists for the next sixty years.

This means that the French scientists did *not* consider that the issue was straightforward—that either the caloric theory was true or the dynamic theory; on the contrary, they held that both were true. Thus it was that Rumford's work had very little impact on them. For example, one of his papers described how he measured the density of caloric by weighing some ice and then reweighing it after it had melted, concluding that the density of caloric, if it existed at all, was negligible. Subsequent accounts of the caloric theory therefore incorporated the additional statement that the mass of the caloric atoms was very small—like electricity. Further, in his other experiments, Rumford showed that the supply of heat produced by friction was apparently inexhaustible. Subsequent statements of the caloric theory therefore included the additional statement that the number of caloric atoms which could be rubbed off by friction was negligible compared with the number actually inside a body—like frictional electricity.

It is usually said that the first symptom of the inadequacy of any theory is observed when each new experiment demands that a new hypothesis be added. From our modern viewpoint these additions to the caloric theory were of just this kind. But from the con-



Pierre Simon Laplace, who dominated the French Academy of Sciences in his later years.

(Culver Pictures, Inc.)

temporary point of view they were extremely reasonable statements. Far from killing the caloric theory, Rumford's experiments added to the understanding of it.

The British scientists, in contrast to the French, were mostly interested in chemistry and atomic theory and therefore adopted the caloric view uncritically. Rarely were the two theories placed side by side for fair comparison in their writings. Even Davy used caloric concepts when he found them convenient. But it was in France that the most significant developments were made, in the decade from 1810 to 1820.

Perfect Differentials

THE mathematical version of the caloric theory gradually evolved in a series of papers by Laplace and Poisson. By 1818, the theory of heat was usually cast in the following form—the quotation is from a brief introductory paragraph in a paper by Poisson:

Let ρ be the density of a gas, θ its centigrade temperature, p the pressure which it exerts on unit area, the measure of its elasticity: then one has

$$p = a\rho (1 + \alpha\theta)$$

where a and α are two coefficients. . . . The total quantity of heat contained in a given weight of this gas, in a gram for example, cannot be calculated: but one can consider the excess of this quantity over that

contained in a gram of gas at an arbitrarily chosen pressure and temperature. Designating this excess by q , it will be a function of p , ρ and θ , or simply of p and ρ since these three variables are connected by the preceding equation; thus we have

$$q = f(p, \rho)$$

where f indicates a function whose form must be found.

By defining q as the excess quantity of heat over an arbitrary zero, Poisson avoided the difficulty that the absolute quantity of heat was much greater than what could be rubbed off by friction. By stating that q was a unique function of the thermodynamic coordinates—for this is the significance of the second equation—he summarized tersely many experimental facts, for example the equality of the latent heats of boiling and condensation, or what we should now call the uniqueness of the enthalpy as a function of pressure and temperature.

We may put this analytical statement into perspective by stating for comparison the starting points of elementary modern thermodynamics. In such treatments, we first restrict ourselves to systems which have single-valued equations of state, and then we postulate that there are two independent heat-like quantities which are single-valued functions of the thermodynamic coordinates—we usually choose the internal energy U and the entropy S , which can be expressed as $U(p, V)$ and $S(p, V)$. In short, the caloric theory differed from our own approach in that it recognized only one law of thermodynamics—one heat function $q(p, V)$ —where we have two.

Laplace and Poisson then used this analytical law to calculate the temperature rise of a gas when it was compressed adiabatically, to explain the experimental results of Clément and Désormes. Since q was a unique function of p and V , dq could be expressed (in modern notation) as

$$\begin{aligned} dq &= (\partial q / \partial p)_v dp + (\partial q / \partial v)_p dv \\ &= (\partial q / \partial T)_v (\partial T / \partial p)_v dp + (\partial q / \partial T)_p (\partial T / \partial v)_p dv \\ &= C_v \cdot V \cdot dp / R + C_p \cdot p \cdot dV / R \end{aligned} \quad (1)$$

putting the specific heats as dq/dT with suitable subscripts, and substituting $pV = RT$. Assuming that the specific heats were constant with temperature the equation was then integrated to give

$$q = f(pV^\gamma). \quad (2)$$

In an adiabatic change the total quantity of heat did not alter; hence such a change was governed by the law

$$pV^\gamma = \text{constant}.$$

It is well known that Laplace corrected Newton's expression for the velocity of sound, assuming that the wave motion was adiabatic instead of isothermal; this was his method of calculation. Thus the assumption that the quantity of caloric was a unique function of the pressure and volume of a gas allowed the velocity of sound to be correlated with direct measurements of the ratio γ . It was something of a triumph and was ob-

viously proof of the correctness of that basic assumption.

