

HEAT

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HEAT

A TEXT BOOK FOR COLLEGES
AND TECHNICAL SCHOOLS

BY

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~~FRANKLIN~~
PREFACE

THE authors have had in mind the following leading ideas in the preparation ~~of this text.~~

1. Undergraduate physics, to be interesting to students must, of course, be presented clearly and intelligibly, *and it must be analytical.*

2. A student must, as a rule, have a definite question in his mind if he is to read a text-book discussion willingly and effectively. Therefore the authors have arranged carefully considered groups of leading questions throughout this text.

3. The authors look upon numerical problems as a means for stimulating a questioning attitude on the part of a student, especially if the problems are stated clearly in physical terms and if the data as given are such as might easily be determined in the laboratory.

This text is a result of a very long development. Three rewritten editions of the first volume of Nichols and Franklin's *Elements of Physics*; then two rewritten editions by Franklin and MacNutt, and now this latest arrangement, which is to replace all of the earlier editions.

FRANKLIN AND MACNUTT.

December 11, 1922.

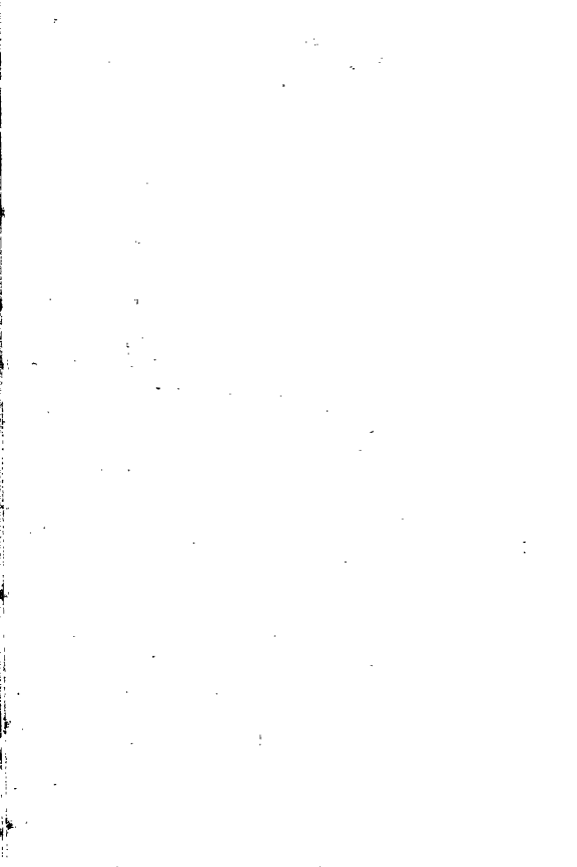


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HELPFUL REFERENCES AND IMPORTANT BOOKS ON HEAT AND THERMODYNAMICS

(a) BOOKS AND REFERENCES FOR COLLATERAL READING BY THE BEGINNER.

Heat, Poynting and Thomson. London: Griffen & Co., 1902.

Heat for Advanced Students, Edser. London: Macmillan & Co., 1899.

The Theory of Heat, Thomas Preston. London: Macmillan & Co., 1894.

(b) BOOKS ON THERMODYNAMICS.

Thermodynamics, Edgar Buckingham. New York: The Macmillan Co., 1900.

Thermodynamik, Max Planck. Leipsig, 1905. This book has been translated into English and into French.

Thermodynamics, by G. N. Lewis and Merle Randall. New York: McGraw-Hill Book Co., 1923.

(c) BOOKS ON THE ATOMIC THEORY AND PROBABILITY.

The Kinetic Theory of Gases, W. P. Boynton. New York: The Macmillan Co., 1904.

The Kinetic Theory of Gases, O. E. Meyer, translated by R. E. Baynes. London: Longmans, Green & Co., 1899.

Vorlesungen über Gas Theorie, Boltzmann. Leipsig, 1896.

See list of books on the electron theory in *Electricity and Magnetism*.

The Mathematical Theory of Probability, A. Fisher, translated by W. Bonyng. New York: The Macmillan Co., 1915.

(d) BOOKS APPLYING THERMODYNAMICS AND THE ATOMIC THEORY TO CHEMISTRY.

Theoretical Chemistry, W. Nernst, translated by R. A. Lehfeldt; new edition, revised by H. T. Tizard. Macmillan & Co., 1916.

Thermodynamics, by G. N. Lewis and Merle Randall. New York: McGraw-Hill Book Co., 1923.

Lewis and Randall's book is a good general treatise and also a good special treatise.

HELPFUL AND IMPORTANT BOOKS

An Introduction to the Principles of Physical Chemistry, E. W. Washburn. New York: McGraw-Hill Book Co., 1915.

The Phase Rule and its Applications, Alexander Findlay. Longmans, Green & Co., 1911.

Theory of Solution and Electrolysis, W. C. D. Whetham. Cambridge, 1902.

Physical Chemistry (3 Vols), Wm. C. McC. Lewis. London: Longmans, Green & Co., 1918.

The third volume of this treatise contains much interesting material relating to the atomic theory (including the electron theory and the quantum theory).

The great work in this field is by Willard Gibbs; see *Gibbs' Scientific Papers*, Vol. I. London: Longmans, Green & Co., 1906.

(e) BOOKS ON RADIATION AND RADIATION PYROMETRY.

Vorlesungen über die Theorie der Wärmestrahlung, Max Planck. Leipzig, 1913; third edition, 1919.

Special Pyrometry volume of Trans. Am. Inst. Mining and Metallurgical Engineers. New York, 1919.

(f) BOOKS APPLYING THERMODYNAMICS TO THE STEAM ENGINE.

Thermodynamics of the Steam Engine, C. H. Peabody. New York: John Wiley & Sons.

Technical Thermodynamics, Gustav Zeuner, translated by J. F. Klein, 2 Vols. London: Constable & Co., 1907.

(g) BOOKS ON THE MATHEMATICAL THEORY OF HEAT CONDUCTION.

The classical book on this subject is Fourier's *The Theory of Heat* (translated from the French).

An important book in this connection is *Fourier's Series and Spherical Harmonics*, W. E. Byerly. Boston: Ginn & Co., 1895.

(h) TABLES.

Tables Annuelles Internationales des Constants.

Physikalisch-Chemische Tabellen, Londolt-Börnstein.

Smithsonian Tables (Towle), publication No. 2269.

Steam Tables, Marks and Davis; see also Peabody's *Steam Tables*.

HEAT

CHAPTER I

TEMPERATURE AND THERMOMETRY

THERMAL EXPANSION

1. **Thermal equilibrium. Temperature.** When a substance (or a system of substances) is left to itself and shielded from all outside disturbing influences it settles to a quiet state or condition in which there is no tendency to further change of any kind. This quiet state is called a state of *thermal equilibrium*. For example, the various objects in a closed room or cellar settle to thermal equilibrium; when a piece of red-hot iron is thrown into a pail of water, the mixture, at first turbulent, becomes more and more quiet and finally reaches a state of thermal equilibrium.

A number of bodies which have settled to a common state of thermal equilibrium are said to have the same temperature. Thus a number of bodies left in a closed cellar have the same temperature.

What is the definition of temperature? No definition which involves a flow of heat nor any definition which involves the molecular or atomic theory is helpful at the beginning of a discussion of heat. It is much more useful at this stage to define temperature by stating where a temperature can be found; go to a cellar or a closed

room, or peep into a brick kiln ! Strictly speaking no substance has a definite temperature unless it is in thermal equilibrium.

A cellar is cool, a closed room is warm and a brick kiln is hot ; the measurement of temperature by a thermometer is familiar to nearly everyone, and it is common usage to speak of a cool cellar as having a *low temperature* and of a hot brick kiln as having a *high temperature*.

Although the various objects in a closed cellar are all at the same temperature, some of the objects may feel cooler than the others to the hand. In fact, a cold piece of metal feels cooler than a piece of dry wood at the same temperature. Likewise a piece of metal taken out of an oven feels hotter than a piece of wood taken out of the same oven.

2. Thermal expansion of gases. Boyle's Law and Gay Lussac's Law. Imagine a body of any gas (such as air, for example) in a cylinder with a piston arranged so that the volume (and pressure) of the gas can be changed at will. *When the temperature of the gas is raised, the pressure increases if the volume is kept constant, or the volume increases if the pressure is kept constant.*

Before considering changes of pressure with temperature when the volume of a gas is kept constant, or changes of volume with temperature when pressure is kept constant, it is helpful to consider the relation between volume and pressure when the temperature is kept constant. *When the temperature of a body of gas is kept constant, the pressure of the gas is inversely proportional to the volume of the space occupied by the gas.* That is to say,

$$p = \frac{k}{v}$$

$$\text{or } pv = k \dots\dots\dots(1)$$

in which p is the pressure of a given amount of gas, v is the volume of the space occupied by the gas, and k is a proportionality factor. This relation was discovered by Robert Boyle* in 1660 and it is called **Boyle's Law**.

Boyle's law is very nearly exact for such gases as hydrogen, nitrogen and oxygen at ordinary temperatures and at moderate pressures, but all gases deviate more or less from equation (1) especially at very high pressures and low temperatures.

A very interesting commercial situation grew out of the inexactness of Boyle's law several years ago in the natural gas districts of Ohio and Indiana. The gas companies piped the gas at high pressure, and sold it at so much per thousand cubic feet *reckoned at atmospheric pressure*, but the gas was actually measured at high pressure and its volume at atmospheric pressure was calculated by Boyle's law, and the volume so calculated was very considerably in excess of the actual volume of the delivered gas at atmospheric pressure. The excess charge by the gas companies on this basis ran up into the hundreds of thousands of dollars per year. The law now requires the volume at atmospheric pressure to be calculated from the measured volume at high pressure, not by Boyle's law, but by the actual experimentally determined law for natural gas under the given conditions.

Gay Lussac's Law. *All gases expand equally for the same rise of temperature.* The exact meaning of this statement may be made clear as follows: A number of cylinders contain equal volumes of gases in a cellar as shown in Fig. 1, and the cylinders are carried to a warm room (given rise of temperature). *Then, when the volume*

* See Boyle's memoir entitled *New Experiments touching the Spring of Air*, Oxford, 1660.

of each gas is allowed to increase so that its pressure may be the same as it was in the cellar, the increase of volume is the

in cool cellar

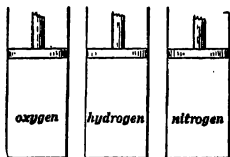


Fig. 1.

same for all, as indicated by the changed positions of the pistons in Fig. 2.

Following are two precise statements of Gay Lussac's law :

(a) When equal volumes of various gases are heated, they all expand equally (for the same rise

of temperature) if their pressures are kept constant.

(b) When various gases at the same initial pressure are heated and not allowed to expand, the pressure increase is the same for all for the same rise of temperature.

3. Expansion of liquids and solids. Liquids and solids, generally, increase in volume with rise of temperature,

or, if not free to expand, an enormous increase of pressure is produced by a rise of temperature.* Thus 1000 cubic centimeters of water at 20° C. becomes about 1000.19 cubic centimeters at 21° C. if it is in an open vessel and subject to normal atmospheric

pressure ; but if the water is kept from expanding,†

in warm room

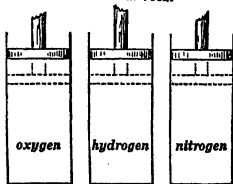


Fig. 2.

* Exceptions to this general rule are mentioned in Art. 11.

† It is not sufficient merely to have the water in a closed vessel, because the volume of the vessel increases with temperature—and also the increase of pressure of the water would stretch the vessel (cause it to become larger).

its pressure will rise to about 8000 "pounds" per square inch when its temperature is raised from 20° C. to 21° C.

The expansion of liquids and solids is discussed more at length in Arts. 11, 12 and 13.

4. The measurement of temperature. To measure a thing is to divide it into equal parts and count the parts, as so many feet of length, or so many seconds of time.* But one cannot divide a temperature into equal parts, and therefore, in a certain fundamental sense, temperatures cannot be measured. Indeed temperature can be measured only in terms of some temperature effect which is measurable, and the temperature effect which is most easily used for this purpose is expansion.

There is, however, an objection to the use of expansion for the measurement of temperature, because every substance has its own characteristic irregularities of expansion, so that there is an element of extreme arbitrariness in the choice of a particular substance in terms of whose expansion we agree to measure temperature. But, according to Gay Lussac's law, all gases expand alike, and therefore it would seem to be best to measure temperature by the thermal expansion of a gas, or by the increase of pressure† of a gas with increase of temperature.

* In many kinds of measurement the two distinct operations: (a) *dividing into equal unit parts*, and (b) *counting of parts*, are obscured by the use of more or less elaborate measuring devices, but every measurement does in fact consist of these two fundamental operations. In measuring a length by means of a *scale of inches* the operation of dividing into equal parts has been performed once for all by the maker of the scale, and the counting is also "ready-made" by the numbers stamped on the scale. In weighing a consignment of coal the operation of dividing into equal parts has been performed once for all by the maker of the *set of weights*, and the counting is also "ready-made" by the numbers stamped on the weights and on the balance beam.

† Volume being constant.

5. Air-thermometer temperatures and the air thermometer.

Let us agree to consider one temperature T' as twice as great as another temperature T when the pressure of a constant volume of air is twice as great at temperature T' as at temperature T . This agreement can be expressed by the equation

$$\frac{T'}{T} = \frac{p'}{p} \dots\dots\dots(2)$$

in which a constant volume of gas has pressure p at temperature T and pressure p' at temperature T' .

The *air thermometer* is an arrangement for measuring the ratio of two temperatures in accordance with equation (2). A glass or porcelain bulb contains a fixed quantity of dry air, and a small tube connects the bulb to a pressure measuring device. Of course the bulb expands slightly with rise of temperature, and the air in the connecting tube is not heated with the air in the bulb, but for the sake of simplicity let us assume that the volume of the bulb is constant and that the volume of the connecting tube is negligible.* Then to measure the ratio of two temperatures we place the bulb in the region where the temperature is T and measure the pressure p of the air in the bulb, then we place the bulb in the region where the temperature is T' and measure the pressure p' of the air in the bulb. Then $T'/T = p'/p$ according to equation (2).

Example showing the use of the air thermometer. The bulb of an air thermometer is placed in a steam bath at temperature S , and the pressure p' of the air in the bulb is measured; the bulb is then placed in ice water at temperature I , and the pressure p of the air in the bulb

* These two complications are always taken into account in precise air-thermometer measurements.

is measured. The ratio p'/p is found to be equal to 1.367, and, therefore, according to equation (2) we have

$$\frac{S}{I} = 1.367 \dots\dots\dots(3)$$

The steam bath is supposed to be pure steam (without admixture of air) in the presence of condensed droplets of water, and the pressure of the steam is supposed to be standard atmospheric pressure, namely, 760 millimeters of mercury. The temperature S under these conditions is called *standard steam temperature*; and the temperature I is called *ice temperature*.*

Further data needed before the value of any given temperature can be measured. It is evident from the above discussion that the air thermometer measures only the ratio of two temperatures. *To be able to measure the value of any given temperature with the air thermometer it is necessary to assign an arbitrary value to some fixed reference temperature* such as standard steam temperature S or ice temperature I . Instead of doing this, however, an arbitrary value of 100 degrees has been chosen for the *difference* ($S - I$). That is, by agreement, we have

$$S - I = 100^\circ \dots\dots\dots(4)$$

Therefore, solving equations (3) and (4), we get

$$I = 273^\circ \dots\dots\dots(5)$$

$$S = 373^\circ \dots\dots\dots(6)$$

Having thus determined the values of I and S (partly by choice, of course), the value of any temperature can be determined by measuring its ratio to I or to S by means of the air thermometer.

* The ice water is supposed to be pure. The pressure of the ice water need not be specified, because the ordinary variations of atmospheric pressure produce only imperceptible variations of the melting temperature of ice.

Temperature values measured in this way are called absolute temperatures, or, preferably, Kelvin temperatures, to distinguish them from temperatures reckoned upwards from the ice point. Thus $I = 273^{\circ}$ K., $S = 373^{\circ}$ K., and the temperature of melting lead is 600° K.

Remark. The air or hydrogen thermometer is very inconvenient and troublesome, and it is never used except in standardizing laboratories.

6. Formulation of Gay Lussac's law and Boyle's law.

When temperatures are measured by the air thermometer as above explained, then, as a matter of course, the pressure of a constant volume of *air* is proportional to its Kelvin temperature; and Gay Lussac's law reduces merely to the substitution of the words *any gas* for the word *air* in this statement.

Representing Kelvin temperature by T , Boyle's law and Gay Lussac's law may both be formulated thus:

$$pv = R'T \dots\dots\dots(7)$$

in which p is the pressure and v is the volume of a given amount of gas at any Kelvin temperature T , and R' is a proportionality factor the value of which depends on the amount of the gas in grams. A more general form of this equation is

$$pv = MRT \dots\dots\dots(8)$$

in which M is the mass of the gas in grams and R is a constant which depends only on the molecular weight* of the gas.

* When p is expressed in millimeters of mercury, v in cubic centimeters, M in grams and T in Kelvin-centigrade; then R is equal to 62,200 divided by the molecular weight of the gas (0 = 16).

LEADING QUESTIONS

L. Q. 1. What is meant by thermal equilibrium?

L. Q. 2. When are two bodies said to have the same temperature? Give an example.

L. Q. 3. Is it entirely correct to state Gay Lussac's law thus: "The pressure of a gas, at constant volume, is proportional to the absolute temperature"? Does this statement include more than experimental fact? If so, what?

L. Q. 4. How could you subject two gas containers to exactly the same rise of temperature without using a thermometer? If the two containers remained unchanged in volume and if they contained different gases initially at the same pressure (at the lower temperature), what would be the relation between the pressures of the two gases at the higher temperature?

L. Q. 5. The hydrogen thermometer is the accepted standard for the precise measurement of temperature. Define the ratio of two temperatures as measured by the hydrogen thermometer.

L. Q. 6. A gram-mol of any gas is a grams of the gas, where a is the molecular weight of the gas. Find the value of the constant R in equation (8) of Art. 6 when M is expressed in gram-mols, p and v being expressed as specified in the footnote to Art. 6. The value of R is the same for all gases when M is expressed in gram-mols.

PROBLEMS

Note. *Gage pressure* means pressure reckoned above the pressure of the atmosphere; *absolute pressure* means the total actual pressure in a vessel or container.

Standard atmospheric pressure is 1,013,200 dynes per square centimeter, or 760 millimeters of mercury, or 14.7 "pounds" per square inch.

1. An oxygen tank will hold 3.5 cubic feet of water. Oxygen is stored in the tank at a gage pressure of 200 "pounds" per square inch, and oxygen is drawn out of the

tank until the gage pressure falls to 10 " pounds " per square inch. How many cubic feet of oxygen, reckoned at atmospheric pressure, is drawn out of the tank? Assume no change of temperature. Ans. $45\frac{1}{2}$ cubic feet.

2. An air compressor has a volume of 10 cubic inches left under its piston at the end of the stroke (clearance volume, so-called), the piston is 6 inches in diameter and the stroke is 7 inches. What is the highest gage pressure at which the compressor can deliver compressed air on the assumption that the air is not heated during compression? Using the same assumption calculate the volume of air (reckoned at atmospheric pressure) that will be delivered per stroke when the delivery is at a gage pressure of 147 " pounds " per square inch. In both calculations assume that the air inlet valves permit the complete filling of the cylinder at atmospheric pressure. Ans. 291 " pounds " per square inch; 98.2 cubic inches.

3. A vacuum pump sucks 100 cubic inches of air out of a container at each stroke, that is to say, the volume of the pump cylinder is 100 cubic inches and the clearance volume is zero. The volume of the container is 1000 cubic inches. Find the pressure in the container after 5 strokes of the pump and after 50 strokes of the pump, the initial pressure in the container being 760 mm. Assume container and pump to be at the same invariable temperature. Ans. (a) 472 mm.; (b) 6.47 mm.

4. Suppose that one cubic inch of space (clearance space or volume) is left under the piston of the vacuum pump of problem 3 at the end of the stroke so that one cubic inch of air at atmospheric pressure would remain in the pump cylinder at the end of each stroke, and suppose that the pump valves are very light so that no perceptible pressure difference is required to open them. Find the lowest pressure that can be produced by a long-continued operation of the pump.

5. An air-tight steel tank in a cellar contains 200 cubic feet of air at atmospheric pressure, and 175 cubic feet of

water is pumped into the tank. Find the gage pressure in the tank, assuming no temperature change and neglecting the minute effect of water vapor. Water is delivered by the tank to upstairs hydrants, and the minimum gage pressure required for delivery is, say, 20 "pounds" per square inch in the top of the tank. Find the volume of water that can be delivered. Ans. 44.1 "pounds" per square inch; 17.4 cubic feet.

Note. Each time the steel tank is filled with fresh water some of the air in the tank is absorbed by the water. This effect is to be neglected in the problem, but this effect is by no means negligible in practice, because no air will be left in the tank after repeated fillings and emptyings. In practice the water pump must be arranged to suck a little air on its intake side and deliver this air to the tank so as to keep up the supply of air in the tank. How about the air in the chamber of a pump?

6. Air in a cylinder initially at atmospheric pressure (14.7 "pounds" per square inch) is suddenly compressed to one-tenth of its initial volume, and the gage pressure, as shown by a steam engine indicator, rises to 366 "pounds" per square inch. Explain why the pressure rises so high. To what value will the pressure rise if the air is compressed slowly?

7. The pressure of the air in an air thermometer bulb at standard steam temperature is 1.367 times as great as the pressure of the air in the bulb at ice temperature. The difference $S - I$ is taken as 180° on the Fahrenheit scale. Find Kelvin (or absolute) temperature of freezing water in Fahrenheit degrees.

8. The air in the bulb of an air thermometer has a pressure of 750 millimeters of mercury when the bulb is placed in a steam bath (at standard atmospheric pressure), and it has a pressure of 1203 millimeters of mercury when the bulb is placed in a bath of lead at its melting point. What is the temperature of melting lead reckoned from the ice point?

9. The initial temperature of the air in the cylinder in problem 6 is 25° C. To what temperature does the air rise when quickly compressed to one-tenth of its initial volume?

10. Given 1000 cubic centimeters of air at 20° C. and 720 millimeters pressure. Find the volume of the air at 100° C. and 780 millimeters pressure.

Note. When pressure, volume and temperature of a gas all change, calculations are most easily made by using the equation

$$\frac{p_1 v_1}{T_1} = \frac{p_2 v_2}{T_2}$$

because this form of equation obviates the necessity of considering the values of the constants R' and R in equations (7) and (8).

11. The density of dry air at 0° C. and 760 millimeters pressure is 0.001293 gram per cubic centimeter. What is the volume of 25 grams of air at 25° C. and at a pressure of 730 millimeters? Ans. 21,970 cubic centimeters.

12. A quantity of dry carbon dioxide is collected over mercury in a eudiometer tube. The observed volume of the gas is 50 cubic centimeters, its temperature is 10° C., the level of the mercury in the eudiometer tube is 10 centimeters above the level of the mercury in the basin, and the pressure of the atmosphere is 750 millimeters. Find the volume of the carbon dioxide at 0° C. and 760 millimeters, making no allowance for the fact that the mercury is not at standard temperature (0° C.). Ans. 41.26 cubic centimeters.

Note. Carbon dioxide at ordinary temperatures and pressures departs perceptibly from Boyle's law, and also from Gay Lussac's law; but equation (8) of Art. 6 is to be used in the solution of the problem.

13. One cubic foot of air at 14.7 "pounds" per square inch (absolute) is compressed to 0.1 cubic feet at constant temperature. Find by integration the amount of work done on the air which is compressed. How much of this work is done by the surrounding air (at 14.7 "pounds" per square inch)? Ans. (a) 4875 foot-"pounds"; (b) 1905 foot-"pounds."

Note. The work dW which is done while pressure p is acting and while the volume is reduced by dv , is $dW = p\,dv$; and systematic units must be used in this equation, either c.g.s. units or units of the engineer's system. Using the latter, we put $p = 14.7 \times 144$ "pounds" per square foot and $v = 1$ cubic foot in equation (8) of Art. 6, and we get the value of the constant MR for the given amount of air and for the chosen units. Put the value of p from equation (8) in the expression $dW = p\,dv$ and integrate between specified limits.

7. The mercury-in-glass thermometer.* The most convenient device for measuring temperature is the ordinary mercury-in-glass thermometer with which everyone is familiar. A glass tube AB , Fig. 3, of fine, uniform bore, with a bulb at one end, is filled with mercury at a temperature somewhat above the steam point, and the tube is sealed at A . As the instrument cools, the mercury contracts more rapidly than the glass and thus only partly fills the stem. The instrument is then placed in an ice bath and the position of the surface of the mercury in the stem is marked at I . Then the instrument is placed in a steam bath at standard atmospheric pressure, and the steam point is marked at S .

In the centigrade scale (Celsius),† which is the scale universally used in scientific work, the distance SI is divided into 100 equal parts, which divisions are continued above S and below I . These marks are numbered upwards, beginning at I , which is number zero. The marks below I are numbered negatively from I .



Fig. 3.

Any temperature is specified by giving the number of the mark at which the mercury stands when the

* A good description of the construction of a mercury-in-glass thermometer is given on pages 4-14, and special forms of thermometer for indicating maximum temperatures and minimum temperatures are described on pages 18-20 of Edser's *Heat for Advanced Students*. London: Macmillan & Co., 1908.

† The only other thermometer scale of which mention need be made is that of Fahrenheit, in which the distance SI is divided into 180 equal parts, which divisions are continued above S and below I . These marks are numbered upwards, beginning with the thirty-second mark below I , which is number zero. The marks below zero are numbered negatively.

thermometer is brought to that temperature. For example, 65° C. (read *sixty-five degrees centigrade*) is the temperature at which the mercury in a mercury-in-glass thermometer stands at mark number 65 of the centigrade scale.

Remark. To reduce ordinary *centigrade temperature* (reckoned from the ice point) to *Kelvin temperature* add 273.

8. Mercury-in-glass temperatures. The indications of an accurately constructed mercury-in-glass thermometer are slightly different from air-thermometer temperatures (reckoned from ice point) because of the irregularities in the expansion of mercury and glass, and temperature values as indicated by an accurate mercury-in-glass thermometer made of a standard variety of glass are called *mercury-in-glass temperatures*.

The following table shows corresponding hydrogen-thermometer temperatures reckoned from ice point, air-thermometer temperatures reckoned from ice point, and mercury-in-glass temperatures (Jena normal glass). All three thermometers agree, of course, at ice point and at steam point, and the differences for the intervening temperatures depend upon irregularities of expansion. Thus, the differences between the hydrogen-thermometer temperatures and the air-thermometer temperatures show that these gases do not expand in exactly the same way with rise of temperature, and another difference between the hydrogen and the air thermometers which does not appear in the table is that the ratio of steam temperature to ice temperature as measured by the hydrogen thermometer is slightly different from the ratio as measured by the air thermometer.

TABLE

COMPARISON OF HYDROGEN, AIR AND MERCURY-IN-GLASS
TEMPERATURES*(Centigrade degrees)*

Hydrogen-thermometer temperatures (reckoned from ice-point)	Air-thermometer temperatures (reckoned from ice point)	Mercury-in-glass temperatures (Jena Normal Glass)
0. ^o	0. ^o	0. ^o
10.	10.007	10.056
20.	20.008	20.091
30.	30.006	30.109
40.	40.001	40.111
50.	49.996	50.103
60.	59.990	60.086
70.	69.986	70.064
80.	79.987	80.041
90.	89.990	90.018
100.	100.	100.

For most purposes the variations in this table are negligible.

9. **Standard thermometers.** It is impracticable to draw a glass tube (a thermometer stem) with a uniform bore, and there are nearly always appreciable errors in the location of ice and steam points on a thermometer stem. Therefore a very carefully made thermometer does not give correct indications. A *standard thermometer* is a thermometer of which the errors have been determined* so that the true mercury-in-glass temperature corresponding to each reading of the thermometer is known. No thermometer which has not been standardized is to be depended upon for work even of moderate accuracy.†

* A good discussion of the standardization of a mercury-in-glass thermometer is given on pages 23-38 of Edser's *Heat for Advanced Students*.

† A well-made thermometer can be sent to the United States Bureau of Standards, Washington, D. C., or to the National Physical Laboratory in London, where it will be standardized for a small fee.

Errors which depend upon the way in which a thermometer is used. The most perfect standard thermometer is subject to three kinds of error, namely: (a) Stem exposure error; (b) Error due to abnormal pressure on or in the bulb; and (c) Error due to sluggish expansion and contraction of the glass.

Error due to stem exposure. The whole of a thermometer, bulb and stem, is supposed to be at the temperature t which is to be indicated by the thermometer; it often happens, however, that a portion of the mercury filament or column is not at temperature t , but at a lower temperature t_0 . Then, if l is the length in degrees of the portion of the column which is at temperature t_0 , a correction equal to $0.000156l(r-t_0)$ must be added to the thermometer reading r . This correction is sometimes very considerable. Thus in indicating the temperature of a hot oil bath a thermometer reads 350°C . with $250^\circ(-l)$ of the mercury column at $t_0 = 50^\circ$, so that the correction is $0.000156 \times 250 \times 200$, or 7.8° .

Errors due to abnormal pressure in or on the bulb. A thermometer is always standardized in a vertical position with its bulb in a region at atmospheric pressure, and a high reading (with long mercury column) is increased if the thermometer is placed in a horizontal position because of the reduced pressure in the bulb. Similarly the reading of the thermometer is increased if the bulb is placed in a high pressure region.

Errors due to sluggish expansion and contraction of the glass. When a thermometer is kept for a long time at a fixed temperature the mercury column settles to what is called the "stable reading" for that temperature. Stable readings only are supposed to be used on a standard thermometer.

A standard thermometer which has been for a long time at room temperature is put into a cold solution and the reading of the thermometer is taken after, say, five minutes. This is called a "temporary reading" because it rises slowly (temperature being constant) on account of the continued slow contraction of the bulb. If one cannot wait for the "stable reading" of the thermometer one can take the "temporary reading," and then one can arrange at leisure to change the thermometer from room temperature to approximately the same cold temperature, take the "temporary reading" after five minutes, and then, keeping the temperature constant by the use of an auxiliary thermometer, wait for the "stable reading." The difference between temporary and stable readings so obtained may then be used as a correction to the original temporary reading.

This tedious procedure is seldom followed. It is outlined here to show how much care is required to get extremely accurate results with a mercury-in-glass thermometer.

LEADING QUESTIONS

L. Q. 7. If the bore of a thermometer stem were a little larger towards *S* and a little smaller towards *I* in Fig. 3 and if the distance *I* to *S* were divided into 100 equal parts, would a reading of 50° on this thermometer be too high or too low? Why?

L. Q. 8. Find, by interpolation in the table in Art. 8, the true hydrogen thermometer temperature (reckoned from the ice point) corresponding to 65° C. on a standard mercury-in-glass thermometer.

PROBLEMS

14. The stem of a thermometer has upon it a scale of equal parts. One of the division marks is at ice point, and the steam point is at 90 divisions above the ice point. At what point on this scale will the mercury stand at 67° C.? at 120° F.?

15. A thermometer stem has 140 spaces between ice point and the steam point, and the division marks are numbered upwards from the 10th mark below the ice point so that the ice point is at mark No. 10. Reduce a reading of 100° on this thermometer to centigrade and to Fahrenheit.

10. Pyrometry.* The measurement of very high temperatures is called *pyrometry*, and a device for measuring high temperatures is called a *pyrometer*.

* Optical and radiation pyrometry is discussed in Arts. 47 and 48 of Chapter IV.

A very comprehensive and authoritative treatise on pyrometry is the Special Volume on Pyrometry of the *Transactions of the American Institute of Mining and Metallurgical Engineers*, published in September, 1919. For sale separately; price \$6.00. Address Sec'y A.I.M. & M.E., 29 W. 39th St., New York City.

The most accurate pyrometer for temperatures up to the softening temperature of porcelain is the porcelain-bulb air or nitrogen or hydrogen thermometer, and the melting points of many of the pure metals have been carefully determined by the nitrogen thermometer to

TABLE*
FREEZING OR MELTING POINTS OF PURE METALS

Tin	232° C.	Gold	1063° C.
Cadmium	321°	Copper	1083°
Lead	327°	Nickel†	1450°
Zinc	419°	Palladium	1550°
Antimony	630°	Platinum	1755°
Aluminium	658°	Alumina	2050°
Copper-silver (Eutectic)	779°	Tungsten	3400°
Silver	961° C.		

serve as a basis for the calibration of purely indicating pyrometers like the thermo-electric pyrometer and the electrical-resistance pyrometer.

The thermoelectric pyrometer.

The essential parts of a thermoelectric pyrometer are shown in Fig. 4. Two wires of suitable metals are connected together at *H*, they are connected to copper wires at *C*, and the copper wires are connected to a

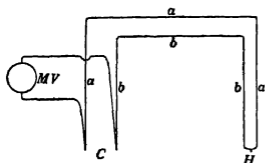


Fig. 4.

millivoltmeter *MV*. The junction *H* is protected by a quartz or porcelain tube and placed in the region whose high temperature *t* is to be determined, and the junctions

* From U.S. Bureau of Standards Circular No. 7. Standard samples of metals for thermometric and pyrometric fixed points are supplied by the Bureau. See Circular No. 66.

† All points above about 1400° C. have been determined by radiation or optical methods.

C are placed in a region at $0^{\circ} C$. Then, if the instrument has been calibrated, the millivoltmeter reading gives the value of t . For very high temperatures the wires a and b are made of platinum and of a platinum-rhodium alloy respectively.

To calibrate the instrument the millivoltmeter readings are taken for a series of known temperatures (melting points of pure metals) of the hot junction H .

11. Irregularities of expansion of liquids and solids. The expansion of a gas (at constant pressure) is very much greater than the expansion of a liquid or solid, and all gases expand very nearly alike (Gay Lussac's Law), whereas every liquid and every solid exhibits characteristic peculiarities, expanding more rapidly at certain temperatures than at others, and in some cases actually contracting with rise of temperature. Most liquids exhibit marked irregularities of expansion near their freezing points. Thus, water contracts as it is heated from $0^{\circ} C$. to $4^{\circ} C$., at which temperature the volume of a given mass of water is a minimum or its density is a maximum; and beyond $4^{\circ} C$. water increases in volume with rise of temperature, at first slowly and then more and more rapidly as the temperature rises.

Steel expands with rise of temperature until a temperature of about $800^{\circ} C$. is reached, and then it contracts. See Art. 35 on the recalescence of steel.

Solids exhibit peculiarities of expansion which are not exhibited by liquid and gases. Thus, many solid substances do not expand promptly with rise of temperature or contract promptly with fall of temperature, the ultimate change of dimensions corresponding to a given change in temperature requiring in some cases days or even months before it is established. The best-known

example of this time-lag of expansion is furnished by ordinary glass. The mercury column of a mercury-in-glass thermometer which has been kept for a long time at room temperature and which is suddenly brought to steam temperature rises at first too high, and as the bulb slowly expands to the ultimate size which corresponds to steam temperature the mercury column slowly drops to its correct position.

TABLE
DENSITY AND SPECIFIC VOLUME OF WATER
(Water containing no air)

Temperature °C.	Density, grams per cubic centimeter	Specific volume, cubic centimeters per gram
0	0.99987	1.00013
1	0.99993	1.00007
2	0.99997	1.00003
3	0.99999	1.00001
4	1.00000	1.00000
5	0.99999	1.00001
6	0.99997	1.00003
7	0.99993	1.00007
8	0.99988	1.00012
9	0.99981	1.00019
10	0.99973	1.00027
20	0.99823	1.00177
30	0.99567	1.00435
50	0.98807	1.01207
100	0.95838	1.04343

A most interesting substance is the non-expansible nickel-steel alloy which was discovered by Guillaume, a nickel-steel containing 36 per cent of nickel, and known as *invar*. The increase in length of a meter scale made of invar when it is heated from 0° C. to 100° C. is a little less than one-tenth of a millimeter, whereas a meter scale made of ordinary steel would increase in length by about 1.3 millimeters for the same rise of temperature. This alloy, invar, is also very sluggish in its expansion and contraction. When the increase of temperature is small

the increase of length does not fully reach its final value in two months. Therefore, when a bar of invar is subjected to fluctuations of temperature which are neither very large nor very long continued, the change of length of the bar is extremely small and for many purposes negligible.

12. Mean coefficient of linear expansion. Let L_0 be the length of a metal bar at 0° C., and let L_t be the length of the bar at t° C. The increase of length, $L_t - L_0$, is accurately proportional to the initial length L_0 of the bar and in most cases approximately proportional to the rise of temperature t . Therefore we may write

$$L_t - L_0 = \alpha L_0 t \dots\dots\dots (i)$$

where α is a proportionality factor. Solving this equation for α , we get

$$\alpha = \frac{L_t - L_0}{L_0 t} \dots\dots\dots (ii)$$

from which it is evident that α is the increase of length per unit of initial length per degree rise of temperature; it is called the mean or average coefficient of linear expansion of the bar throughout the temperature range from 0° C. to t° C.

The most convenient form of equation (i) is

$$L_t = L_0(1 + \alpha t) \dots\dots\dots (9)$$

13. Mean coefficient of cubic (volume) expansion. Let V_0 be the volume of a substance, liquid or solid, at 0° C., and let V_t be its volume at t° C. The increase of volume, $V_t - V_0$, is accurately proportional to the initial volume V_0 of the substance and in most cases approximately proportional to the rise of temperature t . Therefore we may write

$$V_t - V_0 = \beta V_0 t \dots\dots\dots (i)$$

where β is a proportionality factor. Solving this equation for β , we get

$$\beta = \frac{V_t - V_0}{V_0 t} \dots\dots\dots(ii)$$

from which it is evident that β is the increase of volume per unit of initial volume per degree rise of temperature; it is called the mean or average coefficient of cubic (volume) expansion throughout the temperature range from 0°C. to $t^\circ \text{C.}$

TABLE*

COEFFICIENTS OF EXPANSION (MEAN)

α = increase of length per unit initial length per centigrade degree.

β = increase of volume per unit initial volume per centigrade degree.

To reduce to values for Fahrenheit degrees, divide the tabulated values by 1.8.

Coefficient of volume expansion = three times coefficient of linear expansion.

<i>Solids.</i>		α
Aluminium	mean value between 16°C. and 250°C.	..0.0000244
Lead	" 17°C. and 100°C.	..0.000029
Wrought iron and mild steel	" 0°C. and 100°C.	..0.000011
" "	" 600°C. and 700°C.	..0.0000165
Cast iron (5% of carbon)	" 16°C. and 250°C.	..0.0000114
Hardened steel (1.5% of carbon)	" 0°C. and 100°C.	..0.000010
Pure copper	" 16°C. and 250°C.	..0.0000171
Platinum	" 16°C. and 250°C.	..0.0000092
Zinc	" 19°C. and 100°C.	..0.000017
Tin	" 18°C. and 100°C.	..0.000027
Brass (62Cu + 38Zn)	" 16°C. and 250°C.	..0.0000198
Nickel-steel (36.1% Ni)	" 0°C. and 20°C.	..0.0000090
Crown glass	at 10°C.	..0.000009
Flint glass (light)	between 13°C. and 98°C.	..0.0000079
Jena thermometer glass 16 III	" 15°C. and 92°C.	..0.00000802
Porcelain (Berlin)	" 16°C. and 250°C.	..0.0000034
Ice	" -27°C. and -2°C.	..0.000051
Mahogany wood with grain	" 2°C. and 34°C.	..0.0000036
" " across the grain	" 2°C. and 34°C.	..0.000040
<i>Liquids.</i>		β
Mercury	between 0°C. and 200°C.	..0.000181
Petroleum (kerosene)	" 7°C. and 38°C.	..0.0009
Paraffin oil	at 16°C.	..0.00076

* Taken from Landolt-Börnstein, *Physikalisch-Chemische Tabellen.*

The most convenient form of equation (i) is

$$V_t = V_0(1 + \beta t) \dots\dots\dots(10)$$

Thermo-stresses. Unequal heating or cooling of different parts of a body causes non-uniform expansion or contraction and sets up stresses in the body. These stresses are called *thermo-stresses*.

When a casting of iron or steel has thick and thin parts, the thin parts solidify and cool considerably while the thick parts are still plastic. Then when the thick parts solidify and cool their contraction often develops excessive stresses in the thin parts. These stresses often cause a poorly designed casting to pull itself to pieces. To remove such stresses a casting must be thoroughly annealed.

LEADING QUESTIONS

L. Q. 9. What is the exact volume of 1000 grams of water at 20° C. ?

L. Q. 10. Does a hole in a sheet of metal grow larger or smaller as the metal expands with rise of temperature? Explain.

L. Q. 11. The piston and the cylinder of an ordinary gasoline engine are both made of cast iron, but if the piston fits the cylinder when both are cold it gets very tight and causes excessive wear when the engine is running. Explain. The piston rings are elastic and they fit the cylinder under all conditions.

L. Q. 12. When moderate weather follows a bitter cold spell the thick ice on a lake is likely to crush an ordinary wharf. Explain.

L. Q. 13. Many of the lakes of New England are fringed with a sort of "wind row" of small boulders, whereas the lake bottom near the shore where the water is shallow is nearly free of small boulders. Explain.

L. Q. 14. When a pane of ordinary window glass is heated on one side it is very perceptibly bent. Make a sketch

showing a flame heating one side of a pane of glass and show which way the pane is bent. Why is the pane bent?

L. Q. 15. When a pane of window glass is held horizontally over a flame the pane usually breaks, and a piece of the glass is often thrown sidewise with considerable velocity. Explain.

L. Q. 16. A tightly stoppered bottle is full of water. What happens if the bottle is heated? Why? What happens when an ordinary thermometer is heated above the temperature at which the mercury completely fills bulb and stem? How much does it cost to try this experiment?

PROBLEMS

16. A steel meter scale is 99.981 centimeters long at 10° C. and 100.015 centimeters long at 40° C. At what temperature is the scale exactly 100 centimeters long, assuming the expansion from 10° C. to 40° C. to be uniform?

17. A piece of soft wrought iron was found by Andrews to have a length of 101.50 centimeters at a temperature of 100° C. and a length of 101.77 centimeters at a temperature of 300° C. Find the mean coefficient of linear expansion of the iron between 100° C. and 300° C.

18. An iron steam-pipe is 1000 feet long at 0° C. and it ranges in temperature from -20° C. to 115° C. What must be the range of motion of an expansion joint to provide for expansion?

19. A clock with a seconds pendulum (one complete vibration in two seconds) is correct at 25° C. How many seconds will it gain in a day at 20° C., the pendulum being of steel, let us say?

Note. The number of vibrations (complete) of a pendulum in 86400 seconds is

$$n = \frac{86400}{2\pi} \sqrt{\frac{g}{l}} \quad (i)$$

where g is the acceleration of gravity in centimeters per second per second and l is the "length" of the pendulum in centimeters.

The length l becomes $l(1-5a)$, and, since $5a$ is very small as compared with unity, equation (i) becomes

$$n' = \frac{86400}{2\pi} \sqrt{\frac{g}{l}} \times (1 + 2\frac{1}{2}a)$$

20. A steel meter scale is correct at 20°C . Find highest and lowest temperatures at which the scale can be used to measure a distance of 65 centimeters correctly to 0.1 millimeter.

21. A surveyor's steel tape is correct at 0°C . A distance measured by the tape at 22°C . is 500 "feet." What is the true value of the measured distance, coefficient of linear expansion of steel being 0.0000111?

Note. The measured distance is 500 times as long as the portion of the tape between two adjacent foot-marks at the temperature at which the tape is used.

22. A steel shaft is 20 inches in diameter at 70°F . A steel collar is to be shrunk upon this shaft. The collar is to be heated to 650°F . and have at that temperature an inside diameter of 20.01 inches, so that it may be easily slipped over the shaft. Required the inside diameter to which the collar must be turned in the shop, shop temperature being 70°F .

23. The gap between the jaws of a micrometer caliper (steel), as indicated by the reading of the caliper, is 0.735 inch. The temperature of the caliper is 34°C . and the caliper is correct at 20°C . What is the correct distance between the caliper jaws?

24. A glass bottle is weighed as follows: (a) empty, 24.608 grams; (b) full of mercury at 0°C ., 258.723 grams; and (c) full of mercury at 100°C ., 255.183 grams. Find the mean coefficient of cubic expansion of the glass of which the bottle is made. Ans. 0.000,009.

Note. The space inside of a vessel increases exactly as if it were a solid piece of the material of which the vessel is made. The density of mercury at 0°C . is 13.5956 grams per cubic centimeter, and at 100°C . it is 13.3524 grams per cubic centimeter.

25. One "pound" per square inch increase of pressure decreases the volume of a block of steel by one part in thirty million. How great a pressure would be produced by 20° centigrade rise of temperature if the steel were kept from expanding? Ans. 19,800 "pounds" per square inch.

26. A steel rod one square inch in sectional area is stretched

to 1.001 of its initial length by a tension of 30,000 "pounds." Calculate the tension in a steel rod 5 square inches in sectional area when the rod is cooled from 25° C. to 20° C. but not allowed to shorten. Ans. 8250 "pounds."

27. A fine steel wire 0.01 inch in diameter is stretched straight between clamps which are fixed to a large brass bar. At 30° C. the tension of the steel wire is zero. What is the tension of the steel wire at 45° C. ? Ans. 0.31 "pound."

28. Two ribbons of brass and steel each one millimeter thick are riveted together to form a compound steel-brass bar two millimeters thick. This bar is straight at 20° C. What is its radius of curvature at 100° C. ? Ans. 138 centimeters.

Note. Treat the compound bar as two indefinitely thin ribbons of brass and steel one millimeter apart. The curvature as calculated is a little too great (radius as calculated is a little too small) on account of the stiffness of the two ribbons.

CHAPTER II

HEAT AS A FORM OF ENERGY. CALORIMETRY

14. Thermodynamics and atomics. In the study of the phenomena of heat there are two distinct methods of attack.

(a) *Thermodynamics.* One method in the study of heat is exemplified by the discussion of temperature in Art. 1 and by the discussion of Boyle's and Gay Lussac's laws in Arts. 2-6. This method is called *thermodynamics*, and it does not depend in the least on any understanding of physical actions and physical things in themselves. What *is* temperature? What *is* a gas, and why does a gas follow Boyle's and Gay Lussac's laws? These questions are out of place in the method which is used in Chapter I and which must be used more or less throughout our entire study of heat. The method of thermodynamics has to do only with temperature as an actual condition, and with such things as measured volumes, pressures and temperatures.

(b) *Atomics.* Another method which is extensively used in the study of heat is the method of the atomic theory, *atomics*, as it is now called. This method involves the building up of more or less elaborate mental pictures or conceptions of physical processes and physical things as illustrated by the following very meager examples.

When a hammer strikes a piece of lead, the energy of the hammer appears to be entirely lost. But there is no

loss. The visible motion of the hammer produces an invisible molecular motion in the lead, and the energy of the hammer is transformed into the energy of this invisible motion. The greater the amount of energy thus invested in a piece of lead the more violent the molecular motion; that is to say, the molecules vibrate more and more energetically, and, seeking wider room, as it were, they urge each other apart and cause the piece of lead to expand.

The molecules of a solid substance vibrate more or less, but each molecule retains a certain mean position. In a crystal the molecules are arranged in regular rows and layers somewhat like the rows and layers in a regular pile of cannon balls. When the crystal is heated the molecules vibrate more and more energetically, and ultimately the regular crystal structure (the *lattice structure* it is called) breaks to pieces. This breaking to pieces of the lattice structure is the process of melting, and in the melted or liquid form of the substance the molecules wander about individually; but the attractive or cohesive forces between the molecules are still sufficient to keep the liquid together in a body—a small amount of liquid does not automatically swell up and fill a large and otherwise empty vessel!

Further heating of a liquid causes still further increase of molecular commotion, and if a hot piece of iron is dipped into a liquid like water, the heat causes the molecules of the water to break the last bonds of cohesion and fly apart to form bubbles of vapor. A vapor or gas always completely fills any closed and otherwise empty vessel in which it is placed.

Every student of elementary chemistry is familiar with the chemist's conceptions of elements and compounds.

The molecule of water, for example, is a group of two atoms of hydrogen and one atom of oxygen, H_2O . The burning of carbon is the rushing together of one atom of carbon and two atoms of oxygen to a form violently quivering (hot) molecule of carbon dioxide (CO_2).

The above examples illustrate some of the simpler phases of the atomic theory. In Chapter V the earlier stages of a highly mathematical phase of the atomic theory are developed.*

It requires some power of imagination to think of a substance as being composed of a great number of small particles (molecules) in incessant and irregular motion, and to think of the energy of a moving hammer as still existing by virtue of an increased violence of molecular motion after a hammer blow. Every student of physics should see the irregular and incessant to-and-fro motion of very fine particles suspended in water, using a good microscope. This motion was discovered by the English botanist, Brown, in 1827, and it is called the *Brownian motion*. The Brownian motion is the irregular molecular motion of the water rendered visible (and greatly reduced in amplitude) by the small suspended particles.

To see the Brownian motion, grind a small amount of insoluble carmine in a few drops of water by rubbing with the finger in a shallow dish, place a drop of the

* The atomic theory is now used in every branch of physics. Thus the electron theory is the application of the atomic theory to the study of electrical phenomena.

Most of the important uses of the atomic theory are very exacting in that they involve severe mathematical conceptions and arguments.

A very interesting discussion of the status of the atomic theory in 1909 was given by Sir Ernest Rutherford in his address before the Physics Section of the British Association for the Advancement of Science at Winnipeg. See *Science*, Vol. 3, 1909.

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mixture on a microscope slide, lay a thin cover glass on the drop, and use a magnifying power of about 400 diameters. The particles in India ink are much finer than the particles of carmine, and a higher magnifying power is required to see them.

Further characterization of the method of thermodynamics.

In the study of mechanics the theory of energy was discussed in connection with mechanical changes only, changes of position, changes of velocity and changes of shape; thermal and chemical changes were ignored. We are now to take up the study of thermal and chemical changes, and it is important at the outset to understand two things as follows:

(a) Our study is not to be concerned with thermal and chemical actions themselves, but with their results. The actions themselves are, as a rule, extremely complicated. Thus, the details of behavior of the coal and air in a furnace are infinitely complicated. The important practical thing, however, is the amount of steam that can be produced by burning a pound of coal, and this depends only upon (1) the condition of the water from which the steam is made, that is, whether the water is hot or cold to start with, (2) the condition of the air and of the coal which are to combine in the furnace, (3) the pressure and temperature of the steam which is to be produced, and (4) the condition of the flue gases as they enter the chimney. That is to say, *it is necessary to consider only the state of things before and after the combustion takes place, and the only measurements that need be taken are measurements of substances in thermal equilibrium.*

(b) The other important thing is that in studying thermal and chemical changes we have to do with a new kind of energy. The gravitational energy of an elevated

store of water can be wholly converted into mechanical work,* the energy of two electrically charged bodies can be wholly converted into mechanical work, the kinetic energy of a moving car can be wholly converted into mechanical work, and so on. On the other hand, the energy of the hot steam which enters a steam engine from a boiler *cannot be wholly converted into mechanical work.*

Any store of energy which can be wholly converted into mechanical work may be called *mechanical energy*. The energy of the hot steam which enters a steam engine from a boiler is called *heat energy*. The important difference between mechanical energy and heat energy, namely, that one can be wholly converted into mechanical work whereas the other cannot, may be clearly understood in terms of the atomic theory: Every particle of a moving car travels in the same direction and all of the particles work together to produce mechanical effect when the car is stopped; the molecules of hot steam, however, fly to and fro in every direction, and no method can be devised whereby the whole of the energy of the erratically moving molecules of hot steam can be used to produce mechanical effect.

15. The dissipation of mechanical energy.† Preliminary statement of the first law of thermodynamics. In the attempt to exclude all thermal changes from the purely mechanical discussion of energy we were confronted

* Any energy which is converted into heat because of friction exists in the form of mechanical energy or work before it is so converted, and this fact must be kept in mind in connection with the above statements as to the conversion of gravitational and electrical energy into mechanical work.

† The *dissipation* of energy is sometimes spoken of as the *degradation* of energy from any form which is wholly available for the doing of mechanical work into heat.

by the fact that friction (with its accompanying thermal changes) is always in evidence everywhere.* In every actual case of motion, the moving bodies are subject to friction and to collision, their energy is *dissipated*, and they come to rest. This dissipation of energy is always accompanied by the generation of heat.

It is important to understand that the term "dissipation of mechanical energy" refers to the conversion of mechanical energy into heat by a process which cannot be reversed, by what is called an irreversible process, like friction or collision. When a gas is compressed, the work done on the gas goes to heat the gas, but this action is reversible, because when the gas is expanded the work is regained and the gas is cooled. But if you drag a box along the floor the box does not tend to fly back to where it started and return the work done! When an electric current is forced through a wire work is done and the wire is heated, but if the current is reversed the wire is not cooled by the current!

The atomic theory enables one to form a clear idea of the dissipation of mechanical energy. Thus the energy of the regular motion of a hammer is converted into the energy of irregular molecular motion when the hammer strikes a piece of lead.†

16. The first law of thermodynamics. The recognition of heat as a form of energy, to be expressed, if you please, in ergs or joules or foot-"pounds," and the extension of

* This refers to the discussion of energy in the previous study of mechanics.

† This statement is evidently incomplete as it stands, because as it stands it applies to the heating of a gas by compression which is *not* the dissipation of mechanical energy.

the principle of the conservation of energy to include both mechanical energy and heat energy are of supreme importance in the study of heat phenomena.

Everyone knows that a coin can be heated by rubbing it on a board, or a kettle of water can be heated by means of an electric heater (the energy which is delivered to the heater is to be classed as mechanical energy), or a gas can be heated by the work done in compressing it. Contrariwise, any reversible process which involves the conversion of work into heat can be worked backwards so as to convert the heat into work. Thus an expanding gas which does work on a piston is cooled, heat is lost and work is gained.