It took later scientists many years to realize that this same result, that the ratio of adiabatic and isothermal elasticities of a gas is equal to the ratio of two suitably defined specific heats, follows straight from the definitions, and results from any physical model of heat whatever.

Pistons and Cycles

THE mathematical approach to thermodynamics is essentially the same as that which we use today. The other approach, using cycles of operations with frictionless pistons, was evolved by Sadi Carnot. He was capable of an extraordinary precision of thought and was no mean mathematician. But his single published work, *Reflections on the Motive Power of Fire* (1824), was conceived as a popular book for engineers, to stimulate them into designing better heat engines. Thus all his proofs and theorems are based on the actions of engines, however idealized. His concept of the cycle of operations was consciously based on the assumption of the uniqueness of the quantity of heat as a function of coordinates; he had probably been taught that theorem at his Army Engineering School, the Ecole Polytechnique, where Laplace and Poisson were instructors.

In perspective, we can see that this pictorial approach had a comparatively short life. After Clausius used it in 1865 to derive the concept of entropy and thereby show that the two laws of thermodynamics could be expressed in the same way as the old caloric theory, the more mathematical approach became dominant once more; pistons and cycles were relegated to teaching textbooks.

Experimental Proofs

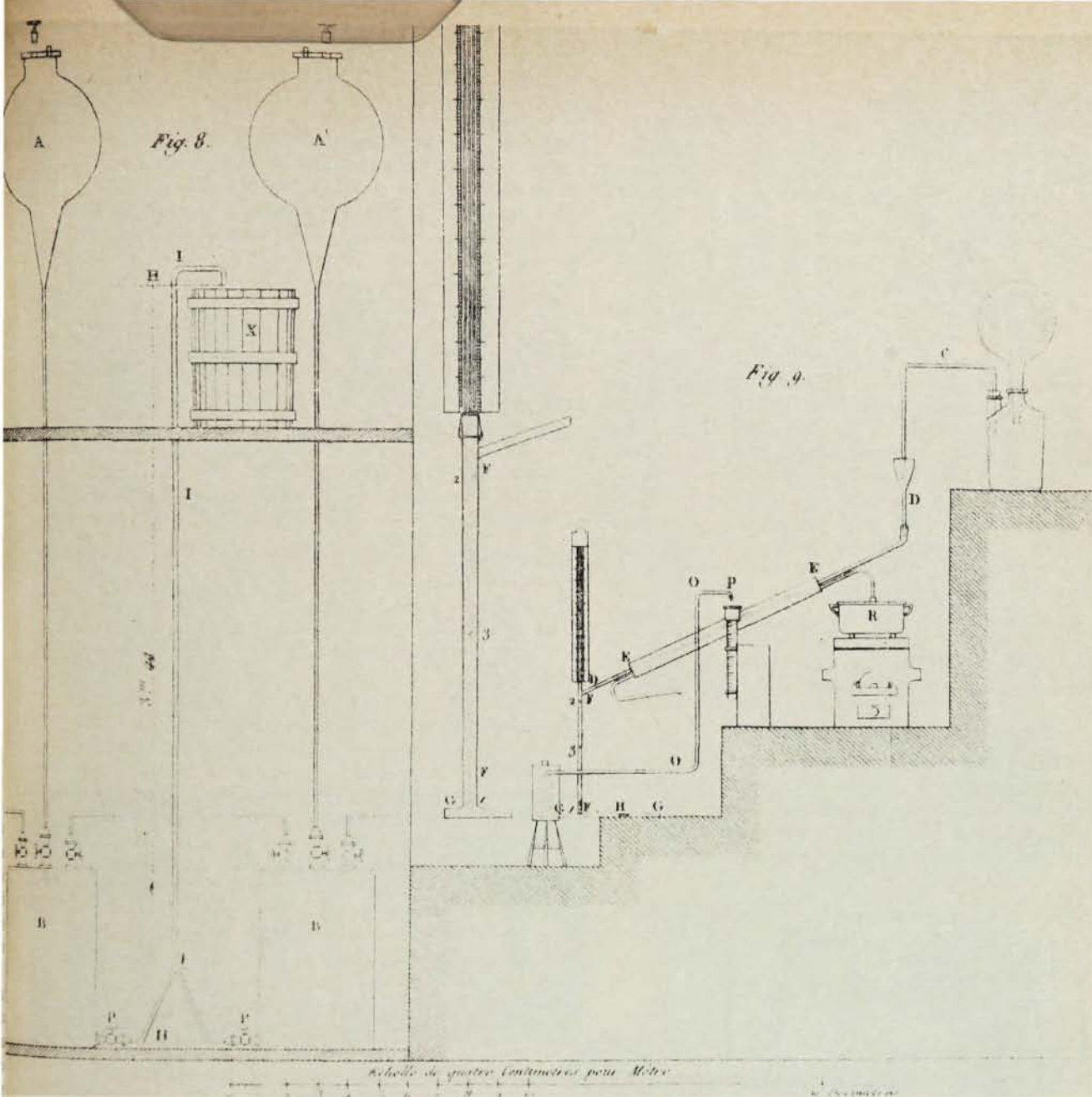
THE rise of temperature of a gas when it was compressed suddenly would be easily explained on the model that caloric itself was atomic—the heat atoms were squeezed out from the gas atoms “like water from a sponge”. This qualitative idea was however given quantitative expression; it followed from equation (2) above.