Suppose that a body A is heated by the expenditure of a certain amount of work. That is to say, work is spent on A (as in an electric heater), and *a definite thermal change is produced in A* . The body A can then be brought back to its initial condition by being brought into contact with another cooler body B . **THEN THE THERMAL CHANGE WHICH IS PRODUCED IN BODY B IS EXACTLY THE CHANGE WHICH WOULD BE PRODUCED IN B IF B HAD BEEN HEATED DIRECTLY BY THE EXPENDITURE OF THE ORIGINAL AMOUNT OF WORK.***

The body A may therefore be thought of as containing or storing *something* which is exactly equivalent to the work which has been spent on A , because A in being brought back to its initial condition can produce exactly the same effect on B by the original amount of work; and this something we call *heat energy* or simply *heat*.

* The operations which are here referred to are very difficult to perform, because body A is assumed to heat only the body B and no other body whatever. What is of importance here, however, is that the statement be understood, not that the operations be easily feasible.

The above statement in Italics and in bold-faced type, rightly understood, means that heat is a form of energy, and that the principle of the conservation of energy must include thermal effects. This statement is called *the first law of thermodynamics*.*

The atomic or molecular conception of heat. When a substance is heated, by the dissipation of mechanical energy or otherwise, there is, in general, *an increase of velocity* of its molecules and *a change in the configuration or arrangement* of its molecules; and the heat energy which is given to the substance is stored in the substance partly as increased *kinetic energy of molecular motion* and partly as increased *potential energy of molecular configuration*.

17. The heating of water by the dissipation of mechanical energy. The relation between the amount of work dissipated in heating water and the rise of temperature produced has been determined with great care by H. A. Rowland.† His results are given in the accompanying

* One of the most important steps in the establishment of the principle of the conservation of energy in its general form, which includes heat energy, was made by Count Rumford in his experiments on the generation of heat in the operation of boring cannon. The results of these experiments were published in the *Philosophical Transactions* for 1799. The first clear statement of the principle of the conservation of energy in its general form was published in 1842 by Julius Robert Mayer. The celebrated experiments of Joule on the heating of water by the dissipation of work were commenced in 1840. These experiments are described on pages 274-278 of Edser's *Heat for Advanced Students*.

† Rowland's experiments, which were carried out in 1879, are described in the *Proceedings of the American Academy of Arts and Sciences*, new series, Vol. VII. A good account of this work of Rowland's and of the work of other experimenters in the same field, is given on pages 267-286 of Edser's *Heat for Advanced Students*.

table and are shown graphically in Figs. 5 and 6. The ordinates of the curve in Fig. 5 represent the work in joules required to raise the temperature of one gram of water from 0° C. to t° C.

of the hydrogen scale. This same quantity of work is given in the table in the column headed *E*.

The curve in Fig. 5 is very nearly a straight line. Therefore, for most practical purposes the amount of energy required to heat water may be taken to be proportional to the rise of temperature, and the amount of heat required to raise the temperature of unit mass of water one degree may be very conveniently used as a unit of heat.

The *gram-calorie* is the amount of heat required to raise the temperature of one gram of water one centigrade degree. In accurate work the gram-calorie is understood to be amount of heat required to raise the temperature of one gram of water from $14^{\circ}.5$ C. to $15^{\circ}.5$ C. and it is equivalent to 4.1893 joules. For most practical calculations, however, the gram-calorie is taken to be 4.18 joules.

The *British thermal unit* is the amount of heat required to raise the temperature of one pound of water one

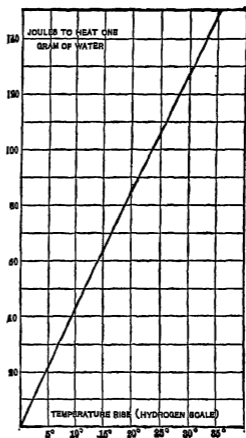


Fig. 5.

Fahrenheit degree,* and it is equivalent to about 778 foot-“pounds” of energy or work. One British thermal unit is equal to 252 gram-calories.

18. Measurement of Heat. *An amount of heat, for example, the amount required to melt a gram of ice, or to produce a given rise of temperature of a gram of lead, is measured when the amount of work required to produce the effect has been determined.* This measurement may be

TABLE†

ROWLAND'S DETERMINATION OF THE WORK REQUIRED TO HEAT WATER

Temperature rise from 0° C. to	Energy in joules to heat one gram of water
(<i>t</i>)	(<i>E</i>)
5°	21·040
10°	42·041
15°	63·005
20°	83·935
25°	104·834
30°	125·708
35°	146·745

made by the direct determination of the work required to produce the given effect. The accomplishment of this method of heat measurement is, however, very tedious and subject to a very considerable error.‡ This is partly

* To be precise it should be stated that the British thermal unit is the amount of heat required to raise the temperature of one pound of water from, say, 59°·5 F. to 60°·5 F.; but this degree of precision is not demanded by the steam engineer, and it is the engineer, chiefly, who uses the British thermal unit.

† From Rowland's results reduced by W. S. Day to the hydrogen scale (*Physical Review*, Vol. VIII, April, 1898).

‡ The work spent in any portion of an electric circuit can be measured with considerably accuracy and it can be easily applied to the accomplishment of any given thermal effect, and this electrical method for measuring heat values is perhaps the most accurate method at present available.

due to the difficulty of measuring work mechanically and partly due to the difficulty of applying mechanical work wholly to the heating of a given substance.

The water calorimeter. Heat is generally measured by the water calorimeter, which is a vessel containing a weighed quantity of water and arranged to absorb the heat to be measured. For example, if the heat produced

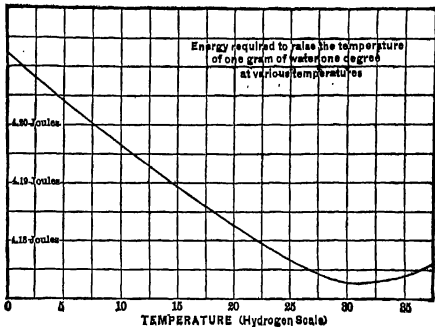


Fig. 6.

by the burning of a given quantity of coal is to be measured, the coal is burned in a chamber which is completely surrounded by the water of the calorimeter, and the waste gases from the combustion pass through a coil of metal pipe also surrounded by the water of the calorimeter. If the heat given off by the cooling of a given amount of metal is to be measured, the hot metal is dropped into the water of the calorimeter.

Let M be the mass of the water in grams, let t' be the initial temperature of the water, and let t'' be the

temperature of the water after the heat H is absorbed. Then, neglecting the heating of the vessel and stirrer and thermometer bulb,* the value of H is calculated as follows.

(a) *Accurate calculation.* Let E' be the energy in joules required to heat one gram of water from 0° C. to t' , and let E'' be the energy in joules required to heat one gram of water from 0° C. to t'' as given in the table in Art. 17. Then $E'' - E'$ is the energy in joules required to heat one gram of water from t' to t'' , and $M(E'' - E')$ is the energy in joules required to heat M grams of water from t' to t'' . Therefore the energy equivalent of H in joules is :

$$H = M(E'' - E') \dots \dots \dots (11)$$

(b) *Approximate calculation.* The amount of heat required to heat water is of course proportional to the mass M of the water and it is approximately proportional to the rise of temperature as pointed out in Art. 17, so that the amount of heat required to heat mass M of water from t' to t'' is :

$$H = M(t'' - t') \dots \dots \dots (12)$$

where H is expressed in calories when M is expressed in grams and temperatures on the centigrade scale, or in British thermal units when M is expressed in pounds and temperatures on the Fahrenheit scale.

19. Specific heat-capacity of a substance. The number of thermal units required to raise the temperature of unit mass of a substance one degree is called the *specific heat-capacity* or simply the *specific heat* of the substance. Thus the ordinate of the curve in Fig. 6 at the 5° point is 4.204, indicating that the specific heat of water at 5° C.

* The method for making allowance for this source of error and for the exchange of heat between the calorimeter vessel and the surrounding air may be found in any laboratory manual.

is 4.204 joules per gram per degree. Specific heats are, however, usually expressed in gram-calories per gram per centigrade degree or in British thermal units per pound per Fahrenheit degree. Thus the specific heat of copper is about 0.093 gram-calories per gram per centigrade degree or 0.093 British thermal units per pound per Fahrenheit degree.

The specific heat of a substance usually varies consider-

TABLE
SPECIFIC HEATS

Aluminium, 0° C. to 100° C.	0.215	Zinc, 20° C. to 100° C.	0.0931
Copper, 20° C. to 100° C.	0.0936	Ice, -21° C. to -1° C.	0.502
Iron, at 20° C., about	0.113	Air (atmospheric) at constant pressure	0.237
Lead, 15° C. to 100° C.	0.0305	Hydrogen at constant pressure	3.41
Mercury, at 0° C.	0.0334	Petroleum, 21° C. to 58° C.	0.511
„ at 50° C.	0.0330	Alcohol, ethyl, at 0° C.	0.548
„ at 100° C.	0.0327	Glass, crown, 10° C. to 50° C.	0.161
Platinum, at 100° C.	0.0275	Glass, flint, 10° C. to 50° C.	0.117
„ at 500° C.	0.0356		
„ at 1000° C.	0.0385		
„ at 1500° C.	0.0407		

ably with temperature. Thus the ordinates of the curve in Fig. 6 show the specific heats of water (in joules per gram per degree centigrade) at different temperatures, and the ordinates of the curves in Fig. 7 show the specific heats of iron and crystalline carbon at different temperatures in calories per gram per degree centigrade.

Determination of specific heat. Example. A copper vessel weighing V grams contains W grams of water at t° C. Into this vessel K grams of hot copper at T° C. is dropped, and the whole settles to a medium temperature m° C. All quantities so far specified are supposed to be known by observation, and it is required to find the specific heat c of copper.

One gram of copper cooling one degree gives off c calories, and K grams of copper cooling from T° to m° gives off $cK(T - m)$ calories. The heat thus given off by the cooling copper is used to heat the vessel and the contained water.

To heat one gram of water one degree requires one calorie, and to heat W grams of water from t° to m° requires $W(m - t)$ calories.

To heat one gram of the copper vessel one degree

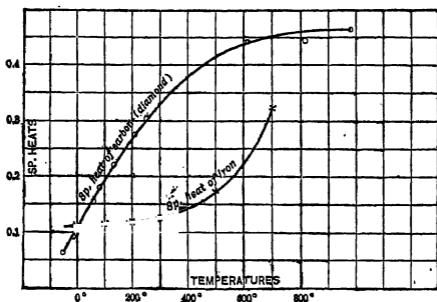


Fig. 7.

requires c calories, and to heat V grams of copper from t° to m° requires $cV(m - t)$ calories.

But the heat given off by the cooling of the hot copper is the heat that raises the temperature of the vessel and water. Therefore we have :

$$cK(T - m) = W(m - t) + cV(m - t) \dots (i)$$

in which c is the only unknown quantity so that the value of c may be calculated.

20. Heat of reaction. Heat of combustion. When zinc (Zn) dissolves in dilute sulphuric acid ($H_2SO_4 + \text{water}$), zinc sulphate ($ZnSO_4$) is formed, there is a rise of temperature of the solution, and to bring the solution back to the initial temperature of the zinc and acid a certain amount of heat must be *taken from* the solution. This heat amounts to 578 gram-calories per gram of Zn or to 377 gram-calories per gram of H_2SO_4 , and it is called the *heat of reaction* of Zn and H_2SO_4 .

In some cases a chemical reaction *cools* the reacting substances so that heat has to be *given to* the residual substance to bring it to the initial temperature of the reacting substances. An example of this kind of reaction is the combination of nitrogen and oxygen in the electric furnace.

A reaction like the dissolving of zinc in sulphuric acid is said to *evolve* or *develop* heat, and it is called an *exothermic* reaction.

A reaction like the combining of nitrogen and oxygen in an electric furnace is said to *absorb* heat, and it is called an *endothermic* reaction.

The most familiar example of an exothermic chemical action is ordinary combustion, the burning of fuel; and the number of thermal units developed by the burning of unit mass of a fuel is called the *heat of combustion* of the fuel.* Thus the heat of combustion of soft-wood charcoal is 7070 gram-calories per gram.

Exothermic reactions are common and endothermic reactions are unusual at low temperatures, whereas the reverse is true at very high temperatures. Thus, living in a cool world we can burn fuel to keep warm, and if we

* Heats of combustion of a great number of substances are given in Landolt and Börnstein's *Physikalisch-Chemische Tabellen*.

lived in a very high temperature world we could burn nitrogen to keep cool.

The breaking up of water vapor to form oxygen and hydrogen is a chemical action and it is endothermic, because the combination of oxygen and hydrogen to form water is exothermic. Now the general rule is that endothermic reactions take place at very high temperatures, and, as a matter of fact, water vapor does break up into oxygen and hydrogen at very high temperatures with absorption of heat. If we lived in a very high temperature world we could keep cool by unburning water! Indeed if it were not for the extreme slowness of chemical action at low temperatures* we might in our cool world keep warm by unburning a substance like nitrous oxide.

LEADING QUESTIONS

L. Q. 17. When the air in the cylinder of an air compressor is compressed all the work done in compressing the air is converted into heat and heats the gas. Is this an example of the dissipation of mechanical energy? If not, why not? Give an example of the dissipation of mechanical energy.

L. Q. 18. The usual statement of the first law of thermodynamics is as follows: "Heat and mechanical work are mutually convertible, when work is lost by dissipation an exactly equivalent amount of heat is produced." However, every principle and every definition in physics, rightly understood, refers to actual operations of some kind, to something that is actually done. State the first law of thermodynamics in terms of actual operations.

L. Q. 19. The spark on a gasolene engine can be adjusted so that the engine will run at full speed and burn its full quota

* There are strong theoretical reasons for believing that any substance like nitrous oxide (which is formed by endothermic reaction) decomposes very slowly at low temperatures.

of gasolene but without doing work. Under these conditions the exhaust is extremely hot. Explain.

L. Q. 20. How many joules of energy is required to heat 500 grams of water from 10° C. to 30° C.? See table in Art. 17.

L. Q. 21. Define the calorie. Define the British thermal unit.

L. Q. 22. What is meant by the specific heat of a substance?

L. Q. 23. The ordinates of the curve in Fig. 6 are, strictly speaking, the specific heats of water at different temperatures. Thus the specific heat of water at 30° C. is 4.173 joules per gram per degree. What does this mean? Is the joule a legitimate unit of heat?

L. Q. 24. What is an exothermic reaction? Give an example.

L. Q. 25. What is an endothermic reaction? Give an example.

L. Q. 26. When moist air is blown into a blast furnace instead of dry air the hot zone of the furnace cools very appreciably and the stack of the furnace becomes hotter. Explain.

PROBLEMS

29. How much power is required to raise the temperature of 5000 grams of water from 0° C. to 35° C. in 10 minutes? Express the result in watts and in horse-power.

Note. A watt is one joule per second. A horse-power is 746 watts.

30. How much does it cost to raise the temperature of 5 gallons (18,500 grams) of water from 20° C. to 100° C. by an electric heater when electric energy costs 10 cents per kilowatt-hour and 20 per cent. of the energy is wasted (not given to the water)? Ans. 21.6 cents.

Note. Compare the result of this problem with the result of problem 41. Why is electrical heating sometimes more economical than coal or gas heating in spite of the fact that heat energy developed electrically is much more costly than heat energy developed by the burning of coal or gas?

31. The great forging press (a hydraulic press) of the Bethlehem Steel Works uses water at a pressure of 8000 "pounds" per square inch (equivalent to a head of 18,400 feet), and at a certain stage in the operation of the press the pressure is relieved by the opening of a by-pass valve. What is the rise of temperature of the first water which escapes through the by-pass valve?

32. A copper vessel weighing 50 grams contains 500 grams of water at 16.00°C . A piece of copper weighing 65 grams is heated to 100°C . and dropped into the water, and the final steady temperature is 17.02°C . Find the specific heat of copper, neglecting exchange of heat between the copper vessel and the surrounding air.

33. A piece of lead weighing 1500 grams is heated to 100°C . and dropped into a 50-gram copper vessel containing 400 grams of water at 15.35°C ., and the final steady temperature is 24.36°C . What is the specific heat of lead, the specific heat of copper being 0.093? Neglect exchanges of heat between the calorimeter vessel and the surrounding air.

34. A steel tank weighing 200 pounds contains 500 pounds of oil at 70°F . A piece of steel weighing 100 pounds is heated to 1800°F . and quenched in oil. Assuming that all the heat given off by the hot piece of steel is used to heat the oil and the containing vessel, calculate the rise of temperature of the oil. Take the specific heat of the steel tank as 0.12, and take the mean specific heat of the piece of quenched steel as 0.22 (see Fig. 7 on page 40). The specific heat of the oil is 0.52.

Notes. A very considerable part of the heat given off by the quenched piece of steel is used to vaporize oil.

35. A 2-kilogram copper vessel contains 24 kilograms of water at 20°C . Into this are dropped 2 kilograms of copper at 100°C ., 2.4 kilograms of zinc at 60°C ., and 6.4 kilograms of lead at 50°C . Find the resultant temperature.

Notes. When there is no question as to the freezing of a portion of the water or the boiling of a portion of the water, the simplest argument of a problem of this kind is as follows: Let t be the resultant temperature, and, for the sake of argument, let us think of t as being

higher than any of the given temperatures. Then the specific heat of any one of the given substances multiplied by its mass and multiplied by (t minus initial temperature of substance) is the amount of heat required to raise the substance up to the resultant temperature. Adding all such products together gives the total heat required to raise the mixture up to its resultant temperature, and this total heat is equal to zero, under the conditions of the problem.

36. Coal giving 7770 calories per gram and costing \$6 per 1000 kilograms is used in a cook stove, and about 5 per cent. of the heat of combustion is utilized, for example, in heating water. Find the cost of heating 18,500 grams of water from 20° C. to 100° C. making no allowance for wear and tear on stove and cooking utensils. Ans. 2.3 cents.

37. A steam boiler and engine plant develops steadily 200 horse-power, and uses 12,000 pounds of coal per day. As burned under the boiler the coal gives 12,000 British thermal units per pound. What fraction of the total heat developed in the burning of the coal is represented by the mechanical energy developed by the engine? Ans. 0.085.

38. The heat of combustion of pure charcoal is 4000 British thermal units per pound when the product of combustion is carbon monoxide (CO) and 14,500 British thermal units per pound when the product is carbon dioxide (CO_2). What is the heat of combustion of carbon monoxide per pound? Ans. 4500 British thermal units per pound.

CHAPTER III

THERMAL PROPERTIES OF SOLIDS, LIQUIDS AND GASES. CHANGES OF STATE

21. Melting points and boiling points.* When heat is imparted to a solid the temperature rises until the solid begins to melt; the temperature then remains constant until all of the substance is changed to liquid; the temperature then begins to rise again and continues to rise until the liquid boils; the temperature then remains constant until the liquid is entirely changed to vapor (pressure being unchanged); and then the temperature begins to rise again as heat is continually imparted to the substance. There are thus two periods during which heat is imparted to a substance without producing rise of temperature, namely, when the substance is melting and when the substance is boiling under constant pressure.

Examples. Heat is imparted to very cold ice and the temperature rises until the ice begins to melt at 0° C., after the ice is all melted the temperature rises to 100° C. (if atmospheric pressure is 760 millimeters of mercury), and after the water is all converted into steam the temperature of the steam may be raised by further addition of heat.

The **melting point** of a substance is the temperature at which the solid and liquid forms of the substance can

* Extensive tables of melting points and boiling points are given in Landolt and Börnstein, *Physikalisch-Chemische Tabellen*.

exist together in thermal equilibrium. This temperature varies but slightly with pressure.

The **boiling point** of a liquid *at a given pressure* is the temperature at which the liquid and its vapor can exist together in equilibrium. This matter is discussed more fully in the next article.

Every substance, so far as known, has a definite boiling point at any given pressure ;* but crystalline substances, only, have definite melting points. Thus, ice crystals and water exist side by side in equilibrium at a given temperature, whereas amorphous substances, such as glass and resin, seem to have no definite melting point. These substances grow softer and softer with rise of temperature.

22. Maximum pressure of a vapor at a GIVEN TEMPERATURE ; and minimum temperature of a vapor at a GIVEN

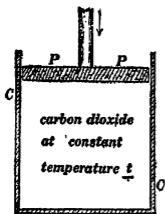


Fig. 8.

Pressure being increased.

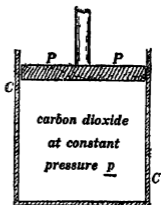


Fig. 9.

Temperature being reduced.

PRESSURE. Consider a cylinder filled with carbon dioxide gas, as shown in Fig. 8, and suppose it is *kept at a constant GIVEN temperature while the piston PP is being pushed downwards.*

* Below what is called the *critical pressure*. See Edser's *Heat for Advanced Students*.

At first the pressure of the gas increases as its volume decreases (in accordance with Boyle's law); but when the increasing pressure reaches a certain value, further decrease of volume does not cause further increase of pressure, but results in the condensation of a portion of the carbon dioxide into liquid form.* *There is a limit to the pressure that gaseous carbon dioxide can exert, or at which gaseous carbon dioxide can exist, at a GIVEN temperature, and if an attempt is made to increase the pressure beyond this limiting value a portion of the gas condenses to liquid.*

Or, consider a cylinder filled with carbon dioxide gas, as shown in Fig. 9, and kept at a constant GIVEN pressure (by pushing the piston downwards if necessary) while the temperature of the whole is slowly decreased. At first the temperature of the gas decreases as heat is taken from the arrangement; but when the decreasing temperature reaches a certain value, further taking of heat from the arrangement does not cause further decrease of temperature, but results in the condensation of a portion of the carbon dioxide into liquid form. *There is a limiting temperature below which gaseous carbon dioxide cannot exist as a gas at a GIVEN pressure, and if an attempt is made to cool the gas below this limiting temperature a portion of the gas condenses to liquid.*

In discussing the change of a substance from a liquid to a gas or from a gas to a liquid it is customary to speak of the gaseous form of the substance as *vapor*. When the vapor is at its maximum pressure for a given temperature or at its minimum temperature for a given pressure, it is

* If the temperature does not exceed a certain value which is called the *critical temperature* of the substance. See Edser's *Heat for Advanced Students*.

said to be a *saturated vapor*. A saturated vapor cannot be cooled without a portion of it being condensed if the pressure remains the same. A saturated vapor cannot be compressed without a portion of it being condensed if the temperature remains the same.

TABLE
PRESSURES AND TEMPERATURES OF SATURATED WATER VAPOR
(Boiling Points of Water at Various Pressures)

Temp.	Pressure in centimeters	Temp.	Pressure in centimeters	Temp.	Pressure in centimeters	Temp.	Pressure in centimeters
-10° C.	0.2151	50° C.	9.1978	110° C.	107.537	170° C.	596.166
0°	0.4569	60°	14.8885	120°	149.128	180°	754.692
10°	0.6971	70°	23.3308	130°	203.028	190°	944.270
20°	1.7363	80°	35.4873	140°	271.763	200°	1168.896
30°	3.1510	90°	52.5468	150°	358.123	210°	1432.480
40°	5.4865	100°	76.0000	160°	465.162	230°	2092.640

What is said here of carbon dioxide is true so far as known of every substance. Thus, water vapor at a given temperature cannot exert more than a certain maximum pressure, or at a given pressure it cannot be cooled below a certain minimum temperature without condensation. The accompanying tables give the maximum pressures and minimum temperatures of water vapor, and of anhydrous ammonia.*

TABLE
PRESSURES AND TEMPERATURES OF SATURATED AMMONIA VAPOR (NH₃)
(Boiling Points of Liquid Ammonia at Various Pressures)

Temperature	Pressure in atmospheres	Temperature	Pressure in atmospheres
-30° C.	1.14 atm.	20° C.	8.41 atm.
-20°	1.83	40°	15.26
-10°	2.82	60°	25.63
0°	4.19	80°	40.59
10°	6.02	100°	61.32

* For more extensive tables see Landolt & Börnstein's *Physikalisch-Chemische Tabellen*.

The boiling point of a liquid at a given pressure is defined in Art. 21 as the temperature at which the liquid and its vapor stand together in equilibrium at the given pressure, and this is the same thing as the minimum temperature of the vapor at the given pressure. The temperature at which a liquid at a given pressure boils, in the ordinary sense of that term, meaning the formation of bubbles of vapor near the bottom of the containing vessel, is slightly variable; it depends to some extent upon the rapidity at which heat is given to the liquid, and to some extent upon the absence of dust particles

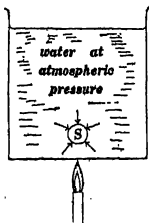


Fig. 10.

and the cleanness of the containing vessel. The connection between *boiling temperature* and the *minimum temperature of vapor* at a given pressure may be explained as follows: Figure 10 represents a bubble *S* of water vapor or steam underneath water at atmospheric pressure. Therefore the steam itself must be at atmospheric pressure,* and if its temperature (the temperature of the water) is less than that for which steam can exert one atmosphere of pressure, the bubble of steam will condense into liquid and collapse. The temperature of the water must be at least as great as the minimum temperature of water vapor at atmospheric pressure in order that the bubble of steam may continue to exist, and if the temperature of the water is slightly greater than this the bubble of

* As a matter of fact the bubble of steam must be slightly above atmospheric pressure because of the weight of the overlying water.

steam will continue to grow in size as more steam is formed at its boundaries.

23. Superheating* and undercooling of liquids. When water which is free from air and dust is heated in a clean glass vessel, its temperature is likely to rise 10 degrees or more above its boiling point (corresponding to the given pressure); and when it begins to boil it does so with almost explosive violence and the temperature quickly falls to the boiling point. If pure water is cooled in a clean glass vessel, its temperature is likely to fall considerably below its normal freezing point; and when freezing begins a large amount of ice is suddenly formed and the temperature quickly rises to the normal freezing point. It seems that water cannot change to vapor or to ice except there be some nucleus at which the change may begin. Most liquids show these phenomena of superheating and undercooling.

Supersaturation of a salt solution. When a solution of a salt stands in equilibrium in contact with undissolved crystals of the salt the solution is said to be *saturated*. A slight cooling of the saturated solution in the presence of the crystals causes additional crystals to be formed and the residual solution is weakened, but it is still saturated at the lower temperature.

When a salt solution free from air and dust is set aside to cool in a clean glass vessel it generally becomes *super-saturated*, and crystallization of the dissolved salt takes

* The term *the superheating of a liquid* must not be confused with the term *the superheating of steam*. Superheated steam is unsaturated steam, that is, steam of which the pressure is less than the maximum pressure at the given temperature, or of which the temperature is greater than the minimum temperature for the given pressure. Steam may be superheated by passing saturated steam from a steam boiler through a coil of pipe in a furnace.

place suddenly when a minute crystal of the same salt is dropped into the solution or when the solution is given a vigorous shake. Supersaturation is the same thing as undercooling.

24. Variation of boiling (or condensing) temperature with pressure. The boiling (or condensing) temperature of water varies greatly with pressure. Thus at normal atmospheric pressure the boiling point of water is 100° C., at half-of-an-atmosphere the boiling point is about 81° C., and at two atmospheres the boiling point is about 122° according to the table in Art. 22. This dependence of boiling point upon pressure may be emphasized as follows: Given a vessel of water at 75° C. There are two ways to bring the water to boiling, namely, raise the temperature of the water to its "normal boiling point" for atmospheric pressure, or lower the "boiling point" to the actual temperature of the water by reducing the pressure.

Another illustration of the dependence of boiling (or condensing) temperature on pressure is afforded by the ammonia refrigerating machine, the essential features of which are shown in Fig. 11. A system of "cooling pipes" in the cold room and a system of "condensing pipes" in the warm outside air contain anhydrous ammonia (NH_3), and a pump draws ammonia vapor out of the "cooling pipes" and forces it into the "condensing pipes," thus maintaining a low pressure in the "cooling pipes" and a high pressure in the "condensing pipes." Under these conditions the liquid ammonia in the "cooling pipes" continues to boil, and the ammonia vapor in the "condensing pipes" continues to condense to liquid. The condensed liquid flows back into the "cooling pipes" and is used over and over again. The usefulness of the

refrigerating machine depends on the fact that the continued boiling or vaporization of the liquid ammonia in the cooling pipes keeps the pipes cold while they take in heat from their surroundings. Indeed the continued boiling of a liquid requires a continued giving of heat to the liquid, and the continued condensing of a vapor requires the continued taking of heat away from the vapor. This matter is discussed in Art. 29.

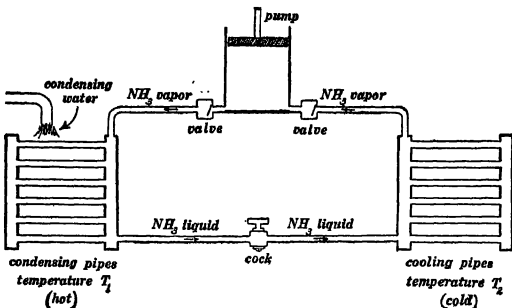


Fig. 11.

25. Variation of freezing points with pressure. Any substance which expands on freezing (as water does when it changes to ice) has its freezing temperature lowered by increase of pressure, and vice versa.

Consider the ice on a pond in moderate winter weather when the temperature of the surface of the ice is only a few degrees below the normal freezing point. When the edge of a skate rests on the ice there is a small region of very high pressure, and in this region the melting temperature is reduced by the pressure below the actual

temperature of the ice. Therefore the ice melts and forms a minute layer of liquid water under the skate, and the skate slides over this layer of water with very little friction. When the skate passes by, the minute quantity of water freezes again because it is, of course, very cold.* A skate does not slide very easily over extremely cold ice because the pressure does not lower the freezing point to the actual temperature of the ice, and therefore no water forms under the skate.

The cohesion of small particles of ice when pressed together, as in the packing of a snow ball, is due to the melting of the ice at the points of contact where the pressure is great, and the immediate freezing of the resulting water as it flows out of the small regions of high pressure.

LEADING QUESTIONS

L. Q. 27. Can pure steam at atmospheric pressure be hotter than 100°C .? If so, state precisely how this condition could be brought about.

L. Q. 28. Can pure steam at 100° have a pressure less than one atmosphere? If so, state precisely under what conditions.

L. Q. 29. What is meant by superheated steam and how is it produced?

L. Q. 30. How could you, possibly, dry out sawdust by blowing steam through it?

L. Q. 31. A cylinder contains water vapor at low pressure and at 110°C . The volume of the vapor is steadily decreased and its temperature is kept constant by taking heat from it.

* Suppose for example the ice is at -3°C . and that the pressure is increased to a value which lowers the freezing point to -5°C . Then in the high-pressure region the ice at -3°C . is much warmer than its melting point, and it quickly melts, and the heat absorbed in melting (see Art. 29) lowers the actual temperature of *ice and water* to -5°C . That is to say, there is a momentary melting and cooling of ice and water under the skate.

Sketch a curve showing the approximate relation between volume and pressure.

L. Q. 32. A cylinder contains water vapor at 200° C. and at atmospheric pressure. Heat is taken from the vapor steadily and its pressure is kept constant by reducing its volume. Sketch a curve showing the approximate relation between volume and temperature.

L. Q. 33. The atmospheric pressure at the summit of Pikes Peak (14,000 feet above sea-level) is ordinarily about 450 millimeters of mercury, and the atmospheric pressure at the Dead Sea (1300 feet below sea-level) is ordinarily about 795 millimeters of mercury. What is the boiling point of water at each place?

L. Q. 34. In an artificial ice plant the pipes in which the ammonia vapor condenses are at, say, 110° F., and the pipes in which the liquid ammonia boils (the cooling pipes) are at, say, 10° F. What is the pressure in each set of pipes?

L. Q. 35. The freezing point of water is lowered about 0.0075 of a centigrade degree for each atmosphere increase of pressure. A steel ball completely filled with pure water is put out of doors where the temperature is 20° below zero centigrade. When some of the water freezes it expands (the ice which is formed is more bulky than the water from which it is formed) and the pressure rises. To what pressure will the water and ice in the steel ball rise? Will all of the water in the steel ball freeze? If not, why not?

L. Q. 36. When a bottle of milk freezes, the frozen milk (which is mostly water) bulges out of the mouth of the bottle. When melted paraffine is left in a jar to cool and harden (to freeze), a deep conical depression or "pipe" is left in the surface of the solid paraffine. Similarly a deep sink hole or "pipe" is always left in the top of an ingot of cast steel. What can you infer from these facts as to the relative density of water and ice? Of fluid and solid paraffine? Of fluid and solid steel?

L. Q. 37. Does snow waste away during a dry, bitter cold spell? If so, why and how?

L. Q. 38. Why can you not press very cold snow into a coherent ball?

L. Q. 39. A fine steel wire can cut through a block of ice in the course of an hour or more, the wire being pulled strongly against the ice; but the ice remains as one block after the wire has cut through. Explain.

26. Boiling points and freezing points of solutions. When a moderately dilute solution of common salt in water freezes, pure ice is formed, and the whole of the salt is left in the residual liquid. When a solution of salt in water boils, pure water vapor is formed, and the whole of the salt is left in the residual liquid. In every such case, namely, when the dissolved substance does not pass off with the water vapor or crystallize with the ice, the boiling point of the solution is higher than the boiling point of pure water and the freezing point of the solution is lower than the freezing point of pure water.*

27. The freezing of solutions and of metallic alloys. There are usually two distinct ways in which a solution can freeze, namely, (a) By the deposition of crystals of ice, and (b) By the deposition of crystals of the dissolved salt. The following example will make this clear.

Freezing of solutions of ammonium sulphate, $(\text{NH}_4)_2\text{SO}_4$. When a weak solution of ammonium sulphate is cooled it deposits crystals of pure ice, the residual liquor grows richer and richer in ammonium sulphate, and the freezing temperature lowers more and more. Thus the ordinates of the curve *I* in Fig. 12 show the freezing temperatures (the *ice points*) of weak solutions of ammonium sulphate.

* A good discussion of this subject may be found in Whetham's *Theory of Solution*, Cambridge University Press, 1902. It is also discussed at considerable length in Nernst's *Theoretical Chemistry* (English translation, Macmillan & Co., London, 1916), and in Jones's *Physical Chemistry* (The Macmillan Co., New York, 1902).

When a hot concentrated solution of ammonium sulphate is cooled it deposits crystals of pure ammonium sulphate, the residual liquor becomes less and less rich in the amount of dissolved salt it contains, and the freezing temperature lowers more and more. Thus the ordinates of the curve *S* in Fig. 13 show the freezing points (the *salt points*) of solutions of ammonium sulphate of high concentration.

The curve *I* is called the *ice curve* and the curve *S* is called the *salt curve*. Figure 14 shows both curves, and

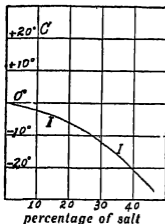


Fig. 12.

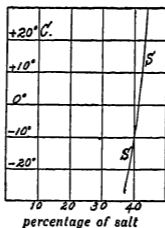


Fig. 13.

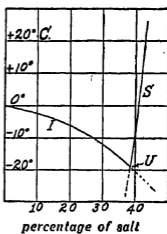


Fig. 14.

the point of intersection *U* is called the *eutectic point*. There is, of course, a definite temperature corresponding to *U* and a definite concentration of the solution. The former is called the *eutectic temperature* and the latter is called the *eutectic concentration*.

The dotted portion of *S* corresponds to an unstable undercooled condition of the solution in the absence of ice crystals but with salt crystals present, and the dotted portion of *I* corresponds to an unstable undercooled condition of the solution in the absence of salt crystals but with ice crystals present.

A solution of a salt cannot exist, stably, at temperatures below the eutectic temperature, and therefore the eutectic temperature is often called the minimum freezing temperature. For ammonium sulphate in water the eutectic temperature is -19.05° C. and the eutectic concentration is 38.4 per cent. ammonium sulphate.

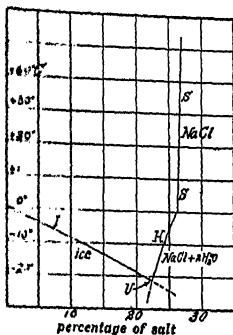


Fig. 15.

When the eutectic solution freezes, ice crystals and salt crystals are deposited simultaneously, and the temperature remains constant until the whole of the solution is frozen.

The freezing point curves of sodium chloride solutions are shown in Fig. 15. Along the curve *I* the freezing solution deposits crystals of pure ice, along the curve *S* the freezing solution deposits crystals

of pure NaCl, and along the curve *H* the freezing solution deposits crystals of $\text{NaCl} + 2\text{H}_2\text{O}$.

Solutions of NaCl have two eutectic points or eutectic temperatures, namely at -21.2° C. with 22.42 per cent of NaCl and at $+0.15^{\circ}$ C. with 26.34 per cent NaCl.

The phenomena of freezing of fused mixtures of salts* and the phenomena of freezing of metallic alloys are similar to the phenomena of freezing of salt solutions,

* Freezing point curves of about 150 two-salt mixtures are given on pages 611-633 of the 4th edition of Landolt and Börnstein's *Physikalisch-Chemische Tabellen*.

and the above described behavior of a solution of ammonium sulphate is perhaps the simplest case. Thus Heycock and Neville* have found many cases in which the freezing of a metallic alloy causes the deposition of pure crystals of one metal or the other, in the same way that the freezing of an ammonium sulphate solution causes the deposition of pure crystals of ice or pure crystals of salt. The freezing point of the residual alloy is steadily lowered by the deposition of pure crystals of either metal until a certain point (the eutectic point) is reached when the residual alloy (the eutectic alloy) continues to freeze without further drop of temperature.

Another case which is slightly more complicated is exemplified by alloys of lead and tin, of which the freezing-point diagram is shown in Fig. 16a†. Along the branch AC of the curve, crystals of lead are deposited containing a variable percentage of tin ranging from pure lead at A up to 12 atoms of tin to 88 atoms of lead as the eutectic point C is approached; along the branch BC of the curve, crystals of tin are deposited containing a variable

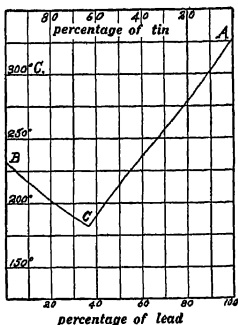


Fig. 16a.

* See Nernst's *Theoretical Chemistry* (Macmillan & Co.), page 402.

† Taken from a paper by W. Rosenheim and P. A. Tucker, *Philosophical Transactions of the Royal Society, Series A, Vol. CCIX, pages 89-122, November 17, 1908.*

percentage of lead ranging from pure tin at *B* up to 1 atom of lead to 500 atoms of tin as the eutectic point is approached. The crystals of lead containing variable

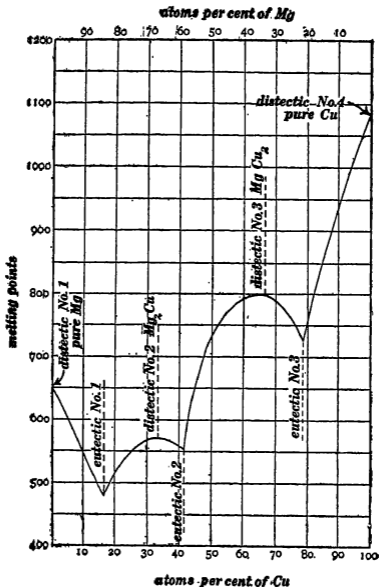


Fig. 16b.

percentage of tin and the crystals of tin containing a variable percentage of lead are called *solid solutions*.

Figure 16b is a melting-point diagram of alloys of

copper and magnesium.* These alloys present three *eutectic points* as indicated in the figure and four so-called *distectic points*, or points of maximum freezing temperature. The first third of this diagram, between distectic points 1 and 2, is a melting-point diagram of mixtures of pure magnesium and the chemical compound Mg_2Cu ; the middle portion of the diagram, between distectic points 2 and 3, is a melting-point diagram of mixtures of the two chemical compounds Mg_2Cu and $MgCu_2$; and the last third of the diagram, between distectic points 3 and 4, is a melting-point diagram of mixtures of the chemical compound $MgCu_2$ and pure copper.

When a cast metal is slowly cooled, the outside portions of the casting differ very considerably in composition from the interior portions of the casting; any substance which is present in the metal in small quantity tends to collect in the central parts of the casting.†

28. The use of ice and salt as a freezing mixture. Ice in a strong solution of common salt has a very low melting point, 15 or 20 degrees below zero centigrade (see Fig. 15). Therefore ice mixed with salt falls to a temperature of 15 or 20 degrees below zero centigrade, and stands at that temperature (if there is no change in the concentration of the brine which bathes the ice, that is if there is an excess of undissolved salt) until all of the ice is melted

* From a paper by G. Urazov, abstracted in the *Chemische Centralblatt*, page 1038, for the year 1908.

† A simple introduction to the study of metallic alloys is R. S. Williams' *Introduction to Metallography*, McGraw-Hill Book Co., New York, 1920. More complete treatises are *Metallography*, by Cecil H. Desch, Longmans, Green and Co., London, 1910, and *Metallic Alloys*, by G. H. Gulliver, Chas. Griffen & Co., London, 1913. An important book on the physical properties of metals and alloys is *Introduction to Physical Metallurgy*, by W. Rosenhain, D. Van Nostrand, London, 1914.

by heat absorbed from surrounding objects. A vessel of pure water or cream surrounded by a mixture of ice and salt gives off heat to the very cold mixture until the water or cream is frozen. The sprinkling of salt on ice or snow in the winter time does not, as commonly supposed, melt the ice; it lowers the melting point below the temperature of the surroundings (if this is not more than 15 or 16 degrees below zero centigrade) and the ice is melted by the heat abstracted from its surroundings.

LEADING QUESTIONS

L. Q. 40. There are three distinct modes of freezing of a solution of common salt. Explain. What are the eutectic points (temperatures) of solutions of common salt, and what are the eutectic compositions?

L. Q. 41. The formation of a "pipe" in a steel ingot as described in L. Q. 36 is not the only serious trouble that is connected with the freezing of a steel ingot. What would you expect as to percentages of carbon, phosphorus, sulphur, etc., in the outer portions of the ingot which freeze first and the inner portions which freeze later?

L. Q. 42. Plumbers universally believe that hot "water pipes freeze much oftener than cold water pipes," meaning that pipes which are filled with water that has been freed from air by boiling are much more frequently burst by freezing than are pipes which are filled with ordinary tap water. This matter has been recently studied experimentally at the University of Iowa and the belief of the plumbers has been completely verified. What can you offer as an explanation? Would a pipe closed at both ends and wholly exposed to cold be more likely to burst if filled with air-free water than if filled with tap water?

29. Latent heat of fusion and latent heat of vaporization.
When heat is imparted to a substance which is at

its melting point or at its boiling point, a portion of the substance is melted or vaporized and the temperature remains unchanged. The number of thermal units required to change unit mass of the solid substance at its melting point into liquid at the same temperature is called the *latent heat of fusion* of the substance. The number of thermal units required to change unit mass of a liquid* at its boiling point into vapor at the same temperature is called the *latent heat of vaporization* of the liquid.

It is believed† that all the heat energy required to

TABLE

	Melting point	Latent heat of fusion, calories per gram.	Boiling point at atmospheric pressure	Latent heat of vaporization, calories per gram.
Water . . .	0° C.	80	100° C.	536
Alcohol . . .			78·3	209
Lead . . .	327	5·86	1500 about	
Mercury . . .	-39·5	2·82	357	62
Sulphur . . .	115	9·36	444·7	
Ether . . .			34·9	91
Carbon bisulphide			46·8	86·6
Chloroform . .			61·1	58·5

change a solid at its melting point into liquid at the same temperature is stored in the liquid as an increase of molecular potential energy, and that all the heat energy required to change a liquid at its boiling point into vapor at the same temperature is stored in the vapor as an increase of molecular potential energy.

The boiling point of a substance varies greatly with pressure, and the latent heat of vaporization varies

* In some cases the substance changes directly from the solid form to vapor without passing through the liquid state.

† Many of the ideas of the atomic theory are not known to be true in fact, although such ideas may be quite generally accepted and used.

greatly with the temperature of the boiling point of the given substance. Thus, the latent heat of vaporization of water is 1043 British thermal units per pound at a pressure of one "pound" per square inch (absolute) and at a temperature of 102° F., whereas it is 965.7 British thermal units per pound at standard atmospheric pressure and 212° F., and it is 844.4 British thermal units per pound at 200 "pounds" per square inch (absolute) and 381° F.

The accompanying table gives freezing and boiling points and latent heats of fusion and vaporization of a number of substances at standard atmospheric pressure.

30. Critical states. When a liquid and its vapor (confined in a vessel) are heated, a portion of the liquid vaporizes, the pressure is increased, the density of the vapor increases and the density of the liquid decreases.* When a certain temperature is reached, the density of the liquid and the density of the vapor become equal, and the vapor and liquid are identical in their physical properties. This temperature is called the *critical temperature* of the liquid, and the corresponding pressure is called the *critical pressure*. The heat of vaporization of a liquid is less the higher the temperature (and pressure) at which vaporization takes place and it becomes zero at the critical temperature.†

31. Pressure of mixed gases. When two or more gases are mixed in a vessel, the total pressure is equal to the sum of the pressures which each component gas would exert if it occupied the vessel alone (*Dalton's Law*). For

* This statement may not be exactly correct in some cases. The densities of liquid and vapor become more and more nearly equal in every case.

† A good discussion of the subject of critical temperatures and pressures, including the celebrated experiments of Andrews on carbon dioxide, is given in Edser's *Heat for Advanced Students*, pages 201-219. An introduction to van der Waal's theory of corresponding states is given in Edser's *Heat for Advanced Students*, pages 304-314. A very full discussion of van der Waal's theory of corresponding states is given in Nernst's *Theoretical Chemistry*, pages 224-230. Macmillan & Co., London, 1904.

example, if the amount of air in a vessel is such that it alone would exert a pressure p , and if the amount of water vapor in the vessel is such that it alone would exert a pressure w , then the mixture will exert a pressure $p + w$.*

A result of Dalton's law is that a definite portion of the total pressure of a mixed gas may be considered to be due to each of the component gases of which the mixture is made. Thus the total pressure of the atmosphere is due in part to the nitrogen, in part to the oxygen, in part to the carbon dioxide, in part to the water vapor, in part to the argon, etc., of which the atmosphere is a mixture.

32. Evaporation versus boiling. It is a common observation that water evaporates into the air at temperatures far below 100° C. *A liquid at a given temperature continues to evaporate as long as the pressure of its vapor is less than the maximum pressure its vapor can exert at the given temperature.* This is true whether the space above the liquid is filled with vapor alone or with vapor mixed with any gas at any pressure. For example, water vapor can exert a pressure of 355 millimeters of mercury at 80° C., and if a vessel at 80° C. contains water, the water will vaporize until *the pressure of the water vapor* in the vessel is 355 millimeters. If the vessel contains nothing but water vapor, then, of course, the total pressure will be 355 millimeters when equilibrium is reached. If the vessel contains dry air at atmospheric pressure, some of the air will be driven out by the vapor which is formed, and when equilibrium is reached the water-vapor pressure in the vessel will be 355 millimeters and the air pressure

* This statement is very nearly true, the degree of approximation being about the same as in the case of Boyle's law and Gay Lussac's law. See Art. 72.

will be 405 millimeters, making a total of 760 millimeters.* If the vessel is filled with dry air at any pressure p and suddenly closed before any perceptible amount of water vapor is formed, then water vapor will form until the total pressure is $p + 355$ millimeters, p being the pressure due to the air alone and 355 millimeters being the pressure of the water vapor.

33. Atmospheric moisture. Hygrometry. Dew Point. The dew point is the temperature to which the atmosphere must be cooled in order that the water vapor which is present may be saturated. Further cooling of the atmosphere would cause some of the moisture to condense.

Vapor pressure. That part of the pressure of the atmosphere which is due to the water vapor which is present is called the vapor pressure. This pressure varies from nearly zero to 30 millimeters, or more.

Absolute humidity. The amount of water in the air, usually expressed in grams of water per cubic meter of air, is called the absolute humidity of the air. The absolute humidity varies from 1 gram of water, or less, per cubic meter of air on a very cold, dry winter's day to 30 or 35 grams of water per cubic meter of air on a moist summer's day.

Relative humidity. The amount of water in the air expressed in hundredths of what the air would contain if it were saturated at the given temperature is called the relative humidity. When the relative humidity is low, the air is said to be dry; when the relative humidity is high, the air is said to be moist, irrespective of the actual amount of water which is present. For example, 20 grams of water per cubic meter would correspond to a relative

* The outside air pressure is assumed to be 760 millimeters.

humidity of about 60 per cent. on a warm summer's day, and the air would seem to be extremely dry, whereas about 5 grams of water per cubic meter of air would saturate the air at 0° C. and the air would seem extremely moist.

The method usually employed for the determination of the hygrometric elements (dew point, pressure of vapor, absolute humidity, and relative humidity) is by use of wet and dry bulb thermometers, from the readings of which the various quantities may be determined from empirical tables. Such tables are published by the United States Weather Bureau.*

LEADING QUESTIONS

L. Q. 43. A bottle has a little hot water poured into it, after which the bottle is quickly closed and shaken, and the pressure in the bottle rises considerably. Name the two causes of this pressure rise.

L. Q. 44. A closed bottle contains a small bulb of water, and by giving the bottle a quick shake the bulb can be broken and the water released. The bottle is submerged in a bath at 100° C.

(a) The bottle contains no air (interior is a vacuum), and when the bulb is broken the pressure rises quickly to one atmosphere.

(b) The bottle contains dry air at normal atmospheric pressure, and when the bulb is broken the pressure rises *very slowly* to two atmospheres.

Explain why the pressure rises much more slowly in case (b) than in case (a), and why the pressure rises to two atmospheres in case (b) although the temperature is 100° C.

L. Q. 45. The bottle in L. Q. 44 is in a water bath at 80° C. and the pressure of the dry air in the bottle is, let us say,

* Weather Bureau Bulletin No. 235. Price, 10 cents.

760 millimeters. To what value does the pressure rise when the bulb of water is broken?

L. Q. 46. In North Western Canada a winter wind sometimes blows over the mountains from the Pacific coast region, and this wind when it reaches a low altitude east of the mountains is actually warmer than it was at the same altitude on the western slope of the mountains. Explain.

PROBLEMS

39. How much ice would be required per hour to cool 10 cubic feet of air per second from 90°F. to 75°F. , assuming ice-water to escape at the freezing point? The density of the air is about 0.081 pound per cubic foot.

40. One thousand cubic centimeters (1.29 grams) of air at 0°C. and at standard atmospheric pressure (1,013,200 dynes per square centimeter) is heated to 100°C. and allowed to expand so as to keep its pressure constant. Find the amount of heat in joules required. Find the work in joules done by the expanding gas.

How much more heat energy does the hot expanded gas contain than the original 1000 cubic centimeters at 0°C. ? Explain. Take one gram-calorie equal to 41,800,000 ergs or 4.18 joules.

41. One gram (one cubic centimeter very nearly) of water at 100°C. becomes 1646 cubic centimeters of steam at 100°C. and at standard atmospheric pressure. Calculate the amount of work done by the expanding steam in pushing the surrounding air out of the way.

42. It takes 536 calories of heat to convert one gram of water at 100°C. into steam at the same temperature and at standard atmospheric pressure. How much greater is the heat energy content of the steam than the heat energy content of the water? Ans. 496.1 calories.

43. What becomes of the difference (536 calories—496.1 calories) in Problem 42?

34. Transformation points of solid substances. Everyone is familiar with the three forms in which water can exist, namely, as a vapor or gas, as a liquid, and as a solid; but recent researches have shown that water can

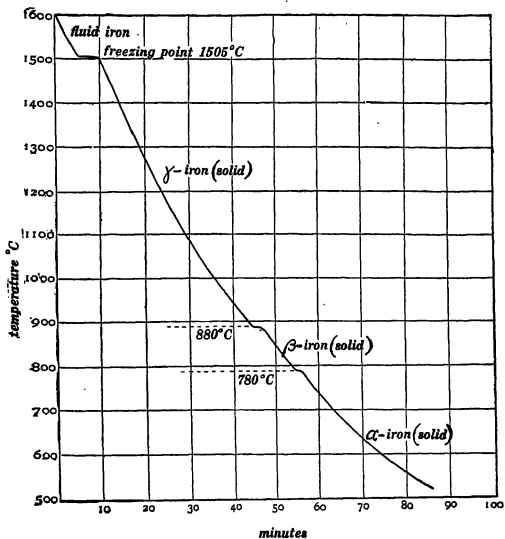


Fig. 17.

exist as a solid in several distinct crystalline forms. Ordinary ice changes to these several forms in succession as it is cooled, each change or transformation takes place at a definite temperature (at a given pressure), and these

temperatures are called *transformation points* or *transformation temperatures*.

This matter may be illustrated by considering pure iron as follows. A crucible filled with melted pure iron is allowed to cool, its temperature is observed at stated times, and the ordinates of the curve in Fig. 17 show the decreasing temperature as a function of the time. As the crucible loses heat its temperature drops until it begins to freeze, then the temperature remains constant until all of the iron is frozen. Pure iron shows two other constant-temperature stages of short duration, one at 880°C . and one at 780°C . In fact, solid iron exists in three distinct states or forms which are called γ -iron, β -iron and α -iron, respectively. Let us consider what takes place at 880°C . for example, and let us compare it with what takes place when the iron freezes at 1505°C .

The physical properties of a substance change when the substance changes from liquid to solid.

The volume of a substance changes when the substance changes from a liquid to a solid.

A certain amount of heat (latent heat) is given off without any change of temperature when a substance changes from liquid to solid.