Laplace made the assumption that the function f was the simplest possible—that it was linear. Thus the heat content of a gas could be written

$$q = A + B \cdot T \cdot p^{(1-\gamma)/\gamma}$$

where A and B were constants, p and T being chosen

Delaroché & Berard's apparatus. Gas contained in B and B' was driven through apparatus by heads of water in vessels A and A' in the room above. Normally it exchanged heat in the little spiral in the other half of diagram; the apparatus is, however, shown arranged for finding the heat capacity of the spiral by forcing hot water through it.



here as the appropriate variables. The specific heat C_p followed by differentiating with respect to T , showing at once that it was proportional to the pressure raised to the power $(1 - \gamma)/\gamma$. Putting $\gamma = 1.4$, the specific heat of air should decrease approximately as the cube root of the pressure.

Carnot on the other hand deduced a number of theorems leading to a slightly different result—his method gave the form of the function explicitly and showed that the heat content and the specific heat decreased with the logarithm of the pressure. But both Carnot's and Laplace's expressions, though different in detail, predicted decreases of specific heat with pressure, showing that a rise of pressure should release heat and so cause a rise of temperature. They were the quantitative expressions of the "squeezing out" process.

The experimental measurements of Delaroche and Bérard of the specific heats at atmospheric pressure of a large number of gases were performed in 1812 and deservedly won a prize award by the Institut de France. Their apparatus was beautifully designed, their techniques were highly developed, and most of their results were accurate. Unfortunately they also performed two measurements of the specific heat of air at one value of the pressure slightly above atmospheric—to be precise, at 1006 mm pressure. They found that for this 30% increase the specific heat of unit mass of air was reduced by about 10%, which agreed almost exactly with Laplace's prediction. This observation remained for years one of the cornerstones of the whole caloric theory.

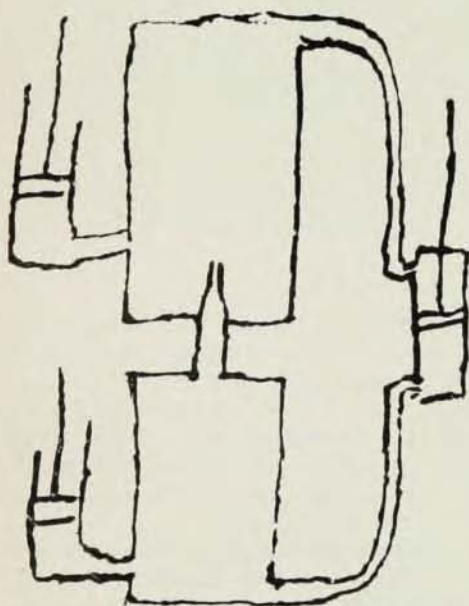
Carnot later compared the same observations with

his own expression and concluded that the coefficient of the $\log p$ term was small. In 1837, von Suerman in Germany performed measurements on air at *reduced* pressures, finding that Carnot's formula (or more precisely Clapeyron's version of the same expression) fitted better and that Laplace's assumption was not correct. But everyone was agreed that there *was* a variation of specific heat, in conformity with the predictions of the caloric theory.

Thus by the late 1830's a considerable body of experimental results had been accumulated and an advanced mathematical technique had been evolved in support of the caloric theory. At the same time, these decades were alive with speculation about the dynamical theory of heat. Claims have been advanced on behalf of several people as the real originators of the First Law—but few of these ever wrote down an equation or quoted numbers other than isolated estimates of J which proved nothing. Even Mayer's brilliant intuitions were largely concerned with qualitative speculations about the conservation of energy in different forms; there was little that was quantitative and even that could be explained on existing theories. In Poisson's phrase, the undulatory theory of heat was sterile.