The change of a substance from liquid to solid

The physical properties of iron change when the iron changes from the γ form to the β form.

The volume of iron changes when the iron changes from the γ form to the β form.

A certain amount of heat (latent heat) is given off without any change of temperature when iron changes from the γ form to the β form.

The change from γ -iron to β -iron takes place at a

takes place at a definite temperature, pressure being given, and this temperature is called the *freezing point* of the substance.

definite temperature, pressure being given, and this temperature is called a *transition temperature* or *point* of the iron.

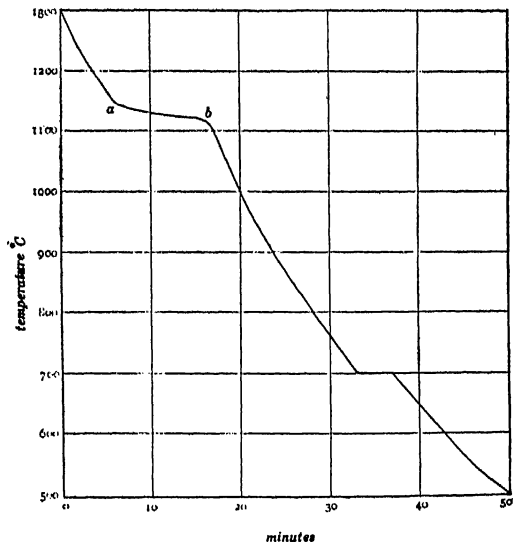


Fig. 18.

Impurities in iron (like salt in water) generally lower the freezing point of the iron, and also lower the transition temperatures. Thus the curve in Fig. 18 is the cooling curve of a crucible containing melted cast iron which

contains five or six per cent of carbon. In this case freezing begins at about 1150°C . (about 350 degrees lower than pure iron), and the freezing temperature drops to about 1120°C . as freezing progresses. Compare this with the freezing of a salt solution as shown in Fig. 12. Below 1100°C . the iron is solid, and but one transition temperature seems to exist, namely, at 700°C . Both transition temperatures in Fig. 17 have been lowered by the carbon, and if both exist in Fig. 18 they are so close together as to show themselves as one.

35. The recalescence of steel. The phenomenon of undercooling shows itself in an interesting way in the transition of steel from the γ -form to the α -form (the two transition temperatures in

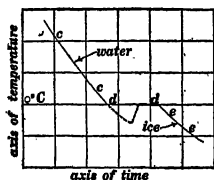


Fig. 19.

pure iron seem to be a single transition in steel as in cast iron), and is called *recalescence*.

To understand the recalescence of steel let us consider the cooling curve of a clean vessel of pure water as shown in Fig. 19. When the water reaches the freezing point it does not begin to freeze, but cools below the freezing point (undercools) as indicated by the dotted line, and when freezing does begin the temperature rises suddenly to 0°C . When a piece of hot steel is cooled, the change from γ -form to α -form does not take place when the transition temperature is reached, but the γ -iron cools below the transition temperature, and when the change to α -iron does begin it takes place rapidly and the temperature rises suddenly on account of the heat which is developed by the change. The recalescence of steel can

be shown by heating a piano steel wire to a bright red heat by an electric current and then allowing the wire to cool. When the cooling wire reaches a low red heat the retarded transformation occurs, and a very decided momentary increase of brightness is seen, due to a momentary rise of temperature. The wire also suddenly lengthens when the transformation takes place, as may be seen by stretching the wire horizontally and observing the variation in the sag.

36. Retarded transformations. The hardening of steel. A familiar example of an almost permanently retarded transformation is afforded by common molasses candy. The crystallization of syrup is a very slow process because, apparently, of the viscosity of the syrup. If the syrup is cooled very, very slowly the crystallization takes place at the true freezing temperature, but if the syrup is cooled quickly it does not have time to crystallize, and the result is the well-known molasses candy. Paradoxical as it may seem, the syrup when it is cooled suddenly does not have time to "freeze" but remains in that physical modification which is the stable modification at high temperatures. If, however, molasses candy is allowed to stand for some months the "freezing" gradually comes about, transforming the substance into the crystalline modification which is stable at low temperatures.

Retarded transformations occur in the hardening of steel. At a high temperature steel settles to thermal equilibrium with a certain crystalline structure, that is, with the iron in a certain modification and with certain crystalline compounds of iron and carbon present. If the steel is very slowly cooled the various transformations take place at approximately the true transition temperatures, and we have what is called *annealed steel* which is the

stable form of steel at low temperatures. If, however, the steel is cooled very quickly the transformation from one modification to another does not have time to take place, the form or modification of the steel which normally exists and is stable at high temperatures is left in existence at ordinary temperatures, and we have the familiar hard form of steel. Hardened steel is an unstable modification and it tends gradually to change to the stable modification (soft annealed steel).* This change is greatly hastened by a slight rise of temperature. Thus hard steel is *tempered* by heating it slightly for a short time.

LEADING QUESTIONS

L. Q. 47. Red-hot iron is " γ -form" iron, and when it cools slowly it changes to " β -form" and " α -form" in succession. What is quenched iron? What is annealed iron?

L. Q. 48. Quenched (glass-hard) steel is "tempered" by moderate heating for a short time. What is supposed to be the change which takes place in tempering, and why the moderate heating?

L. Q. 49. Any viscous liquid like syrup or melted glass freezes (crystallizes) with excessive slowness when cooled to its true freezing point. What happens when such a liquid is quickly cooled? What happens when the cold liquid stands for a very long time?

L. Q. 50. Very old glass comes to have a granular surface. This change is called *devitrification*. What is supposed to be the nature of this change?

L. Q. 51. Ordinary glass or glass-like quartz ("fused" quartz) devitrifies in a short time at a low red heat. Explain this hastening of devitrification as being analogous to the accelerated softening (tempering) of hard steel by moderate heating.

* Extremely hard steel gradually softens. See paper by Carl Barus, *Physical Review*, Vol. XXIX, pages 516-524, December, 1909.

CHAPTER IV

THE TRANSFER OF HEAT

37. Convection, conduction and radiation. There are three processes by means of which heat energy is transferred from one place to another. (a) The carrying of heat energy to the various parts of a building by the hot air which travels through the building from a hot-air furnace is called *convection*; (b) The transfer of heat energy along a metal rod one end of which is in a fire is called *conduction*; and (c) The transfer of heat energy from the sun to the earth across the intervening empty space, or the transfer of heat energy from the hot coffee in a Dewar bulb (popularly known as a thermos bottle) across the empty space between the double glass walls of the bottle is called *radiation*.

Convection, conduction and radiation are nearly always mixed up together. Thus the heat energy from a steam coil, or "radiator," is distributed throughout a room by all three actions. By far the greater part of the heat energy is in this case distributed by air currents (convection); a much smaller portion of the heat energy is distributed by radiation, it shoots through the air and can be felt by the hand at some distance from the "radiator," even though the air surrounding the hand be cool; and an extremely small portion of the heat energy from the "radiator" is distributed by conduction, it spreads or flows along the wall and floor and is handed on from particle to particle of the air.

38. Conduction of heat energy through a wall. Definition of thermal conductivity. Let h be the number of gram-calories of heat which flows through a wall (or slab of material) per second, let a be the area of the slab or wall (area of one side), let l be the thickness of the slab or wall, and let t and t' be the temperatures of the respective faces of the slab or wall. Then h is proportional to a , it is proportional to $(t - t')$, and it is inversely proportional to l . Therefore we may write

$$h = k \frac{a(t - t')}{l} \dots\dots\dots(13)*$$

where k is a proportionality factor whose value depends on the substance of which the wall or slab is made, and it is called the *thermal conductivity* of the substance.

The accompanying table gives the values of k for a number of substances.

TABLE
THERMAL CONDUCTIVITIES

Gram-calories per Second per Square Centimeter of Wall for a Temperature Difference of One Centigrade Degree for Each Centimeter of Thickness of Wall

Substance	k	Substance	k
Wrought iron at 0°C.	0.207	Crown glass at 25°C.	0.00183
" " 100°C.	0.157	Ordinary brick wall at 25°C.	0.0012
" " 200°C.	0.136	Insuforial earth brick at 25°C.	0.0002
Pure copper at 20°C.	0.950	Insuforial earth brick at red heat	0.0004
Pure tin at 20°C.	0.151	85% magnesia pipe covering	0.00016
Pure zinc at 20°C.	0.265	Cork moulded in slabs	0.00010
Yellow brass at 0°C.	0.204	Dry saw-dust (light wood)	0.00015
Red brass at 0°C.	0.246	Flannel, best wool	0.00004
Water at 15°C.	0.00154	Air at 0°C.	0.0000054
Ice at 0°C.	0.0057	Hydrogen at 0°C.	0.000319
Freshly fallen snow	0.00026		
Flint glass at 25°C.	0.00143		

Conductivities as given in this table must be multiplied by 69,800 to give British thermal units per day (24 hours) flowing through each square foot of wall for a temperature difference of one degree Fahrenheit for each inch of thickness of wall.

* This equation applies only to an established, steady flow of heat.

The thermal conductivities of most metals decrease with rise of temperature, and the thermal conductivities of most non-metals increase with rise of temperature. Thus the thermal conductivity of pure lead, in gram-calories per second per square centimeter for a temperature difference of one centigrade degree per centimeter thickness of wall, is about 0.092 at -160°C. , it is about 0.084 at 0°C. , and it is about 0.082 at 100°C. The conductivity of infusorial-earth brick is about twice as much at a low red heat as it is at ordinary room temperature.

39. Heat insulation. To prevent all exchange of heat between a body and its surroundings would be to *insulate* the body thermally; but complete thermal insulation is impracticable, as may be seen from the following examples.

A layer of air between parallel walls is not a very good heat insulator notwithstanding the very low thermal conductivity of air. This is partly because radiation takes place quite freely across a layer of air, but (at low temperatures), mostly because heat is carried across the air layer by air currents (by convection), except when the air layer is horizontal with the hot wall above and the cold wall below.

A layer of saw-dust or cotton or wool is a fairly good heat insulator, because the thermal conductivities of these substances are low, because they hinder convection almost completely, and because radiation is always very small through any extremely non-homogeneous substance like saw-dust or cotton or wool.

The best known heat insulation (for moderately low temperatures) is the empty space between the double glass walls of a Dewar bulb (popularly known as the thermos bottle). If the space is very highly exhausted, heat is carried across it by radiation only, and if the

glass walls are silvered the radiation is reduced to a minimum.

At furnace temperatures radiation is very great (see discussion of Stefan's law in Art. 46), and an empty space between glass or quartz walls, one of which is red-hot is a very poor heat insulator. Light magnesia and the expensive electric-furnace product known as silox are among the best of heat insulators for very high temperatures. Good heat insulation is possible at low temperatures because radiation is relatively small at low temperatures, and because the thermal conductivities of the usual porous insulating materials is low. At high temperatures, on the other hand, good heat insulation is not possible because radiation is very great and because all known porous materials have much higher thermal conductivities at high temperatures than at low temperatures.

40. The steady flow of heat through a cylindrical shell like

a pipe covering. Figure 20 is an end view of a pipe covering of which the inside radius is R_1 , the outside radius is R_2 , the length is L , the inside temperature is T_1 and the outside temperature is T_2 . It is required to find an expression for $T_1 - T_2$ when h gram-calories of heat per second flows through the shell

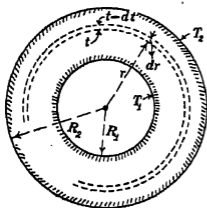


Fig. 20.

or pipe covering from inside to outside, the thermal conductivity of the material being k .

Consider the infinitely thin elementary shell between the dotted circles in Fig. 20 ; its thickness is dr , its area

perpendicular to the direction of heat flow is $2\pi rL$, the temperature of its inner face is t , let us say, and the temperature of its outer face is $t - dt$.

The heat flow across or through the elementary shell is h gram-calories per second, and equation (13) applies to the shell because its radius of curvature is very great in comparison with its thickness. Therefore, substituting $2\pi rL$ for a , dt for $(t - t')$, and dr for l , and solving for dt/dr , we get

$$\frac{dt}{dr} = -\frac{h}{2\pi Lk} \cdot \frac{1}{r} \dots\dots\dots (i)$$

whence, by integration, we get

$$t = -\frac{h}{2\pi Lk} \cdot \log_e r + \text{a constant} \dots\dots\dots (ii)$$

But when $r = R_1$ we know that $t = T_1$, and if we substitute this pair of values in (ii) we find the value of the constant of integration, namely,

$$T_1 + \frac{h}{2\pi Lk} \cdot \log_e R_1.$$

Therefore equation (ii) becomes

$$t = -\frac{h}{2\pi Lk} \cdot \log_e r + \frac{h}{2\pi Lk} \cdot \log_e R_1 + T_1 \dots\dots (iii)$$

or

$$t = \frac{h}{2\pi Lk} \cdot \log_e \frac{R_1}{r} + T_1 \dots\dots\dots (iv)$$

But $t = T_2$ when $r = R_2$ and therefore equation (iv) gives

$$T_1 - T_2 = -\frac{h}{2\pi Lk} \cdot \log_e \frac{R_1}{R_2} \dots\dots\dots (v)$$

This equation is more convenient if solved for h and it is better to put $+\log_e \frac{R_2}{R_1}$ for $-\log_e \frac{R_1}{R_2}$. Therefore

$$h = \frac{2\pi Lk(T_1 - T_2)}{\log_e \frac{R_2}{R_1}} \dots\dots\dots (14)$$

This equation gives the rate of flow of heat, h , in gram-calories per second when L is expressed in centimeters, and $T_1 - T_2$ in centigrade degrees; and when the conductivity k is taken from the table in Art. 38.

Remark. In the derivation of equations (13) and (14) the variation of thermal conductivity with temperature is ignored.

LEADING QUESTIONS

L. Q. 52. A layer of air is used to thermally insulate two large flat parallel plates. In case (a) the layer of air is horizontal and the hotter plate is the upper one; in case (b) the layer of air is vertical; and in case (c) the layer of air is horizontal and the cooler plate is the upper one. In which case is the insulation best and in which case is it worst? Why?

L. Q. 53. Define what is meant by the thermal conductivity of a substance.

L. Q. 54. The thermal conductivity of clothing which is completely water soaked is about the same as the thermal conductivity of water, and yet some recent experiments made in England show that a man's nude body loses heat to cold water about three times as fast as if the man had on a light suit of clothing. Explain.

L. Q. 55. An orchard on the side of a hill suffers much less from late spring frosts than does an orchard in a nearby valley. Explain.

Why is a frost likely to occur on a still clear night; whereas with cloudy sky or with a strong wind, but with the same prevailing temperatures in the early evening, a frost is not likely to occur?

L. Q. 56. The hollow walls of a refrigerator cupboard are filled with saw-dust and arrangements can be made so that the external warm air can enter and circulate through the saw-dust very slowly, or so that the cold internal air can so circulate. The latter arrangement will keep the saw-dust dry, although the internal air has a high relative humidity. Explain.

PROBLEMS

44. A boiler shell is made of iron $\frac{3}{8}$ inch thick and sufficient heat flows through each square foot of the shell to vaporize 72 pounds of water per hour. What is the temperature difference in Fahrenheit degrees between outer and inner surfaces of the boiler shell?

Note. The latent heat of vaporization of water varies with the temperature and pressure of the steam which is produced, and, of course, steam is usually produced in a boiler at pressures greatly in excess of standard atmospheric pressure. Lacking the data as to temperature and pressure of the steam and as to the latent heat of vaporization, assume that the 72 pounds of water is converted into steam at standard atmospheric pressure and at 212° F. (100° C.). Under these conditions the latent heat of vaporization of water is 536 calories per gram or 536×1.8 British thermal units per pound.

45. Let us suppose that the inner and outer surfaces of a glass window pane are at 60° F. and 10° F. respectively. The glass is $\frac{1}{8}$ inch thick and it is of the kind called crown glass. Calculate the amount of heat which flows out of a house in 24 hours through a window containing 9 square yards of this window glass.

Note. By far the greater part of the hindrance to the flow of heat out of a room through a window pane is in the delivery of the heat from the inside warm air to the glass and from the glass to the cold outside air. This problem as stated must not be taken as representing the facts even approximately. See Problem 50.

46. A refrigerator cupboard has 88 square feet of wall area, including top and bottom, and the wall is made of 3-inch cork board (the heat insulation due to the outside wood finish is to be neglected in this problem). Let us suppose that the inner and outer surfaces of the cork board are at 45° F. and 80° F. respectively. The cupboard contains 20 cubic feet of air (about 1.6 pounds), the cupboard is opened 20 times per day, and it is assumed that the entire body of enclosed air (at 40° F.) flows out of the cupboard and is replaced by warm air at 85° F. every time the cupboard is opened. Find the number of pounds of ice that will be

melted in the cupboard in 24 hours, assuming that the ice water escapes at 32° F.

47. How much ice would be melted each 24 hours by the heat that would flow into the cupboard of the previous problem through an iron bolt one square inch in sectional area, the length of the bolt being 4 inches? Assume that the outer end of the bolt is at, say, 70° F., and that the inner end of the bolt is at, say, 50° F.

48. A house wall consists of 8 inches of ordinary brick and one inch of pine (conductivity of pine about $\frac{1}{4}$ of that of ordinary brick) with no air space between. Suppose that the outer surface of the brick is at 20° F. and that the inner surface of the pine is at 65° F. Find the heat that would flow through 250 square feet of the double wall in 24 hours, and find the temperature of the surface of contact of pine and brick.

Notes. To solve this problem find the drop of temperature through the double wall when 1 British thermal unit per day flows through each square foot. Let this drop of temperature be d . Then the flow of heat through each square foot per day for the given temperature difference (45°) will be $45/d$ British thermal units. The brick and pine are supposed to be in intimate contact, which, in fact, is never the case.

49. A metal rod is 5 centimeters in diameter and 40 centimeters long. Starting from end A of the rod the first 20 centimeters is copper, the next 10 centimeters is tin, and the remaining 10 centimeters is lead. The end A of the rod is at 100° C., the other end of the rod is at 0° C., and the rod is surrounded by a vacuum jacket like a thermos bottle so that no appreciable amount of heat can escape sidewise from the rod. Taking the conductivities as given in the table in Art. 38, calculate the amount of heat which flows along the rod per second, and calculate the temperatures where tin and lead, and tin and copper meet.

50. Approximately 50 British thermal units of heat per day per square foot is transferred from air to glass (or from glass to air) for each Fahrenheit degree of temperature difference between the surface of the glass and the air when

the air is still, and heat is transferred about four times as fast when the air is in motion as in case of a moderate wind. Find the amount of heat transferred in one day through 9 square yards of $\frac{1}{8}$ inch window glass (crown glass) when the inside air temperature is 80° F. and the outside air temperature is 20° F. and the outside air temperature is 20 degrees below zero Fahrenheit. Find this result (a) When the air is still outside and inside, and (b) When the air is still inside and windy outside. Ans. (a) 196,800 British thermal units; (b) 309,500 British thermal units.

Note. To solve this problem find the difference of temperature d between inside and outside air when 1 British thermal unit per square foot is transferred per day. Then the required result is $81 \text{ square feet} \times 100/d$.

51. Find the temperature of the inner and outer surfaces of the window glass in part (a) of the previous problem. Ans. Inner surface 31.4° F., outer surface 28.6° F.

52. A steam pipe 4 inches outside diameter has a 85 per cent magnesia covering which is 8 inches outside diameter. The pipe is at 230° F. and the outside of the covering is at 95° F. Find the loss of heat in 24 hours from 100 feet of the pipe. Solve this problem approximately by taking the pipe covering as approximately equivalent to a flat wall 2 inches thick \times 100 feet long \times $\pi/2$ feet wide, where $\pi/2$ feet is the middle circumference of the covering. Ans. 118,400 British thermal units.

53. Solve Problem 52 by using the correct formula as developed in Art. 40. The value of k to be used in equation (14) of Art. 40 must be so chosen that the thickness of the wall may be expressed in feet; that is, $k = 0.00016 \times 69,800 \div 12$. Ans. 113,500 British thermal units.

Note. The near identity of this result and the result of the previous problem shows that the approximate solution is sufficiently accurate for all practical purposes. The approximate solution becomes less and less exact as the ratio R_2/R_1 increases.

A very interesting problem is to show just where in the argument of Art. 40 the step is made which necessitates the use of the modified value of k .

54. Using an argument somewhat similar to the argument in Art. 40, derive an expression for the temperature difference between inside and outside of a spherical shell of conductivity k when h gram-calories per second flows through the shell, using R_1 for inside radius and R_2 for outside radius of shell.

41. Component parts of radiant heat. A beam of white light (of sunlight) is separated into its component parts (colors) when it is passed through a prism, and each component part is light of a definite wave-length. That is to say, sunlight is a mixture of various wave-lengths (colors), and the band of colors which is formed by a prism and as seen in a spectroscope is called the *spectrum*. The spectrum of sunlight contains invisible, long-wave-length rays beyond the red end of the spectrum in what is called the *infra-red*, and invisible, short-wave-length rays beyond the violet end of the spectrum in what is called the *ultra-violet*.

The radiation from any hot body is, like sunlight, a mixture of all wave-lengths. Some of these wave-lengths (from about wave-length 0.39μ to about wave-length 0.75μ , where $\mu = 0.0001$ centimeter) produce a sensation of light when they enter the eye, and these wave-lengths are therefore called light; *but all wave-lengths heat a black body upon which they fall, and therefore all wave-lengths are called radiant heat.*

42. Composition of any given batch or beam of radiation. The relative intensities (energy intensities) of the various wave-lengths in a given beam of radiation can be measured by the spectro-bolometer, as briefly explained in the following article, and these intensities can be represented by the ordinates of a curve of which the abscissas represent the respective wave-lengths.

Thus, Fig. 21 shows three such curves, the curve for the radiation from a black body at 1377° K., the curve for the radiation from a black body at 1087° K., and the curve for the radiation from a black body at 836° K.* The dotted lines in Fig. 21 show the actually observed curves, the deep hollows being due to the excessive absorption of certain wave-lengths (2.7μ and 4.3μ) by the water

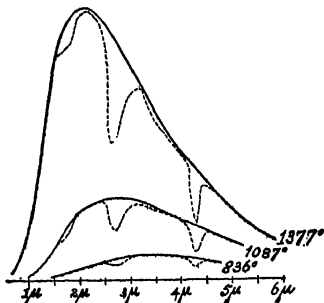


Fig. 21.

vapor and the carbon dioxide in the air through which the radiations passed on their way from the radiating hot body to the measuring instrument.

43. **The spectro-bolometer.** One form of instrument which is used for studying the composition of radiation is the *spectro-bolometer*, which is essentially like a spectro-scope. Radiation from a hot body passes through a narrow slit *S*, through a collimating lens *C*, through a

* From measurements made by Lummer and Pringsheim, see *Verh. d. deutschen Phys. Gesellschaft*, Vol. I, page 23, Berlin, 1899.

prism P and through a second lens L which forms a band of images of the slit (a spectrum) at VR , red at R and violet at V . The spectrum as seen from E , Fig. 22, is shown in Fig. 23. The small portion V , only is visible, the *visible spectrum*, the invisible portion UV corresponding to the shorter wave-lengths is called the *ultra-violet*,

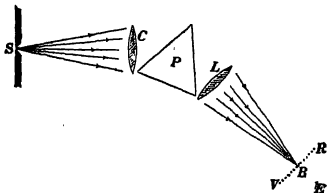


Fig. 22.

and the invisible portion IR corresponding to the longer wave-lengths is called the *infra-red*. The infra-red is shown to scale of wave-lengths in Fig. 23, but a prism always crowds this portion of the spectrum together greatly.

The spectro-bolometer is so called because the intensity

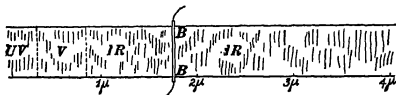


Fig. 23.

of the spectrum at any point B is indicated by a *bolometer*.* A very narrow, thin strip of metal BB (see Fig. 23) is exposed to the radiations at B (see Fig. 22).

* A very sensitive thermo-element or a delicately suspended vane like the vane of Crookes' light-mill may be used.

This strip of metal is connected as one arm of a carefully balanced Wheatstone bridge (see Fig. 24). The radiations at B , Fig. 22, raise the temperature of BB , change its resistance slightly and cause a deflection of the sensitive galvanometer G ; and this deflection is proportional to the energy intensity of the spectrum at B in Fig. 22. The metal strip BB is balanced against a similar strip $B'B'$ (see Fig. 24) which is *not* exposed to the spectrum, thereby avoiding a disturbance of the balance of the Wheatstone bridge by a change of temperature of the whole apparatus.

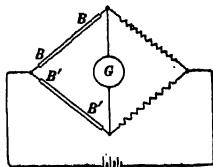


Fig. 24.

The lenses C and L and the prism P must be made of fluorite, or rock salt or other substance which is transparent to a wide range of wave-lengths. Ordinary glass is almost completely opaque to ultra-violet and to infra red rays.

A spectrum which is formed by a prism is crowded together where the dispersion of the prism is small and spread apart where the dispersion of the prism is large; and the intensity of the spectrum is therefore too great where the prism dispersion is small, and too small where the prism dispersion is great. This effect is corrected for in the curves which are shown in Fig. 21.

44. Definition of an ideal black body. The artificial black body. A perfectly black body, or a perfectly black spot on a body, would not reflect any of the radiation which might fall upon it, it would absorb it all or swallow it all, as it were. The ideal or perfectly black body (or spot on a body) is of great importance in the theory of

radiation, and a small hole in the wall of a closed box or chamber is a perfectly black spot. Such a hole swallows up all radiation which falls upon it, it does not reflect any. The full-line curves in Fig. 21 refer to the radiation from

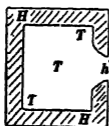


Fig. 25.

a perfectly black body. The dotted curves were obtained by allowing the radiations from the hole h in Fig. 25 to enter the slit S of the spectrometer, and the deep valleys, due to the absorption of certain wavelengths by water vapor and carbon

dioxide, were bridged over, as it were, by the smoothly drawn full-line curves.

45. Normal radiation or black-body radiation corresponding to a given temperature T . When one peeps into a porcelain kiln which has been heated to a fairly uniform temperature one sees nothing at all but a flood of soft yellow light. Radiation of the same composition and of the same intensity comes to the peep-hole from everything in the kiln, from a piece of metal, from a bit of charcoal, from a piece of porcelain, from a pile of ashes, from a deep body of hot air! Objects which are near the peep-hole may cool off slightly and thereby become faintly visible, or a beam of sunlight (or any light that comes from something hotter than the kiln) may be reflected into the kiln through the peep-hole so as to render the objects in the kiln visible as if they were in a dark room.

The similar radiation which comes to the peep-hole from all directions and which, of course, escapes through the peep-hole, is called the *normal radiation* or the *black-body radiation* for the given temperature T of the kiln.

The composition of this normal or black-body radiation at Kelvin* temperature T is given by the equation

$$E_{\lambda} = \frac{C}{\lambda^5(e^{c/\lambda T} - 1)} \dots\dots\dots (15)$$

This is the equation to the full-line curves in Fig. 21, it is due chiefly to Max Planck, and it is called *Planck's equation*. The amount of energy which is carried through each square centimeter of the peep-hole per second by all wave-lengths between λ and $\lambda + d\lambda$ is $E_{\lambda} \cdot d\lambda$, and the quantity E_{λ} so defined is the ordinate of the curves in Fig. 21. When $E_{\lambda} \cdot d\lambda$ is expressed in watts per square centimeter, wave-lengths in centimeters, and T in Kelvin-centigrades, then $C = 3.718 \times 10^{-16}$ and $c = 1.46$.

The chief purpose of this discussion of radiation is to give to the student a clear understanding of the optical or radiation methods for measuring high temperatures. These methods all depend directly or indirectly on Planck's equation, and the question rises: How much dependence is to be placed on Planck's equation? In answer to this question it may be stated that Planck's equation is very largely the result of theoretical considerations, and that it has been verified by experiment throughout a wide range† of temperatures; but, of course, the equation applies only to normal radiation (black-body radiation).

The most useful radiation methods for measuring high

* Sometimes called *absolute* temperature. Centigrade degrees are understood to be used always unless it is expressly stated to the contrary.

† Between 87° K. and 1650° K., temperature measurements being based on the hydrogen thermometer, and 1650° K. being about the highest temperature that can be so measured.

temperatures are discussed in Arts. 47 and 48, but the following is of considerable interest.

Consider the maximum ordinates of the curves in Fig. 21. Let λ_m be the wave-length corresponding to the maximum ordinate for temperature T° K. Then, from Planck's equation it can be shown that

$$T\lambda_m = \text{a constant} \dots\dots\dots(i)$$

and the value of the constant is 2940 if λ is expressed in ten-thousandths of a centimeter ($= \mu$). Therefore if we know the wave-length corresponding to the maximum energy intensity in the radiation from a black body we can calculate the Kelvin temperature of the body. This method of finding temperature is not feasible in practice because of the difficulty of determining λ_m . Equation (i) expresses what is called *Wien's displacement law*. It was discovered by Wien, and it has been derived theoretically from the second law of thermodynamics,* but it is also a consequence of Planck's equation.

46. Stefan's law. The total energy W which is radiated per second by an ideal black body, is

$$W = saT^4 \dots\dots\dots(16)$$

where s is a constant, a is the area of the surface of the body† and T is the Kelvin temperature of the body. This law was discovered experimentally by Stefan in 1879, it was derived for the ideal black body from the second law of thermodynamics by Boltzmann‡ in 1884, and it may now be thought of as a consequence of Planck's equation. Stefan's experiments, however, related to ordinary bodies, not to the ideal black body; indeed equation (16) applies fairly well to any ordinary body, except that the constant

* See *Wiedemann's Annalen*, Vol. LII, page 156, 1894.

† This statement will be qualified later.

‡ Boltzmann's argument is quite simple. See Art. 70.

s has a smaller value for any ordinary body than it has for an ideal black body. Thus for ordinary glass the value of s is 0.85 times its value for the ideal black body.

The value of s for the ideal black body is 5.32×10^{-12} when W is expressed in joules per second (watts), a is square centimeters and T in Kelvin-centigrade.

Equation (16) expresses the rate at which a body gives off energy by radiation, but always the body receives energy by radiation, and the net rate at which a body gives off energy by radiation is

$$w = sa(T^4 - T_0^4) \dots \dots \dots (17)$$

where T is the Kelvin temperature of the body and T_0 is the Kelvin temperature of all surrounding bodies. The conditions under which a may be taken as the total area

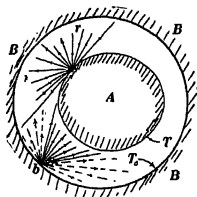


Fig. 26.

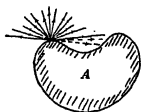


Fig. 27.

of the radiating body are explained in the following discussion.

Consider a body A , Fig. 26, which is entirely surrounded by a hollow body B , the Kelvin temperature of A being T and the Kelvin temperature of B being T_0 . The arrows rr represent radiations from a small part of the surface of A , and if the shape of A is such that none of the rays rr ever come back to A (see Fig. 27), then a in equation

(16) is the area of the surface of A . Furthermore, each square centimeter of the inner surface of BB emits heat energy at the rate sT_0^4 , but many of the rays which are emitted from the inner surface of BB come back to B as indicated by the dotted rays from b in Fig. 26. A careful consideration of this matter leads to the conclusion that BB gives heat energy to A at the rate saT_0^4 , where a is *not* the area of B , but the area of A . Therefore the net rate of loss of heat by body A is $sa(T^4 - T_0^4)$, according to equation (17).

47. Total-radiation pyrometers. The practicable forms of total-radiation pyrometers, that is to say, of pyrometers which depend upon or are actuated by all the wave-lengths which are emitted by the hot body, are briefly described at the end of this article, and, of course, these pyrometers can be used by persons who are totally ignorant of all theory; but a clear understanding of these pyrometers, and, to some extent, a clear understanding of any radiation pyrometer, depends upon several points which are touched upon in the following discussion.

It is desired to find the amount of heat energy per second which comes from the hot spot h in Fig. 28 and falls on the ball b , a being the area of the hot spot, b the radius of the ball and r the distance of the ball from the hot spot as indicated in Fig. 28. In the discussion of Fig. 28 the heat which is given off by the walls ff is ignored and the expression which we get for the heat energy received per second by the ball b will be strictly correct for the arrangement shown in Fig. 29, a being the area of the hole in the screen SS , b the radius of the ball, and r the distance of the ball from the screen SS ; if nothing but the hot spot h is visible through the hole in SS from the front or exposed side of the ball b . The distance D makes no difference.

The beam from h , Fig. 28, when it reaches b carries a certain amount c of heat energy per second per square centimeter of section, and therefore the heat energy per second falling on b is $\pi b^2 c$. It remains therefore to determine c .

Imagine a hemisphere of radius r with its center at the hot spot h

in Fig. 28. Consider the narrow beam from h which falls on the zone zs of the hemisphere. The energy per second per square centimeter of this inclined beam is to the energy per second per square centimeter of the central beam (which is c as above stated) as the full area a of the hot spot is to the projected area, $a \cos \phi$, of the hot spot as seen from the zone zs .* Therefore the energy per second per square centimeter which falls on the zone zs is $c \cos \phi$, and, since the area of the zone is $2\pi r^2 \sin \phi \cdot d\phi$, the total energy per second, dW , falling on the zone is

$$dW = 2\pi cr^2 \sin \phi \cos \phi \cdot d\phi. \quad (i)$$

If we integrate this expression from $\phi = 0$ to $\phi = \pi/2$ we get the total energy per second which falls on the entire hemisphere, namely

$$W = \pi cr^2 \dots (ii)$$

Now the energy per second falling on the entire hemisphere is equal to the total energy per second, saT^4 , which is emitted by the hot spot [see equation (16)]. Therefore

$$c = \frac{1}{\pi r^2} saT^4 \dots \dots \dots (iv)$$

and consequently we get for $\pi b^2 c$ the following expression

$$\left\{ \begin{array}{l} \text{rate at which heat} \\ \text{energy falls on} \\ \text{the ball } b \end{array} \right\} = \frac{b^2}{r^2} saT^4 \dots \dots \dots (v)$$

This equation applies to Fig. 28 on the assumption that the walls ff do not radiate energy to the ball, and it applies to Fig. 29 under the conditions specified above in bold-faced type.

The ball b in Fig. 29 will rise in temperature until it gives off heat energy to its surroundings as fast as it receives heat energy from the hot spot h , and it is of some interest to consider how the rate at which the ball b receives heat from h may be inferred from the observed rise of temperature of b so that, using equation (v) the temperature T of the hot spot may be calculated, b , r , s and a being known. If an electrical resistance coil is mounted inside of the ball b it is easy to determine how many watts of electrical power is required to keep

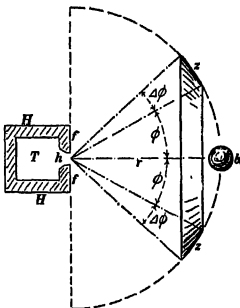


Fig. 28.

* This relation is known as Lambert's Law.

the ball at temperature t when the hole in the screen in Fig. 29 is closed, t being the temperature at which the ball b stands when the hole in the screen is open and no electrical power is delivered to the coil in the ball; the power so determined is the rate at which the ball received energy from the hot spot as expressed by equation (v).

The foregoing discussion covers all of the principles of the so-called total-radiation pyrometer, but the method which is outlined for the determination of T would be out of the question in practice for the following reasons:

(a) The rise of temperature of the ball, which we will call the *indicator*, depends upon the size of the hot spot (on the value of a) and upon the distance r of the indicator from the hot spot, whereas it is highly desirable to devise and use an arrangement in which the rise of temperature of the indicator may be independent, or nearly independent, of a and r . This condition may be met in two ways as follows: (1) The screen SS may be at a fixed distance r from the ball, that is

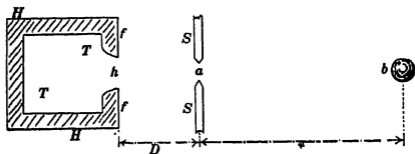


Fig. 29.

to say, the screen SS and the indicator b may both be fixed in a portable structure, then, if the condition which is stated above in bold-faced type is met, the rise of temperature will be independent of the distance D and independent of the size of the hot spot (a now being the area of the hole in the screen SS); or (b) a lens (or a concave metal mirror) may be used to form an image of the hot spot and the indicator b may be placed in the plane of this image, then, if the image is larger than the indicator b the desired condition is realized, as is evident from the following considerations: Suppose the distance of the lens (or mirror) from the hole is doubled, then one-quarter as much energy per second will fall on the lens (or mirror) and one-quarter as much energy per second will be concentrated in the image, but the image will be half as large* in diameter or one-quarter as large in area, and therefore the energy per second which is concentrated in each square centimeter of the image will be the same as before; or suppose the diameter of the hole h to be doubled, then four times as much energy per second

* This assumes that the focal length of the lens (or mirror) is short in comparison with the distance of the lens (or mirror) from the hole.

will fall on the lens (or mirror) and four times as much energy per second will be concentrated in the image, but the image will be four times as large in area, and therefore the energy per second which is concentrated in each square centimeter of the image will be the same as before. A well-polished metal mirror is very much more satisfactory than a lens for concentrating the total radiation (all wave-lengths) because the longer wave-lengths do not pass through glass. A lens is mentioned in the above discussion because the formation of an image by a lens is more familiar than the formation of an image by a concave mirror.

(b) The ball *b* takes much too long a time to settle to a steady temperature when it is exposed to the radiations as indicated in Fig. 28 or Fig. 29. A satisfactory total-radiation pyrometer must therefore have a very minute indicating body which will quickly settle to a steady temperature.

The Fery total-radiation pyrometer.* A concave metal mirror forms an image of the hot spot, one junction of a

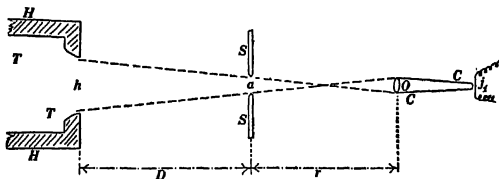


Fig. 30.

thermo-element is placed in the plane of this image and heated thereby, the thermo-element is connected to a sensitive millivoltmeter, and the scale of the millivoltmeter is divided so as to indicate the temperature of the hot spot or hot body directly.

The Thwing total-radiation pyrometer.† The essential features of the Thwing pyrometer are shown in Fig. 30.

* Manufactured and for sale by The Taylor Instrument Company of Rochester, N.Y.

† Manufactured and for sale by The Thwing Instrument Company of Philadelphia, Pa.

The screen *SS* and the polished metal cone *CC* are rigidly fixed to each other, and the hot spot is large enough so that nothing but the hot spot would be visible through α from any point in the opening of *O* of the cone. The radiant heat which enters *O* is thus independent of the distance *D* and independent of the size of the hot spot, and this radiant heat is concentrated upon one junction j_1 of a thermo-element which is connected to a sensitive millivoltmeter which is calibrated so as to read the temperature of the hot spot directly.

Errors of total radiation pyrometers. The indications of these pyrometers are not completely independent of size and distance of the hot spot or hot body, and therefore for accurate work they should be calibrated under the conditions under which they are to be used.

These pyrometers are calibrated so as to give correctly the temperature of an ideal black body. When used to measure the temperature of a body in the open the indicated temperature is too low, as shown in the accompanying table.

TABLE*

TRUE TEMPERATURES AND APPARENT TEMPERATURES AS INDICATED BY A TOTAL-RADIATION PYROMETER WHEN SIGHTED UPON THE FOLLOWING MATERIALS IN THE OPEN

Indicated temperature centigrade	True temperatures centigrade				
	Molten iron	Molten copper	Iron oxide	Copper oxide	Nickel oxide
600	—	1130	630	720	710
700	—	1290	735	830	800
800	1200	—	840	945	895
900	1340	—	945	1060	985
1000	1475	—	1050	1170	1075
1100	1610	—	1155	—	1165
1200	1750	—	1260	—	1255

* From a paper by Paul D. Foote and C. O. Fairchild (of the Bureau of Standards) published in the Special Pyrometry Volume of the American Institute of Mining and Metallurgical Engineers, 29 W. 39th St., New York City.

48. The one-color pyrometer. The method for measuring temperature which is described in Art. 47 depends upon all of the radiations (all of the wave-lengths or colors) emitted by the hot body. Following are possible methods for determining the temperature of a radiating black body by measuring the intensity of one wave-length (or color) only.

(a) If E_λ in Planck's equation (equation (15)) were measured in absolute units for a chosen and known wave-length λ , then the temperature T of the radiating black body could be calculated, using Planck's equation. However, the measurement of E_λ in absolute units is a very difficult thing; it involves complicated allowances for size of the body and its distance from the measuring apparatus (a spectro-bolometer), allowances for width of slit of spectro-bolometer, dispersion of prism, loss of radiation by reflection and absorption, etc. This measurement is entirely out of the question in practice.

(b) The value of E_λ for a chosen wave-length (or color) may be measured in terms of any arbitrary unit, first for a black body at a known temperature and then for a black body at an unknown temperature; then, using Planck's equation, the unknown temperature can be calculated. This is perhaps the best of all the radiation methods for measuring high temperatures, and in the arrangement used in the Leeds and Northrup one-color pyrometer, the measurement is independent of size and distance of the hot body.

The Leeds and Northrup one-color pyrometer.* An image of the hot body or hot spot is formed at F ,

* This pyrometer was developed simultaneously by Holborn and Kurlbaum in Germany and by Morse in the United States. It is manufactured and for sale by Leeds and Northrup of Philadelphia.

Fig. 31, by the objective lens* *O*, and, looking through an eyepiece *E*, the observer sees this image and the filament *F* of a glow lamp superposed on each other. Red glasses *G* are used to cut out all but one color (approximately one wave-length), the rheostat *R* is adjusted until the lamp filament blends with the image of the hot spot and becomes invisible, and the scale of the ammeter *A* is divided so as to read the temperature of the hot body directly.

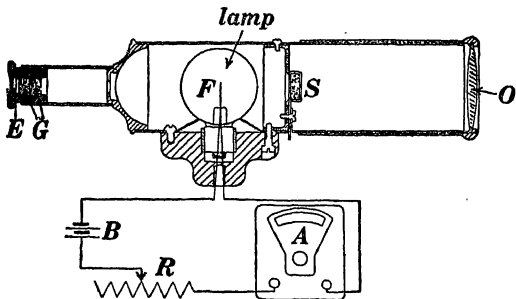


Fig. 31.

When very high temperatures are to be measured the brightness of the hot spot is reduced in a fixed ratio by a smoky glass absorbing plate *S*. This pyrometer is not suitable for temperatures below a red heat.

Errors of the one-color pyrometer. The Leeds and Northrup pyrometer is calibrated so as to indicate correctly the temperature of an ideal black body (see Fig. 25), and when it is used to measure the temperature of a hot

* The wave-length used in this instrument (red light) will pass through glass, and therefore a glass lens can be used.

body in the open its indications are always too low. The errors are sometimes very large and *wholly uncertain* if the hot body is brightly illuminated. Therefore to measure the temperature of a hot body in the open the hot body should not be illuminated, it should be in a very dimly lighted region. Under these conditions the indicated temperatures and true temperatures are related as in the accompanying table.

TABLE*

TRUE TEMPERATURES AND APPARENT TEMPERATURES AS INDICATED BY A ONE-COLOR PYROMETER USING RED LIGHT (WAVE-LENGTH 0.65μ) WHEN SIGHTED UPON THE FOLLOWING MATERIALS IN THE OPEN, GENERAL ILLUMINATION BEING VERY SMALL.

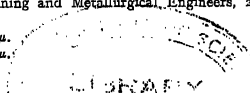
Indicated temperatures centigrade	True temperatures, centigrade						
	Molten copper	Molten† iron	Solid iron oxide	Solid nickle oxide	Nichrome alloy	Molten‡ slag.	Bright platinum
700	—	—	700	701	702	—	750
800	—	—	801	802	804	—	861
900	—	—	902	904	906	—	973
1000	1150	—	1004	1007	1010	—	1087
1100	1277	1183	1106	1110	1116	—	1202
1200	1405	1296	1210	1215	1224	—	1320
1300	1536	1410	—	1320	—	—	1435
1400	—	1525	—	—	—	1455	1555
1500	—	1641	—	—	—	1565	1675
1600	—	1758	—	—	—	1670	—
1700	—	1876	—	—	—	1780	—

Remark. It is interesting to note that the one-color pyrometer does not need to be calibrated when it is used to measure the temperature of an ideal black body, but only standardized. Thus if the brightness of the lamp

* From a paper by Paul D. Footc and C. O. Fairchild (of the Bureau of Standards) published in the Special Pyrometry Volume of the American Institute of Mining and Metallurgical Engineers, 29 W. 39th St., New York City.

† For wave-length 0.40μ .

‡ For wave-length 0.65μ .



filament, as seen through the red glass, has been measured in any arbitrary unit for various ammeter readings by a simple photometric method, and if the reduction ratio of the smoky glass S has been determined by a simple photometric test, then a reading of the ammeter for a single known temperature T (of an ideal black body) is sufficient, because a reading of the ammeter for any unknown temperature T' (of an ideal black body) will give the brightness ratio of the particular wave-length (which is known) for the two temperatures T and T' so that T' can be calculated, using Planck's equation. See Problem 65.

LEADING QUESTIONS

L. Q. 57. What is meant by an ideal black body or by an ideally black spot on a body?

L. Q. 58. What is meant by normal or black-body radiation at a given temperature?

L. Q. 59. State Stefan's law concerning the rate at which heat is radiated by an ideally black body in the form of a sphere. State Stefan's law concerning the rate at which the sphere receives heat by radiation from surrounding bodies at temperature T_0 , the surrounding bodies being supposed to be ideally black.

L. Q. 60. Under what conditions is the area a in equation (16) of Art. 46 the actual area of the radiating body?

L. Q. 61. Equation (17) of Art. 46 applies to two of the bodies A and B in Figs. 26 and 27. What is a in equation (17)?

L. Q. 62. Small dark leaves lying on white snow in the sunshine sink into the snow. Explain. What difference will a strong wind make, assuming the leaves to stick fast to the snow? Explain.

L. Q. 63. Given two similar thermometers the bulb of one of which is blackened with dull black paint. (a) When both thermometers are laid in the sun, the black bulb thermometer

rises considerably above the bright bulb thermometer. Explain. (b) When both thermometers are held near to and to one side of a hot brick or hot can of water, both thermometers rise about equally. The reason is that glass itself is "black" in so far as long wave-lengths are concerned. What does this mean? What bearing does this fact have on (a).

PROBLEMS

55. Figure 32 shows the energy curve of sunlight, and the maximum ordinate is at 0.5μ . Calculate the Kelvin temperature of the sun on the assumption that the sun radiates like an ideal black body.

56. The rate at which heat escapes from or is transmitted into the contents of a good Dewar bulb (thermos bottle) is proportional to $(T_1^4 - T_2^4)$, where T_1 is the Kelvin temperature of the contents and T_2 is the Kelvin temperature of the outer shell of the thermos bottle. The temperature of the bottle full of hot water is observed to drop from 100°C. to 99°C. in 30 minutes when the outer shell of the bottle is at 25°C. Find the time required for the temperature of the bottle full of ice water to rise from 0°C. to 1°C. when the outer shell of the bottle is at 20°C. , neglecting the effects of flow of heat through the cork stopper. Ans. 189 minutes.

57. The inner bottle of a Dewar bulb (unsilvered) contains one liter of ice water, and the outer shell of the Dewar bulb is at 25°C. The coefficient s in equation (17) of Art. 46 for unsilvered glass is about 0.85 times its value for an ideal black body. The area of the outside surface of the inner bottle is 175 square centimeters. Neglecting the flow of heat through the cork (this flow of heat is not, in fact, negligible), find the time required for the contents of the Dewar bulb to rise from 0°C. to 1°C. Ans. $37\frac{1}{2}$ minutes.

58. A steam pipe $1\frac{1}{2}$ inches outside diameter and 10 feet long filled with steam at 212°F. gives off 1100 British thermal units per hour when in a room at 75°F. Calculate the rate at which heat energy is radiated by the pipe, assuming the

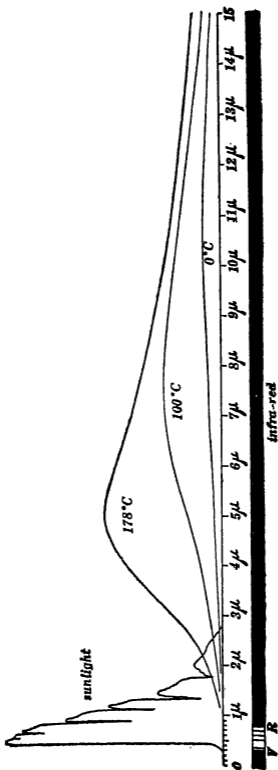


Fig. 32.

pipe to radiate like an ideal black body. What fraction of the heat given off by the pipe is radiated? How is the remainder given off?

59. A black ball 10 centimeters in diameter is placed in front of an opening in a furnace and screened from all radiations from the outside of the furnace walls (see Fig. 29). The hole in the screen has an area of 100 square centimeters ($=a$), the distance of the ball from the screen is 150 centimeters ($=r$) and the ultimate steady temperature of the ball is found to be such as would be steadily maintained (with the hole in the screen closed) by 6.21 watts of electrical energy delivered to a resistance coil placed inside of the ball. Calculate the temperature of the furnace. Ans. 1800° K.

60. The sun's radiation at the distance of the earth is approximately 2 gram-calories per square centimeter per minute, which means approximately 21,800 gram-calories per square centimeter per minute at the sun's surface. Assuming the sun to radiate like an ideal black body, calculate its temperature. Ans. 4120° K.

Note. The sun's temperature as here calculated is certainly much below the sun's actual temperature. The calculation of the sun's temperature as involved in Problem 55 is much more accurate, because the departure of the sun's radiation from ideal black-body radiation is to a great extent allowed for by drawing a smooth curve so as to bridge over the deep valleys in the observed curve in Fig. 32, thus getting a fair estimate of the wave-length which would correspond to the maximum value of E_{λ} if there were no deep valleys in the observed curve. The sun's radiation departs from ideal black-body radiation chiefly because of the very sharp selective absorption of the cooler gases in the upper regions of the sun's atmosphere, and this absorption gives the deep valleys in the observed curve.

61. To what temperature would the blackened spherical bulb of a thermometer rise in full sunlight if the bulb were surrounded by a *perfectly transparent* and highly exhausted glass bulb? The bulb and all the surroundings are at 25° C. Assume the thermometer bulb to behave like an ideal black body. Ans. 74° C.

Note. A glass bulb, whether blackened or not, radiates very nearly as well as an ideal black body at low temperatures; and a blackened glass bulb absorbs nearly all the radiations which fall on it from the

sun. Therefore the result of this problem is a fair estimate of the rise of temperature of a blackened glass bulb under the specified conditions, except that the intensity of the sun's rays is considerably reduced in passing through any actual glass containing bulb.

A polished metal bulb covered with a thin coating of lamp-black absorbs nearly all the heat energy of the sun's rays (is very nearly an ideal black body in its behaviour towards the sun's rays), but it is a very poor radiator at low temperatures (far from being an ideal black body in its emission of long wave-lengths). Therefore a blackened metal bulb would get considerably hotter than a blackened glass bulb under the conditions specified in the problem.

62. The grand-mean temperature of the entire earth's surface is about 60° F. or about 15° C., let us say. Assuming the earth as a whole (including its atmosphere) to absorb the sun's rays like an ideal black body and to emit radiations like an ideal black body, calculate the Kelvin temperature of space, taking the intensity of the sun's rays to be 2 gram-calories per square centimeter per minute. Ans. 131° K. or about 223° below zero Fahrenheit.

63. Taking the intensity of the sun's rays to be 2 gram-calories per square centimeter per minute, calculate the temperature of the moon's surface where the sun's rays fall perpendicularly upon it, assuming the moon's surface to absorb all of the sun's rays like an ideal black body and to emit radiation like an ideal black body. Ans. 130° C. or 403° K.

Note. There is no appreciable atmosphere on the moon. The temperature of space, 131° K., is so low that it may be neglected in the expression $(403^4 - 131^4)$.

The "day" on the moon is about twenty-eight times as long as our day here on earth, and therefore a portion of the moon's surface is under the influence of the sun's rays for so long a time at a stretch that it must rise very nearly to the temperature which is calculated in this problem, namely, about 250° F. On the other hand, the "night" on the moon is about twenty-eight times as long as our night, and the temperature of the moon's surface falls no doubt to nearly the temperature of space every night, namely, about 220 degrees below zero Fahrenheit. This means a "daily" range of temperature on the moon from about 250° F. at "2 p.m." to about 220 degrees below zero Fahrenheit at "2 a.m." Even with our shorter day and night here on the earth, the daily range of temperature which would exist but for the ameliorating influence of our atmosphere would kill everything.

64. Using Planck's formula calculate the ratio of increase of brightness of the radiation of a black body at wave-length 0.0000641 centimeter (in the red) for an increase of temperature from 1200° K. to 1500° K. Ans. 44.7 times.

Note. When $\lambda = 0.0000641$, unity is less than half of one per cent of $e^{c/\lambda T}$ for all temperatures less than 4300° K., and therefore for most practical purposes a simplified form of Planck's equation which is known as Wien's equation can be used, namely

$$E_{\lambda} = \frac{C}{\lambda^5} \cdot \frac{1}{e^{c/\lambda T}}$$

65. A Leeds and Northrup one-color pyrometer shows that black body radiation at wave-length 0.0000641 is 2.50 times as bright at an unknown temperature T as it is at the melting point of pure copper. What is the value of T ? Ans. 1435° K.

Note. See note to previous problem.

CHAPTER V

THE PROPERTIES OF GASES. THE ATOMIC THEORY OF GASES

49. Boyle's law and Gay Lussac's law. A recapitulation. Boyle's law and Gay Lussac's law, as explained in Art. 2, are completely expressed by the equation

$$pv = MRT$$

which is fully explained in Art. 6.