Carnot and the First Law

THE dynamical theory implied that the heat content q was not a unique function of pressure and temperature and that the single law of thermodynamics was wrong. But this essential point was still not recognized by all physicists. Perhaps they took refuge in the



A sketch taken from Carnot's private manuscript notes (the original is one inch high), showing a proposed experiment on free expansion of gases. It was not until 25 years had elapsed that Joule and Thomson proposed and performed this experiment.

postulate that the quantities of heat so evolved were small compared with the total so that the error of the assumption was small; perhaps they did not believe that the supply of heat produced by friction was really inexhaustible. At any rate, it is astonishing to find a person as critical as Clapeyron writing (in 1834) only two or three pages before explicitly stating the uniqueness of the heat function:

It follows that a quantity of mechanical action and a quantity of heat which can pass from a hot body to a cold body are quantities of the same nature, and that it is possible to replace the one by the other; in the same manner as in mechanics a body which is able to fall from a certain height and a mass moving with a certain velocity are quantities of the same order, which can be transformed one into the other by physical means.

Clapeyron was discussing the functioning of heat engines, not the nature of heat, when he wrote this paragraph, but the implication was nevertheless quite clear. The opinion of Laplace and Lavoisier, that there was no conflict between the two theories of heat, was still held.

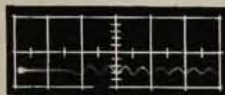
Possibly the only person who grasped the essential conflict was Carnot himself. In fact he occupies a special position in any history of the subject because, though he only published the one short book on heat engines, some notebooks of his have been preserved in which he mused about the shortcomings and improbabilities of the caloric model, and gradually groped toward the equivalence of heat and work. These notes constitute a revealing record of the objections which could at that time be raised against the dynamical theory. Mostly they stem from the fact that there was no clear picture of the structure of atoms or of solids, so that the nature of the thermal agitation of atoms in solids could not be imagined. For example, Carnot states that if heat is what we now call energy then the fact that the whole universe cannot be imagined to run down must imply (on the dynamical theory) that atoms cannot touch one another; for if they did touch there would be friction and the heat vibrations would die down. In that case he was unable to visualize what forces could hold the atoms in position in a solid if they were not touching. Any forces would have to act through an ether; since an ether had to be a fluid, it too had to be atomic in structure, so the difficulty could not be solved. Finally, however, he explicitly stated the equivalence of heat and work, leaving the question of the microscopic picture unsolved. He estimated J quite accurately.

A careful examination of these notebooks together with the *manuscript* of Carnot's book on heat engines and the published version of it shows that he had started on this train of speculation about the First Law at the same time as he was writing about the Second. Certainly by the time he came to correct the proofs of his book he had realized that the very basis of all his theorems and demonstrations was wrong. For example,

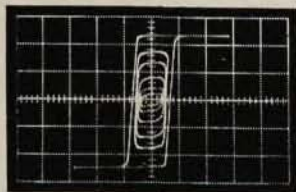


You can do **MORE** with the
NEW TEKTRONIX C-12 CAMERA
than you can with any other
Oscilloscope Camera

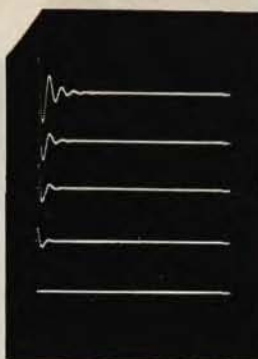
...picture this



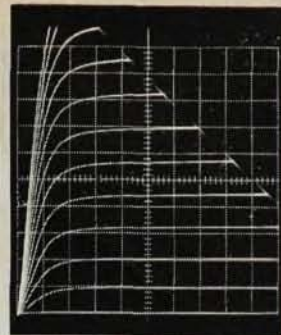
1 KMC damped oscillation
(single shot at 2 nsec/cm).



Typical hysteresis loops (multiple
exposure of varying amplitudes).



Damped sine wave (multiple ex-
posure using all 5 detent
positions).



Family of characteristic curves
(for NPN transistor).

...like this



One-hand portability



Lift-on mounting



Swing-away hinging



Comfortable viewing —
with or without glasses

...only with this C-12 CAMERA

The C-12 Camera combines flexibility with simplicity. It offers you new convenience in undistorted viewing and direct recording of oscilloscope traces.

Here's why:

You can use Polaroid* or any conventional film.

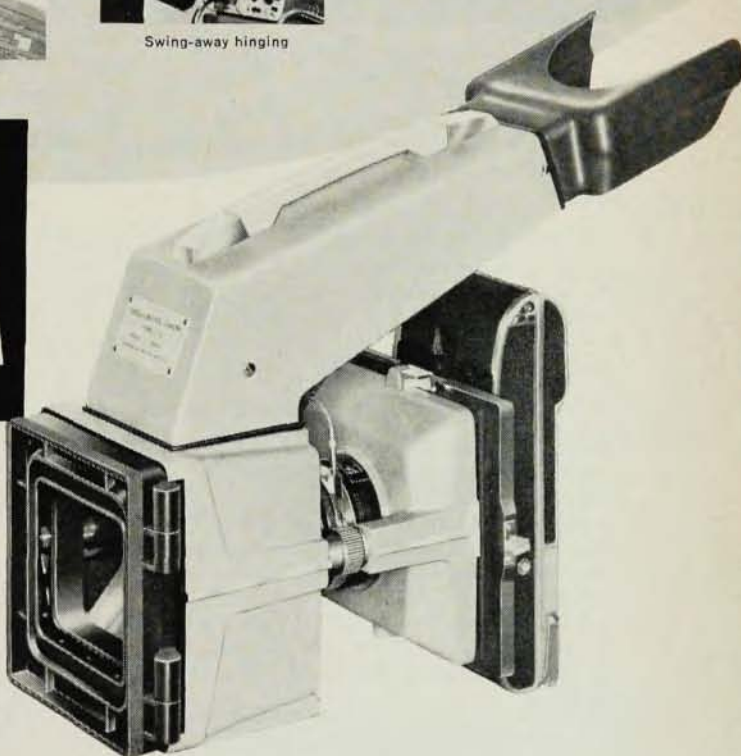
You can use the unique sliding back, adjustable to horizontal or vertical. On this sliding back, you can interchange the par-focal, film-holding backs, lock them securely in 5 detent positions, also rotate them thru 90° increments (with the long axis of the film horizontal or vertical).

You can choose from 8 easily-interchangeable lenses — in varying object-to-image ratios and maximum aperture to f/1.5. The lenses are housed in uniform, pre-focused, calibrated mounts with keyed threads — so the shutter-speed and diaphragm-opening controls always appear at the same accessible position on the camera.

C-12 CAMERA \$500

Includes: f/1.9 Lens (with 1:0.9 object-to-image ratio) complete with cable release, Focusing Back, Polaroid® Back, and Minute Timer.

*Registered by Polaroid Corporation.



For more information about these and other features of the new C-12 Camera . . . and the many accessories designed for specialized applications . . . call your Tektronix Field Engineer.

Tektronix, Inc.

P. O. Box 500 • Beaverton, Oregon

Phone MIltchell 4-0161 • TWX—BEAV 311 • Cable: TEKTRONIX

TEKTRONIX FIELD OFFICES: Albuquerque, N. Mex. • Atlanta, Ga. • Baltimore (Towson, Md.) • Boston (Lexington, Mass.) • Buffalo, N.Y. • Chicago (Park Ridge, Ill.) • Cleveland, Ohio • Dallas, Texas • Dayton, Ohio • Denver, Colo. • Detroit (Lathrup Village, Mich.) • Endicott (Endwell, N.Y.) • Greensboro, N.C. • Houston, Texas • Indianapolis, Ind. • Kansas City (Mission, Kan.) • Los Angeles Area (East Los Angeles, Calif., Encino, Calif. • West Los Angeles, Calif.) • Minneapolis, Minn. • New York City Area (Albertson, L.I., N.Y. • Stamford, Conn. • Union, N.J.) • Orlando, Fla. • Philadelphia, Pa. • Phoenix (Scottsdale, Ariz.) • Poughkeepsie, N.Y. • San Diego, Calif. • San Francisco (Palo Alto, Calif.) • St. Petersburg, Fla. • Syracuse, N.Y. • Toronto (Willowdale, Ont.), Canada • Washington, D.C. (Annandale, Va.).

TEKTRONIX ENGINEERING REPRESENTATIVES: Hawthorne Electronics, Portland, Oregon • Seattle, Washington. Tektronix is represented in twenty overseas countries by qualified engineering organizations. In Europe please write Tektronix Inc., Victoria Ave., St. Sampsons, Guernsey C.I., for the address of the Tektronix Representative in your country.



James Prescott Joule as he appeared at the time of his classic experiments.

concerning his theorem that the motive power of heat is independent of the working substance, he originally wrote:

The fundamental law which we proposed to confirm seems to us to have been placed beyond doubt. . . . We will now apply the theoretical ideas expressed above to the examination of the different methods proposed up to now for the realisation of the motive power of heat.