Dalton's law relating to the pressures of mixed gases is stated and discussed in Art. 31.

The law of multiple volumes. The ratio of the volumes of two gases which combine chemically is always a simple fraction. Thus two volumes of hydrogen combine with one volume of oxygen to form water, volumes being measured at the same temperature and pressure; two volumes of carbon monoxide combine with one volume of oxygen to form carbon dioxide; equal volumes of hydrogen and chlorine combine to form HCl. This law of multiple volumes is, of course, chiefly of interest to the chemist, but it has an important meaning which was first pointed out by Avogadro, namely, *that all gases have the same number of molecules per unit volume at the same temperature and pressure* (Avogadro's principle).

The perfect gas. A gas which would conform exactly to Boyle's law and which would be neither heated nor cooled by free expansion (see next article) would be called a *perfect gas*. The perfect gas is, of course, an ideal; but

hydrogen, oxygen and nitrogen approximate very closely to this ideal at ordinary temperatures and pressures.

The idea of the perfect gas is of great use in theoretical chemistry and thermodynamics because many mathematical arguments can be carried out with comparative ease when applied to the ideal perfect gas, arguments which become extremely difficult when applied to a gas which does not conform to Boyle's law and which does change its temperature during free expansion; and the most remarkable thing about such arguments when applied to the ideal perfect gas is that they lead to conclusions which have in nearly every case been confirmed by experiment.*

50. Latent heat of expansion of a gas. A cylinder contains one gram of gas (nitrogen, for example) at a fairly high pressure. Let us suppose the nitrogen to expand and do an amount of work, W ergs, on a piston; and let us suppose an amount of heat, H ergs, to be given to the expanding nitrogen, *sufficient to keep its temperature constant*. Then the actual net increase of heat-energy content of the nitrogen will be $H - W$, this net amount of heat-energy has been given to the nitrogen without causing a rise of temperature, and it is called the *latent heat of expansion* of the nitrogen. For most gases, however, the latent heat of expansion is very small (H very nearly equal to W in the above discussion) so that the value of $H - W$ cannot be determined from measured values of H and W , because neither H nor W can be measured with sufficient precision.

The latent heat of expansion of a gas is of great importance in the theory of gases, and the first attempt to measure it was made by James Prescott Joule about 1840. Joule's method was essentially as follows: Imagine a glass bulb filled with compressed gas and placed in a larger empty bulb (a vacuum). If the bulb of compressed gas is broken the gas will, of course, expand and fill the

* A good example of such an argument is given in Art. 71.

larger bulb ; but in this case the expanding gas will do no mechanical work, and if the gas has any latent heat of expansion its temperature will drop. This experiment of Joule led to no definite result except to show that the latent heat of expansion of the ordinary gases is too small to be detected in this way.

The celebrated "porous plug" experiment was then devised and carried out by Joule and Thomson as explained below.

Constrained expansion and free expansion. The expansion of a gas against a receding piston in a cylinder is called *constrained expansion*. The expansion of a gas when a bulb of compressed gas is placed in a larger empty bulb and broken is called *free expansion*. If no heat-energy is given to the expanding gas its temperature drops greatly during constrained expansion, chiefly because of the mechanical work done by the expanding gas, but the temperature drops only slightly during free expansion.

The Joule and Thomson porous-plug experiment.* To determine the change of temperature of a gas during free expansion Joule and Thomson used the arrangement shown in Fig. 33. The free expansion of the gas took place

* The object of this experiment is to determine how much a gas is cooled by free expansion, but several complicating effects are involved in Fig. 33 as follows: (a) The uniform velocity of the gas is greater on the low-pressure side of the plug, so that each portion of the gas gains in *mechanical* kinetic energy as it passes through the plug, and this effect tends to produce a drop in temperature; (b) Imagine the high-pressure gas to be fed to the plug by a piston *A* (on the left in Fig. 33), which moves inwards, imagine space to be made for the low-pressure gas by a piston *B* (on the right in Fig. 33), which moves outwards, and suppose the pistons to move so as to keep the pressures constant on both sides of the plug, then the work done on the gas by piston *A* is, in general, not equal to the work done by the gas on piston *B*; and (c) A thermometer does not indicate the exact true temperature of a stream of gas.

through the innumerable minute passage ways in a porous plug, and two thermometers placed as shown in Fig. 33 served to show the change of temperature.

At moderate pressures and at temperatures not greatly different from ordinary room temperature, hydrogen is very slightly warmed when it passes through the porous plug in Fig. 33, and oxygen and nitrogen are slightly cooled. Making due allowance for the effects which are referred to in the foot-note, it is found that hydrogen is not perceptibly changed in temperature by

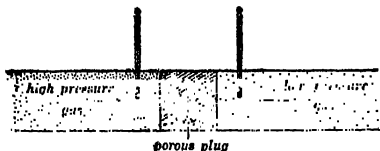


Fig. 33.

free expansion, whereas oxygen and nitrogen are slightly cooled by free expansion. In other words, the latent heat of expansion of hydrogen is zero and the latent heat of expansion of oxygen and nitrogen is small.

At very high pressures all gases are very considerably cooled by free expansion if the initial temperature is low.

Explanation of cooling of a gas by free expansion. Imagine a small bulb of compressed gas to be placed in a large empty bulb and broken. The molecules of the gas move farther apart as the gas spreads out in the large bulb, and, *if the molecules of the gas attract each other*, they will lose velocity and kinetic energy as they move apart, and this loss of molecular kinetic energy

means a drop in temperature. The molecular kinetic energy of the expanding gas decreases and its molecular potential energy (latent heat) increases.

51. The making of liquid air. The cooling effect of free expansion at very high pressures is utilized in the making of liquid air. Air is compressed to about 200 atmospheres and passed through a coil of pipe which is cooled by ice. The high pressure air then flows through a compact coil containing many feet of small copper pipe, and at the end of this coil the air escapes through a small orifice into a low-pressure region whence it flows back over the coil of copper pipe. The free expansion of the air at the small orifice cools the air considerably, and the air thus cooled cools the inflowing high-pressure air in the copper coil; the high-pressure air is then still further cooled by free expansion at the orifice; and so on, until the temperature at the orifice becomes so low as to cause some of the air to condense to a liquid which collects in the low-pressure chamber and is drawn off at will.

52. The kinetic theory of gases.* Imagine a large number of excessively minute particles (atoms or molecules) moving about in a closed vessel. Imagine these

* A good simple discussion of the kinetic theory of gases, including van der Waal's theory, is given in Edser's *Heat for Advanced Students*, pages 287-314.

A good elementary treatise is Boynton's *Kinetic Theory of Gases*, The Macmillan Co., New York, 1904. Another good treatise is *The Kinetic Theory of Gases*, by O. E. Meyer, translated by R. E. Baynes, Longmans, Green & Co., London, 1899.

Boltzmann's *Vorlesungen über Gas Theorie* is a highly important work on this subject, and some interesting points in the kinetic gas theory are touched upon in Planck's *Acht Vorlesungen über theoretische Physik* (Columbia University Lectures), Leipzig, 1910.

particles to have the property of rebounding with undiminished velocities when they strike the walls of the vessel, imagine them to be so small as seldom to collide with each other, and imagine them to exert no perceptible attraction or repulsion on each other. *Such a system of particles would exhibit all the properties of a gas.* Therefore we will speak of our system of particles as a gas in the following discussion.

Let p be the pressure of the gas in dynes per square centimeter, v the volume of the containing vessel in cubic centimeters, N the total number of particles (molecules) in the vessel, $n (= N/v)$ the number of molecules per cubic centimeter, and m the mass of each molecule in grams. The total kinetic energy of the system is constant because the molecules are assumed to rebound from the walls with undiminished velocities. Therefore the *average kinetic energy per molecule*, namely, $\frac{1}{2}m\omega^2$, is constant, ω^2 being the average value of the square of the velocities of all the molecules. Then

$$p = \frac{1}{3}nm\omega^2 \dots\dots\dots(i)$$

or, since $n = N/v$, we have

$$pv = \frac{1}{3}Nm\omega^2 \dots\dots\dots(ii)$$

Proof. The square of the velocity of a given particle is equal to the sum of the squares of the x , y and z components of its velocity. Therefore the sum of the squares of the velocities of all the particles is equal to the sum of the squares of all the x -components, plus the sum of the squares of all the y -components, plus the sum of the squares of all the z -components. The particles move at random in all directions, so that the sum of the squares of the x -components, of the y -components, and of the z -components are equal each to each. Therefore (i) The

sum of the squares, $N\omega^2$, of all the velocities is equal to three times the sum of the squares of the x -components.

Imagine the containing vessel to consist of two parallel walls, of area q , distant d from each other, perpendicular to the x -axis of reference, and between which the gas is confined. Only the x -components of the molecular velocities contribute, by impact, to the pressure on these walls, so that the y and z components may be ignored. Consider a single particle, the x -component of whose velocity is a . This particle strikes first one wall and then the other, traveling back and forth $a/2d$ times per second. At each impact the velocity of the particle changes by $2a$, that is, from $+a$ to $-a$, or the momentum of the particle changes by $2am$. Therefore momentum is lost on each wall by the impact of this particle at the average rate $2am \times a/2d$, or ma^2/d , which is the average force exerted on the wall by this particle. That is, the force on one wall, due to one particle, is equal to m/d times the square of its x -velocity component. Therefore the total force F , exerted on the wall by all the particles, is equal to m/d times the sum of the squares of their x -velocity components. Therefore $F = \frac{1}{2}\omega^2 N \cdot m/d$; see (i). Dividing by q , and putting $qd = v$, we have $F/q = p = \frac{1}{3}N m \omega^2/v$.

The kinetic theory of gases is very important as furnishing a clear conception of what constitutes thermal equilibrium of a gas, as furnishing a rational basis for Boyle's law, Gay Lussac's law, etc., and as enabling one to form clear mental pictures of various gas phenomena, as follows :

Thermal equilibrium of a gas. When a gas is in thermal equilibrium, the erratic movements of its molecules are such that on the average there is the same number of

molecules in each unit of volume of the gas and the same average molecular velocity in the neighbourhood of each point in the gas.

Heating of a gas. When the walls of a containing vessel are heated the molecules of the enclosed gas rebound with increased velocity when they strike the walls and the temperature of the gas rises. When the walls of the containing vessel are cooled, the molecules of the gas rebound with diminished velocity when they strike the walls and the temperature of the gas falls.

Heating of a gas by compression. Cooling of a gas by expansion. When a gas is compressed under a piston in a cylinder, the particles of the gas rebound from the inwardly moving piston with *undiminished velocities relative to the moving piston*, but with increased actual velocities, and the temperature of the gas rises. When a gas is expanded under a receding piston in a cylinder, the particles of the gas rebound from the receding piston with diminished velocities, and the temperature of the gas falls.

Boyle's law and Gay Lussac's law. Let us assume that the Kelvin temperature of a gas is proportional to the average kinetic energy per molecule of the gas, that is, let us assume that T is proportional to $\frac{1}{2}m\omega^2$, then we may write

$$a \text{ constant} \times M \times T \text{ for } \frac{1}{2}Nm\omega^2$$

and equation (ii) becomes

$$pv = MRT$$

which equation expresses Boyle's law and Gay Lussac's law as explained in Art. 6.

Avogadro's principle. Many years ago the law of multiple volumes was interpreted by Avogadro as meaning that all gases have the same number of particles (molecules) per unit volume at the same temperature and

pressure. This result may be shown to be in conformity with equation (i) as follows :

Consider two gases and let p_1 , n_1 , m_1 , and ω_1 be the pressure number of particles per cubic centimeter, etc., of the one gas, and let p_2 , n_2 , m_2 , and ω_2 be the corresponding quantities for the other gas. Then $p_1 = \frac{1}{3}n_1m_1\omega_1^2$ and $p^2 = \frac{1}{3}n_2m_2\omega_2^2$, from equation (i). If the two gases are at the same pressure and temperature, then $p_1 = p_2$; and $m_1\omega_1^2$ must be equal to $m_2\omega_2^2$ according to the above assumption that Kelvin temperature is proportional to the average kinetic energy per molecule. Therefore when temperature and pressure are the same for the two gases, we have $n_1 = n_2$.

Dalton's law is consistent with the kinetic theory of gases inasmuch as the moving particles are assumed to be so small that they do not interfere with each other in any other way. Thus, if a number of oxygen molecules and a number of nitrogen molecules are in a containing vessel, each set of molecules will move exactly as if the others were not present and exert the same pressure as they would exert if they occupied the vessel alone.

The cooling of a gas by free expansion. This effect is explained in Art. 50 as due to forces of attraction between the molecules of a gas. When such a gas expands freely its molecular kinetic energy decreases and its molecular potential energy increases. Latent heat seems always to be associated with increase of molecular potential energy.

Maxwell's law of velocity distribution. Let n be the number of gas molecules per unit volume and ω the root-of-mean-square of the velocities as in the above discussion. Then the number, $d\mu$, of molecules whose velocities lie between c and $c + dc$ (regardless of direction) is

$$d\mu = n \sqrt{\frac{54}{\pi}} \cdot \frac{c^3}{\omega^3} \cdot e^{-3C^2/2\omega^2} dc \dots\dots (i)$$

where e is the Napierian base. A very good discussion of this matter is given by James Rice, M.A., in Appendix I of Volume III of Wm. McC. C. Lewis's *Physical Chemistry*, Longmans, Green & Co., London, 1919. See also O. E. Meyer's *Kinetic Gas Theory*, translated by R. E. Baynes, Longmans, Green & Co., London, 1899. Meyer's book is especially to be recommended for its discussion of mean free path, coefficient of viscosity, diffusion and heat conductivity.

Mean free path. Imagine a vessel to contain n molecules per unit volume *all standing still* and distributed uniformly (on the average) throughout the vessel. Imagine a molecule to enter the vessel at velocity c , or, rather, imagine a large number to enter in succession, and let l be the average distance traveled by them all before colliding with one of the fixed molecules. It is required to find l . The difficulty here is to specify what constitutes a collision; let us therefore, for the sake of simplicity, think of all the molecules as solid spheres of diameter ρ . Then, when an entering molecule comes within a distance ρ of one of the fixed molecules (center to center) we will have a collision. Therefore, when a sphere of radius ρ with its center at the entering and moving molecule sweeps over a volume of $1/n$ th of a cubic centimeter (a volume which, on the average, contains one fixed molecule) we will have, on the average, one collision. That is when $\pi\rho^2l$ is equal to $1/n$ we will have, on the average, one collision. Therefore

$$l = \frac{1}{\pi n \rho^2} \dots \dots \dots (ii)$$

starting with this expression for n stationary molecules per unit volume it is possible to show that the average distance traveled between collisions of the molecules of a gas, when the molecular velocities are distributed in accordance with Maxwell's law, is

$$l = \frac{1}{\sqrt{2} \pi n \rho^2} \dots \dots \dots (iii)$$

Coefficient of viscosity of a gas. (a) *Definition of coefficient of viscosity as applied to any fluid (liquid or gas).* Consider a layer of the fluid between two flat boards AA and BB as indicated in Fig. 34a, and imagine the board BB to slide over the layer of fluid at velocity V . Then because of the viscosity of the fluid a certain force F will oppose the motion of BB . This force F is proportional to the velocity V , it is proportional to the area a of BB , and it is inversely proportional to the thickness D of the layer of fluid. Therefore we may write

$$F = \eta \frac{aV}{D} \dots \dots \dots (iv)$$

where η is a proportionality factor which is called the *coefficient of viscosity* of the fluid. The fluid velocity at any point p in Fig. 34a is

proportional to the distance y , that is, $v = ky$, where $k = V/D$, so that we may write k for V/D in equation (iv).

(b) *Expression for the coefficient of viscosity of a gas.* Imagine a gas to be flowing to the right so that the velocity of flow at any distance y above the plane AA in Fig. 34*b* is $v = ky$. It is required to find an expression for the force which acts across the plane area a , pulling forwards (to the right) on the gas below a and pulling backwards (to the left) on the gas above a . This force is $F = \eta a k$ according to equation (iv); but this force is also equal to the net rate at which momentum is crossing the area a .

An approximate expression for the coefficient of viscosity of a gas can be easily derived on the assumption that $\frac{1}{2}$ of the molecules of the gas are moving at velocity w in each of the following directions upwards, downwards, northwards, southwards, eastwards and westwards.

On this assumption it is easy to show that $\frac{1}{2}nwa$ gas molecules pass

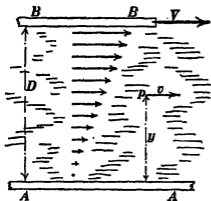


Fig. 34*a*.

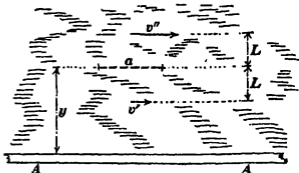


Fig. 34*b*.

downwards through the area a in Fig. 34*b* per second. These molecules come on the average from distance L^* above a , where L is the mean free path. Therefore these molecules all have the velocity $v'' = k(y + L)$ to the right (their heat motion is helter skelter and need not be considered), and consequently the rate at which momentum to the right is carried downwards across a is

$$\frac{1}{2}nwa \times mk(y + L) \dots \dots \dots (v)$$

and similarly it can be shown that the rate at which momentum to the right is carried upwards across a is

$$\frac{1}{2}nwa \times mk(y - L) \dots \dots \dots (vi)$$

the difference, $\frac{1}{2}nwa mkL$, is the net rate at which momentum to the right is carried downwards across a , and this is equal to the force $F (= \eta a k)$. Therefore we have

$$\eta = \frac{1}{2}nmwL \dots \dots \dots (vii)$$

* From a distance somewhat less than L above a , in fact.

This equation expresses the coefficient of viscosity in terms of the density ρ of the gas, but the mean free path is itself inversely proportional to ρ , and if we substitute the value of L from equation (iii) in equation (vii) we get

$$\eta = \frac{m\omega}{3\sqrt{2}\pi\rho^2} \dots\dots\dots(viii)$$

and this equation shows that the coefficient of viscosity of a gas is independent of the density of the gas. This result is confirmed by experiment for a very wide range of density. See O. E. Meyer's *Kinetic Gas Theory* (Bayne's translation), pages 171-200.

53. Degrees of freedom of the molecules of a gas and the principle of the equipartition of energy. The number of degrees of freedom of a body is defined as the number of coördinates which must be specified to fix its position. Thus a point in space has three degrees of freedom because its x , y and z -coördinates must be specified to fix its position; a linear body has five degrees of freedom, because to fix its position we must specify the x , y and z -coördinates of a point in such a body and we must specify two angles (two angular coördinates) to fix its direction; a body like a disk has six degrees of freedom because to fix its position we must specify the x , y and z -coördinates of a chosen point in the disk, we must specify two angles (two angular coördinates) to fix the direction of the axis of the disk, and we must specify one angle (one angular coördinate) to fix the direction of a chosen line on the disk.

A point can move in three ways, namely, by the change of each of its three coördinates; a linear body can move in five ways, namely, by the change of each of its five coördinates; and a disk can move in six ways, namely, by the change of each of its six coördinates.

The principle of the equipartition of energy. *The kinetic energy of the molecules of a gas is, on the average, distributed equally among the various degrees of freedom of the molecules.* Therefore, representing the kinetic energy of translatory motion of the molecules of a gas by $\frac{1}{2}Nm\omega^2$ (see Art. 52), we get $\frac{1}{2}Nm\omega^2$ for the total molecular kinetic energy of a monatomic gas, we get $\frac{5}{3} \times \frac{1}{2}Nm\omega^2$ for the total molecular kinetic energy of a biatomic gas, we get $\frac{6}{3} \times \frac{1}{2}Nm\omega^2$ for the total molecular kinetic energy of a gas having three or more atoms in a molecule (except when the atoms lie in a line), and in general we get $\frac{f}{3} \times \frac{1}{2}Nm\omega^2$ for the total molecular kinetic energy of a gas where f is the number of degrees of freedom of the molecules of the gas.

The ratio C_p/C_v where C_p is the specific heat of a gas at constant pressure and C_v is the specific heat of the gas at constant volume. According to Art. 52 the Kelvin temperature of a gas is proportional to $\frac{1}{2}Nm\omega^2$, and therefore, N and m being constants, a given rise of temperature means a certain increment of $\frac{1}{2}Nm\omega^2$ or $Nm\omega'\Delta\omega$. The amount of heat ΔH which must be given to the gas to produce

the given rise of temperature is equal to the increment of the total molecular kinetic energy of the gas, the Joule and Thomson effect being zero. Therefore

$$\Delta H = \frac{1}{2}fNm\omega \cdot \Delta \omega \dots \dots \dots (i)$$

To produce the same rise of temperature of the gas at constant pressure an additional amount of heat is required because of the work $p \cdot \Delta v$ that is done by the expanding gas. Therefore the heat $\Delta H'$ required to produce the same rise of temperature at constant pressure is

$$\Delta H' = \frac{1}{2}fNm\omega \cdot \Delta \omega + p \cdot v \dots \dots \dots (ii)$$

But $p v = \frac{1}{2}Nm\omega^2$ according to equation (ii) of Art. 52, and therefore, since p is constant, we have

$$p \cdot \Delta v = \frac{1}{2}Nm\omega \cdot \Delta \omega \dots \dots \dots (iii)$$

Using this value of $p \cdot \Delta v$ in equation (ii), and considering that

$$\Delta H' / \Delta H = C_p / C_v,$$

we get

$$k = \frac{C_p}{C_v} = \frac{f+2}{f} \dots \dots \dots (iv)$$

Therefore for monatomic gases like helium and argon for which $f=3$ we should have $k=1.67$, and for biatomic gases like oxygen (O—O) and nitrogen (N—N) for which $f=5$ we should have $k=1.40$; and as a matter of fact these are very nearly the values of k for these gases (see table in Art. 54). This appears to be a strong confirmation of the principle of the equipartition of energy, but the great success of the quantum hypothesis (which is incompatible with the equipartition principle) has discredited the latter, and recent experiments on specific heats at low temperatures have shown that the equipartition principle is not true at low temperature. This matter is discussed at length in Volume III of Lewis's *Physical Chemistry*, pages 18-31; Longmans, Green & Co., London, 1919.

54. Specific heats of a gas.* The number of thermal units (ergs) required to raise the temperature of one gram

* Not only does a gas have two specific heats according as it is kept at constant volume, or at constant pressure during the increase of temperature, but a gas has two important values for its bulk modulus. If the temperature of the gas is kept constant during compression by the extraction of heat from the gas, then the rise of pressure due to a given decrease of volume is less than if no heat is abstracted from the gas during compression. In the one case we have what is called the *isothermic bulk modulus*, and in the other case we have what is called the *adiabatic bulk modulus*.

All substances have two values of specific heat, namely, a specific heat at constant volume and a specific heat at constant pressure, and every substance has isothermic and adiabatic moduli of elasticity. It is only in the case of gases, however, that these differences are large enough to be appreciable.

of a gas one degree is called the *specific heat* of the gas. If the volume of the gas does not change during the rise of temperature, then, inasmuch as no external work is done by the gas, all of the heat applied goes to increase the internal heat energy of the gas. If, however, the gas be allowed to expand as the temperature rises, *to such an extent, for example, as to keep the pressure constant*, then the heat which is supplied to the gas to raise its temperature must not only increase the internal heat energy of the gas but must also make up for the external work done by the gas as it expands. The specific heat of a gas has therefore two important values, namely, the specific heat at constant volume C_v , and the specific heat at constant pressure C_p , of which the latter has the larger value.

Relation between C_v and C_p . To raise the temperature of M grams of a gas ΔT degrees requires $C_v M \cdot \Delta T$ units of heat (ergs) if the volume is kept constant. If the gas is then allowed to expand by an amount Δv sufficient to bring the pressure back to its initial value p , an amount of work equal to $p \cdot \Delta v$ is done by the expanding gas and an amount of heat equal to $p \cdot \Delta v$ must be given to the gas to keep up its temperature, for, according to Joule and Thomson, the only appreciable cause of change of temperature by expansion of a gas is the loss of energy of the gas by the doing of external work. Therefore a total amount of heat equal to $C_v M \cdot \Delta T + p \cdot \Delta v$ is required to raise the temperature of the gas by the amount ΔT when the gas is allowed to expand sufficiently to keep its pressure constant; but according to the definition of C_p the amount of heat required for this change of temperature at constant pressure is equal to $C_p M \cdot \Delta T$. Therefore

$$C_p M \cdot \Delta T = C_v M \cdot \Delta T + p \cdot \Delta v \dots\dots\dots(i)$$

Proposition. The constant R in equation (8) of Art. 6 for a given gas is equal to the difference between the specific heat of the gas at constant pressure (C_p) and the specific heat of the gas at constant volume (C_v)*; that is

$$C_p - C_v = R \dots\dots\dots(ii)$$

TABLE

SPECIFIC HEATS OF GASES AND VAPORS AT CONSTANT PRESSURE
(Gram-calories per gram per degree centigrade)

	C_p	C_p/C_v		C_p	C_p/C_v
Dry air at -183°C	0.253	1.34	Argon, 20°C . to 90°C .	0.123	1.667
,, at 20°C .	0.242	1.405	Carbon dioxide, 15°C .		
,, mean be- tween 20° & 880°C .	0.243		to 100°C .	0.202	1.305
Dry air at 40 at- mospheres and -140°C :	2.607		Carbon dioxide, 0°C .		
Oxygen at 20°C .	0.219	1.402	to 1400°C .	0.270	
Hydrogen, 21°C . to 100°C .	3.410	1.410	Ammonia vapor NH_3 , 23°C . to 100°C .	0.520	1.262
Nitrogen, 0° to 200°	0.239	1.390	Water vapor, 100°C .		
Helium	1.250	1.630	to 125°C .	0.379	1.277
			Water vapor, 100°C .		
			to 1000°C .	0.494	

Proof. Imagine M grams of the gas to have been increased in temperature by the amount ΔT at constant pressure, Δv being the increment of volume. Then we have equation (i) above. The increment of volume necessary to keep the pressure constant when the temperature increases is found by differentiating equation (8) of Art. 6, remembering that T and v , only, vary. This gives

$$p \cdot \Delta v = MR \cdot \Delta T \dots\dots\dots(iii)$$

Substituting this value of $p \cdot \Delta v$ in equation (i), we have equation (ii).

55. Isothermic expansion and compression. When the temperature of a gas is kept at a constant value by supplying heat to the gas as the gas expands, or by

* Both expressed in ergs per gram per degree.

abstracting heat from the gas as the gas is compressed, the expansion or compression is said to be *isothermic*. Equation (8) of Art. 6 gives the relation between p and v of a perfect gas during isothermic expansion or compression, T being then a constant as well as M and R .