But in the printed version he altered this to:

The fundamental law which we proposed to confirm seems to us however to require new verifications in order to be placed beyond doubt. It is based on the theory of heat as it is understood today, and it should be said that this foundation does not appear to be of unquestionable solidity. New experiments alone can decide the question. Meanwhile we can apply the theoretical ideas expressed above, regarding them as exact, to the examination of the different methods proposed up to now for the realisation of the motive power of heat.

He had realized that the Law $q = f(p, V)$ was no longer true and this destroyed the idea of the cycle of operations. He had discovered the First Law to the exclusion of the Second. The essential step of postulating that there were two independent laws was too difficult to take.

The point of this episode is that we know that Sadi Carnot was a reserved and taciturn man, something of a perfectionist. It is therefore extraordinary that he allowed the publication of his book to proceed after he

had begun to doubt his own methods. We can only be thankful that this is what he did.

(It is unfortunate that something of a "mystique" has grown up around Carnot's writings. From his use of the word "caloric" it has been deduced that he had a pre-vision of the concept of entropy. However, the words he used were merely interpretations of the equations he wrote down, and it is clear that together with those written down by all other contemporary physicists, these equations were only true by coincidence.)

Joule's Experiments

JOULE'S first research (started when he was aged 19) was on the design of electric motors. Though these early machines were spidery little affairs hardly recognizable as the forerunners of those familiar to us, Joule envisaged them as the prime movers of the future. At first he thought of them as possible perpetual motion machines, but the i^2R formula for the heating effect of a current was an early result of the investigations. He also found that the attractive force of an electromagnet was proportional to i^2 , and the similarity of the formulas led him to think of a connection between mechanical and heating effects. Eventually he was led to do a remarkable experiment with a simple dynamo whose armature was immersed in a rotating vessel full of water. With the armature stationary and connected to a battery he measured the heating; by rotating the armature he superimposed a second current and found that he could create or *destroy* heat according to the sense of rotation. The change of heating was proportional to the work done in rotating the armature. This experiment, in Joule's view, showed conclusively that the accepted theory of heat was wrong and he started at once on a series of experiments of great variety to prove his point of view.

The electrical experiments had given $J = 4.60$ joules/calorie in our modern units. The heating of water forced through narrow holes in a piston gave 4.25 units; heating by the friction of two solid surfaces rubbing beneath water or mercury gave the same value. He pumped air into a cylinder to 22 atmospheres and measured the heat produced in the cylinder; comparing this with the pV term, J emerged as 4.60 units. Then he allowed the gas to escape slowly—the cylinder cooled and J was found to be 4.38 units. But when the gas escaped slowly from the high-pressure cylinder into another, without performing external work, the cooling of one cylinder was equal to the heating of the other so that there was no net production of heat. These experiments took him five years to do—from 1843 to 1848.

After these experiments were finished Joule allowed himself to speculate on the philosophical and other aspects of the theory. It was, however, the quantitative aspect of his work which eventually carried conviction. The conversion factor was the same within 15% however the work was performed: electromagnetically, by solid or liquid friction, or by the changes of volume of a gas. This could not be plausibly explained on any



Out of this
New England farm house
will grow

A UNIQUE NEW RESEARCH CENTER

The Center's program and facilities have been planned to provide maximum flexibility for a research effort that will cover an unusually broad scientific spectrum:

Materials Sciences

Solids Physics, Mechanics, Magnetism and Dielectrics

Radiation Sciences

*Microwave Physics, Infrared, Optics,
Propagation and Communication, Energy Conversion*

Applied Mathematics and Theoretical Physics

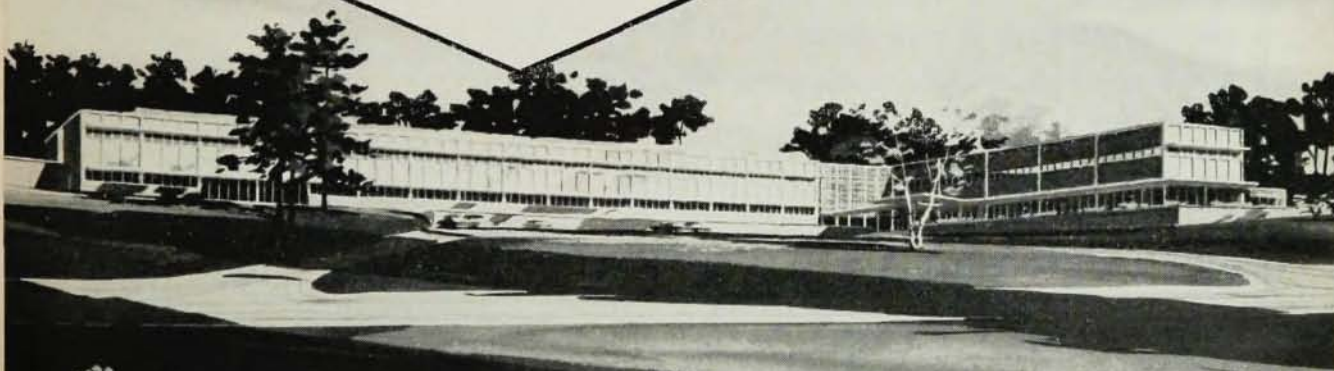
Earth and Life Sciences

*Oceanography, Geophysics, Physiological, Neurological
and Zoological Systems, Human Factors*

Systems Research

*Synthesis/Analysis/Evaluation involving new principles
for systems 5 to 15 years in the future.*

We are now forming the nuclei of these research groups which will grow in importance and scope as the Center itself grows. Especially qualified scientists in the above fields are invited to write to: Frederick M. Swope, Jr., Sperry Rand Research Center, North Road, Sudbury, Massachusetts.



SPERRY RAND RESEARCH CENTER

SUDBURY, MASSACHUSETTS

OUTSTANDING ASSIGNMENTS for OUTSTANDING SCIENTISTS at the OPERATIONS EVALUATION GROUP of M. I. T.

Seeking scientists who have the ability and imagination to apply their broad knowledge with *originality* in the field of research, the Operations Evaluation Group of the Massachusetts Institute of Technology offers stimulating career opportunities to scientists with advanced degrees in mathematics and the physical sciences.

For over 18 years, OEG has served as advisor to the Office of Chief of Naval Operations and the operating fleet. Engaged in both conventional operations research and in the solution of complex problems far out of the realm of the ordinary, OEG has the responsibility for conducting research that cuts laterally across many scientific disciplines.

If you have the interest and the creative ability to apply your basic research findings to the solution of problems that are vital to the Navy and the national security, you are invited to write to OEG. Working in a professional atmosphere and exchanging stimulating ideas with colleagues of the same discipline, you will find a rewarding opportunity for increased scientific stature and personal growth.

OPERATIONS EVALUATION GROUP

An Activity of the Massachusetts
Institute of Technology

Department H
Washington 25, D. C.

Physicists • Physical Chemists • Mathematicians
Economists • Electronics Engineers

caloric model. Two years after this series of experiments he measured J accurately by stirring water with paddle wheels, but these experiments were relatively unimportant.

Joule wrote a number of papers about his work but till almost the end of this important epoch he was intellectually quite isolated. The commonest objection to his theory was that it all depended on temperature rises of a few hundredths of a degree, which could hardly be significant enough. But two papers, Grove's "On the Correlation of Physical Forces" and Helmholtz' "On the Conservation of Force" helped to prepare the intellectual climate for the acceptance of Joule's theory.

Clapeyron's paper on the motive power of heat had been published in England in 1837, in Taylor's *Scientific Memoirs*, a journal which specialized in translations of foreign papers; Joule was familiar with it. By 1844 he was already confident enough to reject Clapeyron's description of the cycle of operations in the steam engine. He flatly contradicted the view that the passage of heat from boiler to condenser was sufficient to produce work. For the first time, the issue appeared to be clear—either Carnot or Joule was right.

Synthesis

WILLIAM THOMSON (Lord Kelvin) seems to have been the key figure in the synthesis of the two theories. He worked in Paris as a sort of research assistant in Regnault's laboratory in 1845 and there learned of Clapeyron's paper. He proposed the work scale of temperature wholly in caloric terms. Though he became a close friend of Joule, had a deep respect for his experiments, and always quoted his opinion, he could not accept the newer theory. His principal objection was that there were no examples of the reverse conversion of heat into work. Joule wrote to him that the Peltier effect could provide one such process, but it took Thomson four years to understand this remark. In 1849, Thomson published an account of Carnot's theory. There were many references to Joule's work but the "ordinarily received and almost universally acknowledged" principle that heat was conserved in a cycle of operations was still the accepted basis. Later in the year William's brother James published theoretical predictions based on Clapeyron's equation for the lowering of the freezing point of water by pressure; experiments confirmed the predictions—and hardened Thomson's conviction that Carnot's methods and the theory it was founded on were true.

The change of viewpoint happened quite suddenly. Probably Clausius was the first to see that there were two *independent* principles. In 1850 he wrote:

It is not at all necessary to discard Carnot's theory entirely, a step which we certainly would find it hard to take since it has to some extent been conspicuously verified by experiment. A careful examination shows that the new method does not contradict the essential principle of Carnot, but only the subsidiary statement that *no heat is lost*, since in the production of work it

Whatever radiation detector electronics system you employ

/insist on
HARSHAW SCINTILLATION CRYSTAL
radiation
detectors

NaI(Tl)
CsI(Tl)
LiI(Eu)
Li⁶I(Eu)
NaI_{PURE}
CsI_{PURE}
Anthracene
Plastic Phosphors

HARSHAW
Mounted NaI(Tl) Scintillation
CRYSTALS / *Standard line*
Matched window line
Integral line

THE HARSHAW CHEMICAL CO.
1945 E. 97TH STREET • CLEVELAND 6, OHIO

- INVESTIGATION OF PHYSICAL PHENOMENA
- BASIC SENSORS
- APPLICATIONS OF NEW MATERIALS & TECHNIQUES
- INSTRUMENTATION SYSTEMS

EXPERIMENTAL PHYSICISTS AND PHYSICAL CHEMISTS

for expansion of a group concerned with the development of basically new techniques and with the solution of advanced instrumentation and measurement problems.

The nature of the problems solved by this group varies widely, so that the principal qualifications required are an inquiring intelligence and a sound background in physics, physical chemistry, and mathematics. Positions are available for both recent graduates and experienced people capable of accepting primary responsibility for specific programs. Present programs include work in the following areas:

- SPACE PHYSICS
- MEASUREMENT OF GEOPHYSICAL AND METEOROLOGICAL PARAMETERS IN AND ABOVE THE ATMOSPHERE
- VISIBLE AND ULTRAVIOLET RADIATION
- NEW TYPES OF ELECTRON MULTIPLIERS
- MASS SPECTROMETRY

Final engineering and packaging are normally carried out by other groups in the organization.

The work is stimulating and satisfying in comfortable and pleasant surroundings in suburban Detroit.

Opportunities for advanced study.

Write or wire A. Capsalis,
Research Laboratories Division,
The Bendix Corporation
Southfield, Michigan

Research Laboratories
Division SOUTHFIELD, MICHIGAN



may well be that at the same time a certain quantity of heat is consumed and another quantity transferred from a hotter to a colder body, and both quantities of heat stand in a definite relation to the work that is done.

At about the same time, Thomson saw the light. Some theoretical work by Rankine on the adiabatic expansion of steam, together with the observation that high-pressure steam escaping from a safety valve does not scald because it comes out dry, abruptly convinced Thomson that steam could be heated by friction. It is difficult to see why this should suddenly have appeared so conclusive to him when Joule had been using the same concepts for seven years. However that may be, Thomson soon embarked on a long paper, stating the two laws explicitly and independently, one ascribed to Joule and the other to Carnot and Clausius. The introductory historical account was of course quite biased and incomplete; it was the forerunner of those which are usually written today. This paper, with the appendixes which were added at various times, included the thermoelectric relations and a discussion of elasticity.

In 1850 Clausius wrote that the "internal work U "

has the properties which are commonly assigned to the total heat, of being a function of V and T and of being therefore fully determined by the initial and final conditions of the gas.

He treated U with the same mathematical techniques as Laplace and Poisson and Clapeyron had applied to q . The quantity $\Sigma dQ/T$ began to appear quite early in papers by Thomson and Clausius, but it was not till 1865 that Clausius deemed it worthy of special definition. He wrote:

We can say of it that it is the *transformation content* of the body, in the same way as we say of the quantity U that it is the *heat and work content* of the body

and coined the name entropy for it. The mathematical methods of the caloric theory were finally recovered; thermodynamics today still bears the impress of Laplace and Poisson, just as surely as electrostatics.

Conclusion

THE conventional description of the caloric theory, as a qualitative model of heat processes which had to be abandoned as soon as Rumford did his cannon-boring experiments, is obviously untrue. The difficulty encountered by the proponents of the dynamic theory of heat was that they had first to break the stranglehold of a glib mathematical formulation, a method which could make a sufficient number of correct predictions to give the illusion of being the whole truth. But probably this was a necessary stage in the development of the subject, since it did after all allow the formulations to be worked out. After that, there just remained the enormous intellectual difficulty of proposing two laws where instinct said that only one existed; when that was done the theory of heat was virtually complete.