The curves T_1 and T_2 in Fig. 34c show graphically the isothermic relations between p and v for air for two

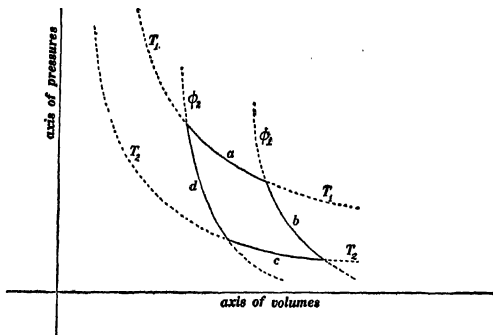


Fig. 34c.

different temperatures. The ordinates of these curves represent pressures and the abscissas represent volumes. The curves are sometimes called the *isothermal lines* of the gas; they are equilateral hyperbolas.

56. Adiabatic expansion and compression. When a gas is expanded or compressed and not allowed to receive heat from, or to give heat to surrounding bodies, the expansion or compression is called *adiabatic*.

The relation between p and v of a perfect gas during adiabatic expansion or compression is

$$pv^k = \text{a constant} \dots\dots\dots (i)$$

in which

$$k = \frac{C_p}{C_v} \dots\dots\dots (ii)$$

The curves ϕ_1 and ϕ_2 in Fig. 34c show the adiabatic relation between p and v for air (for two different values of the entropy ϕ_1 and ϕ_2).

Proof of equation (i). Consider a very slight adiabatic expansion of a gas, and let Δv , Δp and ΔT be the actual changes of volume, pressure and temperature; Δv being an increment, while Δp and ΔT are both decrements and therefore both negative.

The work $p \cdot \Delta v$ done by the gas is all made up by the decrement $MC_v \cdot \Delta T^*$ of the heat energy of the gas; therefore, remembering that $MC_v \cdot \Delta T$ is negative while $p \cdot \Delta v$ is positive we have

$$p \cdot \Delta v = -MC_v \cdot \Delta T \dots\dots\dots (iii)$$

From the equation $p v = MRT$ we have

$$T = \frac{1}{MR} p v \dots\dots\dots (iv)$$

* The simplest point of view concerning the specific heat of a gas is to define it as the actual net increase of heat-energy of one gram of the gas when its temperature is raised one degree. From this point of view a gas whose latent heat of expansion is zero (a gas which is not cooled by free expansion) has only one specific heat. Let C_v be the number of ergs of heat-energy required to raise the temperature of one gram of gas one degree *at constant volume*. Under these conditions the gas does no mechanical work and C_v is the actual net increase of heat-energy of the gas per gram per degree rise of temperature. Then $C_v + W(-C_p)$ is the number of ergs of heat-energy required to raise the temperature of one gram of the gas one degree *at constant pressure*, where W is the mechanical work done by the gas; and, as before, C_v^* is the actual net increase of heat-energy per gram per degree rise of temperature. If M grams of a gas drops in temperature by the amount ΔT the actual decrease of heat-energy of the gas is $MC_v \cdot \Delta T$.

whence

$$\Delta T = \frac{1}{MR}(\phi \cdot \Delta v + v \cdot \Delta \phi) \dots\dots(v)$$

Substituting this value of ΔT in equation (iii), remembering that $R = C_p - C_v$ according to equation (ii) of Art. 53, and that $k = C_p/C_v$, we have

$$\frac{\Delta \phi}{\phi} + \frac{k \Delta v}{v} = 0 \dots\dots(vi)$$

whence by integrating

$$\text{Log } \phi + k \text{ Log } v = \text{a constant}$$

or $\text{Log } (\phi v^k) = \text{a constant}$

or $\phi v^k = \text{a constant}$

57. Rise in temperature of a gas during adiabatic compression. We may eliminate ϕ (or v) from equation (i) of Art. 56 by substituting the value of ϕ (or v) from equation (8) of Art. 6. In this way we find that

$$T v^{k-1} = \text{a constant} \dots\dots(i)$$

or $T \phi^{(1-k)/k} = \text{a constant} \dots\dots(ii)$

during adiabatic expansion or compression.

Examples of adiabatic expansion and compression. The expansion and compression of the air in sound waves is adiabatic, because the expansion and compression take place so quickly that the expanded or compressed portion of the air does not have time to give off or to receive any appreciable amount of heat.

When a large body of air moves upwards, as, for example, when a wind blows up a mountain slope, the pressure of the body of air falls off with increasing altitude and the temperature is reduced. The expansion is adiabatic inasmuch as the body of air is so large that it cannot, during the brief time of the ascent, receive or give off an

appreciable amount of heat. Suppose that the rising body of air was initially at temperature T_1 and pressure p_1 , and that its pressure has fallen to p_2 . The temperature T_2 corresponding to p_2 may be found from equation (ii), which gives

$$T_1 p_1^{(1-k)/k} = T_2 p_2^{(1-k)/k}$$

A very interesting phenomenon, due to the cooling of a rising column of air by adiabatic expansion, is the formation of the beautiful cumulous clouds on a quiet summer day. The warm moist air near the ground starts streaming upwards through the superimposed cold air. This upward stream once started draws like a chimney, and the rising column develops until it becomes very large and very high. At a very sharply defined altitude the pressure reaches a value for which the temperature of the rising air is reduced to the dew point. The further cooling which is produced as the air passes above this level, causes the condensation of water vapor and the formation of mist or cloud. The strikingly flat bottom of a cumulous cloud is at that altitude where the rising air reaches the temperature of the dew point.

The condensation of water vapor as rain is due very largely to the adiabatic cooling of the great rising column of air, sometimes hundreds of miles in diameter, at the center of what is technically called a cyclone.

When a gas is quickly compressed under a piston in a cylinder, the compression is adiabatic. If the initial volume is v_1 , initial temperature T_1 , and final volume v_2 , we may find the temperature T_2 corresponding to v_2 from equation (i), which gives

$$T_1 v_1^{k-1} = T_2 v_2^{k-1}$$

LEADING QUESTIONS

- L. Q. 64.** What is Dalton's law ?
- L. Q. 65.** What is an ideal, perfect gas ?
- L. Q. 66.** What two things cause the temperature of a gas to drop during constrained expansion ?
- L. Q. 67.** What causes the temperature of a gas to drop during free expansion ?
- L. Q. 68.** Explain the principle of operation of the liquid air machine.
- L. Q. 69.** Why is the specific heat of a gas at constant volume less than the specific heat of the gas at constant pressure ?
- L. Q. 70.** What is meant by adiabatic compression ? Does the heat energy content of a gas increase during adiabatic compression ? If so, why ?

PROBLEMS

- 66.** Find the volume of 3.5 pounds of oxygen at a pressure of 3 atmospheres and at a temperature of 27° C., the volume of one pound of oxygen at 0° C. and one atmosphere being 11.204 cubic feet. Ans. 14.36 cubic feet.
- 67.** One volume of oxygen, 2 atoms in the molecule, combines with 2 volumes of hydrogen, 2 atoms in the molecule, to form H_2O . How many volumes of H_2O vapor are produced ?
- 68.** One volume of chlorine, 2 atoms in the molecule, combines with one volume of hydrogen, 2 atoms in the molecule, to form HCl . How many volumes of HCl gas are formed ?
- 69.** Find the density in grams per cubic centimeter of a mixture of equal volumes of oxygen and hydrogen, the pressure of the mixture being 760 millimeters and the temperature of the mixture being 0° C., the density of oxygen at 0° C. and 760 millimeters being 0.00143 and the density of hydrogen

at 0° C. and 760 millimeters being 0.000089 grams per cubic centimeter. Ans. 0.0007595.

Note. Each gas may be thought of as occupying the entire space alone at the given temperature and 380 millimeters pressure, and the density of each gas under these conditions calculated. The density of the mixed gas is then the sum of the densities of the two component gases.

70. Calculate the root-of-mean-square velocity, ω , of hydrogen molecules and of oxygen molecules at 0° C. Ans. 184,200 centimeters per second and 46,050 centimeters per second.

Note. At 760 millimeters pressure ($=1,013,000$ dynes per square centimeter) and at 0° C. the density of H is 0.0000895 gram per cubic centimeter and the density of O is 16 times as great.

71. A bicycle pump is full of air at 15 pounds per square inch, length of stroke 15 inches. At what part of the stroke does air begin to enter the tire at 40 pounds per square inch above atmospheric pressure on the assumption that the compression takes place without rise of temperature? Ans. 4.113 inches from end of stroke.

72. Air at 15 pounds per square inch pressure and at 20° C. is pumped into a bicycle tire at a pressure of 40 pounds per square inch (above atmospheric pressure). Find the temperature of the compressed air, assuming the compression to be adiabatic, and find at what part of the stroke the air reaches 40 pounds per square inch above atmospheric pressure. Ans. $153^{\circ}.5$ C. ; 0.6 of stroke.

73. Air at 200 pounds per square inch (above atmospheric pressure) is used to drive an air engine which exhausts at 15 pounds per square inch (above atmospheric pressure). Required the temperature of the high pressure air in order that there may be no possibility of frost forming in the exhaust ports of the engine, the expansion of the air in the engine being assumed to be adiabatic. Ans. 212° C.

Note. Frost frequently forms in the exhaust ports of an air-driven engine. This occurs when the air (moist) is cooled below 0° C. by the expansion which takes place in the engine.

74. Carbon dioxide gas at 25° C. is suddenly compressed (adiabatically compressed) to one-tenth of its initial volume. Find its temperature. Make the same calculation for helium and for air.

75. The atmospheric pressure at the ground is 755 millimeters. At a distance of 2000 feet above the ground the pressure is 695 millimeters. The temperature of the air at the ground is 31° C. Find the value of the dew point of the air at the ground in order that a rising column of air would form a cloud at 2000 feet above the ground. Ans. $25^{\circ}.5$ C.

Note. In this problem neglect the influence of the water vapor upon the law of adiabatic expansion of the air. Note that the pressure of the water vapor is decreased in the ratio 755 to 695 so that the air will have to be cooled below the temperature which expresses the dew point at the ground.

The following table showing relation between dew point and vapor pressure is needed in the solution of this problem.

Dew Point.	Vapor Pressure.
23° C. 20.9 mm.
24° C. 22.2 mm.
25° C. 23.5 mm.
26° C. 25.0 mm.

CHAPTER VI

THE SECOND LAW OF THERMODYNAMICS.

ENTROPY

58. The second law of thermodynamics. The principle of the conservation of energy in its broadest sense, which covers heat effects, is sometimes called *the first law of thermodynamics*, and it is one of the great generalizations of physics. Another entirely distinct generalization, one which is most deeply seated in the intuitions of all men, is *the second law of thermodynamics*, or *the law of entropy*, as it is sometimes called. No one can have any sort of grasp of the philosophy of physics who does not have some degree of clear understanding of both these great generalizations.

Necessity of a general point of view. Consider the successive stages of the change which takes place when a system of substances is settling to a state of thermal equilibrium; for example, consider the successive stages of the change which takes place when a piece of red-hot iron is dropped into a pail of water, and imagine these stages to follow each other *in a reverse order*. If such a thing could be, it would mean that the piece of cold iron would become red-hot and jump out of the pail. No one ever saw such a thing happen, and the postulate that such a thing can never happen is called *the second law of thermodynamics*.

The bald statement that a piece of iron lying quietly in a pail of cold water cannot become red-hot

spontaneously and jump out of the pail carries with it no general idea, and to say that "nothing of the kind" can take place is too vague to convey any meaning at all. Therefore it is evident that a general statement of the second law of thermodynamics cannot be made until we have developed a point of view which will permit us to speak intelligibly and definitely, but in general terms, of all kinds of spontaneous or impetuous action.

59. Reversible processes. A substance in thermal equilibrium is generally under the influence of external agencies. Thus surrounding substances confine a given substance to a certain region of space, and they exert on the substance a definite pressure; surrounding substances are at the same temperature as the given substance; surrounding substances may exert constant electric or magnetic influences on the given substance; and so on. If the temperature of the surrounding substances be raised or lowered very slowly, or if the influences they exert upon the given substance be made to change very slowly, *then the given substance will pass through a continuous series of states of thermal equilibrium*; such a slow change of the substance is called a *reversible process*, because the substance will pass through the same series of states in a reverse order if the external influences are changed slowly in a reversed sense.

60. Irreversible processes or sweeps. When a substance is settling or tending to settle to thermal equilibrium it may be said to undergo a process. Such a process cannot be arrested or held at any stage short of complete thermal equilibrium, but it always and inevitably proceeds towards that state. Such a process may therefore be called a *sweeping process* or simply a *sweep*.

A **simple sweep** is the settling of a closed system* to thermal equilibrium. For example, the equilibrium of a batch of gunpowder in a large room may be disturbed by ignition, and the explosion of the powder and the subsequent settling of the residual gases to a quiescent state constitute a *simple sweep*. The equilibrium of a gas confined under high pressure in one compartment of a two-compartment vessel may be disturbed by opening a cock which connects the two chambers, and the rush of gas through the opening and the subsequent settling of the gas in both chambers to a state of thermal equilibrium constitute a *simple sweep*.

Trailing sweep. When external influences change continuously and rapidly, a substance is all the time settling towards thermal equilibrium and it never catches up with the changing influences, but trails along behind them as it were, and there exists what may be called a *trailing sweep*. Thus the rapid heating of water in a tea-kettle is a trailing sweep; the bottom of the kettle is always a little hotter than the water.

Steady sweep. A substance may be subject to external action which, although entirely permanent or unvarying, is incompatible with thermal equilibrium, and the substance may settle to a permanent or unvarying state which is not a state of thermal equilibrium. Such a permanent state of a substance may be called a *steady sweep*. For example, the two faces of a slab or the two ends of a rod may be kept permanently at different temperatures, and when this is done the slab or rod settles to a permanent or unvarying state. Heat flows through

* A closed system is a substance or a set of substances which neither receives nor gives off heat, and which neither does work on an outside substance nor has work done upon it.

the slab or along the rod from the region of high temperature to the region of low temperature, and this flow of heat is an irreversible process. The ends of a wire may be connected to the terminals of a battery or dynamo so that a constant electric current flows through the wire, and the heat which is generated in the wire by the electric current may be steadily carried away by a stream of water or air. Under these conditions the wire settles to an unvarying state which is by no means a state of thermal equilibrium ; the battery or dynamo does work steadily on the wire and this work reappears steadily in the wire as heat.

61. **Thermodynamic degeneration.** The most familiar example of a sweeping process is ordinary fire, and, as everyone knows, a fire is not dependent upon an external driving cause, but when once started it goes forward of itself and with a rush. It is not exactly correct to speak of a fire as *spontaneous*, because this word refers especially to the beginning of a process, whereas we are here concerned with the characteristics of a process already begun. Therefore it is better to describe a phenomenon like fire as *impetuous*, because it does go forward of itself. Tyndall, in referring to the impetuous character of fire, says that it was one of the philosophical difficulties of the eighteenth century. A spark is sufficient to start a conflagration, and the effect would seem to be out of all proportion greater than the cause. Herein lay the philosophical difficulty. Under conceivable conditions a fire can be started by a cause more minute and more nearly insignificant than anything assignable. This possibility of the growth of tremendous consequences out of a cause which has the mathematical character of an infinitesimal is the remarkable thing ; and this possibility is not only

characteristic of fire but it is characteristic of impetuous processes in general.

Everyone has a sense of the irretrievable aspects of a disaster, such as the collapse of a bridge, or the wreck of a ship, or the destruction of a house by fire ; and although such things may be forgotten after reconstruction, the fact remains that the destruction is absolute, it cannot be undone.* Also everyone has a sense of the extreme complexity of detail of a disaster. Imagine anyone making the attempt to study the minute details of a conflagration, recording the height and breadth and the irregular and evanescent distribution of temperature throughout each flicker of consuming flame, the story of each crackling sound and the extent and character of every sway of timber and wall ! And consider how utterly useless and uninteresting such a record would be even if it could be made ! From a practical point of view the important thing in the collapse of a bridge or the wreck of a ship or the destruction of a house by fire is the money† loss involved, and money loss is the only basis upon which one disaster can be definitely compared with another.

When a charge of gunpowder is exploded in a large empty vessel, everything remains after the explosion ; all of the material is there and all of the energy is there. And yet the powder cannot be exploded a second time ! You cannot burn your coal twice ; and your cake, you cannot eat it and have it ! The explosion of gunpowder, and the burning of coal, and the utilization of food in the body are what we have called sweeping processes ; in detail they are infinitely complicated, and it is not

* The material of the house is not destroyed nor is any energy destroyed and yet everyone appreciates that something is destroyed.

† Other than money values are here ignored for the sake of simplicity.

only impossible to compare two sweeping processes detail by detail but it would be useless even if it could be done. However, the impetuous character of a sweeping process suggests a certain havoc, a certain *degeneration*, in the substance or substances in which the sweep takes place, and if we can establish this idea of thermodynamic degeneration as a definitely measurable quantity we will have a basis for the comparison of any two sweeping processes, namely, in terms of the thermodynamic degeneration involved in each. Such a quantity does in fact exist, and it is usually called **increase of entropy**.

To establish the idea of thermodynamic degeneration it is necessary to begin with the **ASSUMPTION** that every sweeping process does involve a definite amount of thermodynamic degeneration (increase of entropy); then derive by strict argument the physical consequences which necessarily follow from the assumption; and subject these consequences to the test of experiment. Such a program is, of course, too extensive for an elementary text; but we shall attempt to make the meaning of the assumption clear and develop several of its physical consequences.

To appreciate the following discussion one should consider the idea of thermodynamic degeneration as a purely tentative idea up to the point which is reached in Art. 66, where the first easily verifiable consequence of the second law of thermodynamics is set forth. The application of the second law of thermodynamics to the steam engine as outlined in Arts. 63, 64 and 65 is very important, but no clear cut experimental verification of the law can be devised out of the material given in Arts. 63, 64 and 65.

The first step in the development of the idea of thermodynamic degeneration as a measurable quantity must be based on the consideration of a steady sweep. In a

simple sweep the degeneration must lie wholly in the relation between the initial and final states of the substance which undergoes the sweep, because no outside substance is affected in any way by a simple sweep, no work is done on or by the substance which undergoes the sweep and no heat is given to or taken from it. In a trailing sweep the degeneration may lie partly in the relation between the initial and final states of the substance which undergoes the sweep and partly in the change which takes place in outside substances. *In a steady sweep, however, it is possible to think of the degeneration as lying wholly in the conversion of work into heat or in the flow of heat from a high temperature region to a low temperature region, or both; because the substance which undergoes the sweep remains entirely unaltered.** Therefore the idea of thermodynamic degeneration as a measurable quantity can be reached in the simplest possible manner by a careful consideration of a steady sweep. In speaking of the havoc which is wrought by a sweeping process we have had in mind the impetuous character of such a process, and to consider so mild a thing as a steady sweep may seem to be a weakening of our argument; but the initial steps of any physical argument should have a vivid appeal to sense. It is for this reason that we have directed the reader's attention at first to the quick and spectacular process of burning rather than to the slow and invisible

* This matter requires further explanation. Consider, for example, a rod which conducts heat steadily from a hot region to a cool region; to eliminate all changes of state outside of the rod we must imagine the hot region and the cool region each to consist of an infinite amount of substance. As another example consider the steady generation of heat in a wire by an electric current; in this case we may imagine an ideal, one-hundred-per-cent-efficient dynamo driven by a very heavy fly-wheel or by a heavy weight and cord so that purely mechanical changes, only, take place outside of the wire.

process of rotting, although it is in the end as bad to lose a house by rotting as it is to lose a house by the quick calamity of a conflagration.

Proposition. *The thermodynamic degeneration which is involved in the direct* conversion of work into heat at a given temperature is proportional to the quantity of work so converted.* This proposition may seem to be self-evident, but it is not, because it is meaningless until we connect it definitely with something physical. Let us consider, therefore, a steady flow of electric current through a wire from which the heat is carried away by a stream of water so that everything remains unchanged as time elapses. Such a process is steady, that is, it remains exactly the same during successive intervals of time, and therefore any result of the process must be proportional to the elapsed time. Thus the amount of thermodynamic degeneration must be proportional to the elapsed time, and the amount of mechanical energy converted into heat is proportional to elapsed time. Therefore the amount of thermodynamic degeneration, ϕ , is proportional to the amount of work, W , that is degenerated. That is, we may write

$$\phi = mW \dots\dots\dots (18)$$

where m is a constant whose value depends only on the temperature of the body in which the degenerated energy appears as heat.

The higher† the temperature the smaller the value of m . This is evident from the following considerations: Let a quantity of work be degenerated into heat at a certain temperature, and let the heat so produced flow to a region of lower temperature. This flow is a sweeping process

* By a sweeping process.

† The recognition of what we speak of as a high temperature does not depend upon any method for measuring temperature. See Art. 1.

and it must, according to our assumption, involve *an additional amount of thermodynamic degeneration*. But the final result could be reached directly by the degeneration of the original amount of work into heat at the lower temperature, and if our assumption as to the existence of a quantity called thermodynamic degeneration is to be of value, *we must assume that the amount of thermodynamic degeneration is the same for any two ways in which the same final result is reached from the same initial conditions*. Therefore the lower the temperature the greater the value of ϕ in equation (18) and the greater the value of m , for a given amount of work degenerated into heat.

As yet we have not agreed upon any fundamental measure of temperature.* Therefore we are at liberty to adopt the quantity $1/m$ as our measure of temperature, inasmuch as this quantity always has a definite value for any given temperature and inasmuch as its value is larger and larger the higher the temperature. Consequently we may write $1/T$ for m in equation (18), and we have

$$\phi = \frac{W}{T} \dots\dots\dots(19)$$

or, since W is equal to the heat H which has been produced, we may write

$$\phi = \frac{H}{T} \dots\dots\dots(20)$$

Note. It is a remarkable and significant fact that the simplest line of argument concerning thermodynamic

* The measurement of temperature as explained in Art. 5 is entirely arbitrary, and it depends upon the particular gas which is used in the "air" thermometer. A fundamental measure of temperature must be independent of the peculiar properties of any particular substance.

degeneration should make it proportional to elapsed time. Indeed the two quantities, time and thermodynamic degeneration, do refer to the same condition in nature, to the universal forward movement of things which we all have come to think of as inevitable, and never to be reversed.

Kelvin temperature values.* The definition of temperature values which is involved in the above discussion of thermodynamic degeneration and which is stated in explicit terms in Art. 64, is due to Lord Kelvin, and therefore these temperature values are called Kelvin temperatures. In Art. 71 it is shown that temperature values as measured by the air thermometer are very nearly identical to temperature values according to the Kelvin definition. **Therefore the temperature T as used throughout this chapter is Kelvin temperature as measured by the air thermometer.** To get Kelvin temperature add 273° to ordinary centigrade temperature. Thus $40^{\circ}\text{C.} = 313^{\circ}\text{K.}$

62. Statements of the second law of thermodynamics.

(a) The thermodynamic degeneration which accompanies a sweeping process cannot be directly repaired, nor can it be repaired by any means without compensation.

This is an entirely general statement of the second law and the two terms *direct repair* and *compensation* must be explained.

The direct repair of the havoc wrought by a sweeping process means the undoing of the havoc by allowing the sweep to perform itself backwards, an idea as absurd as the idea of allowing a burned house to unburn itself!

One can, of course, rebuild a burned house, but a certain

* Kelvin temperatures are frequently called "absolute" temperatures.

amount of expense is involved. Also the havoc wrought by a sweeping process can be repaired, but when such repair is finished some other substance is always left in what may be called a degenerated state. The original sweep represents a certain degeneration of the substance involved, and when the effects of the sweep are repaired, even by ideal reversible processes, this degeneration is handed along to some other substance. This equivalent degeneration of the other substance is what is referred to by the use of the word compensation.

(b) Heat cannot pass directly from a cold body to a hot body, nor can heat be transferred from a cold body to a hot body by any means without compensation.

This reference to the direct passage of heat from a cold body to a hot body should recall what has been said about a piece of iron lying quietly in a pail of cold water and becoming suddenly red hot and jumping out of the pail !

(c) Heat cannot be converted directly into work, nor can heat be converted into work by any means without compensation.

The direct conversion of heat into work would mean the simple reverse of any ordinary sweeping process which involves the degeneration of work into heat. For example, work is degenerated into heat in the bearing of a rotating shaft, and everyone knows that to reverse the motion of the shaft does not cause the bearing to grow cold and the heat so lost to appear as work helping to drive the shaft ! That would be a rotary engine indeed !

(d) A gas cannot pass directly from a region of low pressure to a region of high pressure, nor can a gas be transferred from a low-pressure region to a high-pressure region by any means without compensation.

Imagine a gas squirting itself backwards through a nozzle into a high-pressure reservoir! But the second law of thermodynamics is the statement of a fact which everyone knows coupled with a generalizing clause or postulate which no one can understand until some of its consequences are derived and tested by experiment.

Here is one more statement of the second law of thermodynamics, the oldest English version of it :*

Humpty Dumpty sat on a wall.
 Humpty Dumpty had a great fall.
 All the King's horses and all the King's men
 Cannot put Humpty Dumpty together again !

This is perhaps the most sensible of all the statements of the second law, for which we will allow it to pass for the moment, because it ignores direct repair and refers at once to the most powerful of external means. It is important to understand, however, that in Humpty Dumpty's case we are concerned with structural degeneration, not with the vastly simpler kind of degeneration which, for example, takes place when you produce turbulence in a pail of water by stirring. Of course the water can be easily brought back to its initial condition, but a certain compensation is always involved.

Of all the generalizations of physics the second law of thermodynamics is the most deeply seated in human experience and intuition, and one of the most humorous

* The reader must not think of the humor that is involved in the use of this old verse. The second law of thermodynamics relates to a condition which is entirely familiar to everyone, but when a formal statement of the law is made, especially a statement such as can be used like an axiom in geometry as a basis for mathematical argument, then, it seems, every common-sense view of the matter is apt to be crowded out of the mind.

of children's verses refers to the man whose wondrous wisdom enabled him to circumvent it by direct repair !

There was a man in our town,
And he was wondrous wise ;
He jumped into a bramble bush
And scratched out both his eyes,
And when he found his eyes were out,
With all his might and main,
He jumped into another bush
And scratched them in again.

But let us return to the fourth statement (*d*). A gas can be transferred from a low-pressure region to a high-pressure region by means of a pump, and the work that is used to drive the pump, even supposing the pump to be frictionless, is all converted into heat. This conversion of work into heat is the compensation for the transfer of the gas as specified.

Or consider the second statement (*b*). In an artificial ice factory heat is transferred from the freezing room to the warm outside air, but the work required to drive the ammonia pump, even supposing it to be frictionless, is converted into heat.

Or consider the third statement (*c*). An ordinary steam engine converts heat into work, but even with an ideal or perfect engine a large amount of heat must be supplied to the engine at boiler temperature and a large portion of this heat must be let down to the temperature of the exhaust and pass out with the exhaust to compensate for the conversion of the remainder into work.

63. The steam engine. One of the most important consequences of the second law of thermodynamics is that a steam engine working between *given* boiler temperature

and *given* condenser temperature has a limiting efficiency beyond which it is impossible to go, whatever the design of the engine and however carefully it may be made. Furthermore it can be shown that any sweeping process which takes place in the operation of a steam engine must necessarily reduce its efficiency. These two consequences of the second law of thermodynamics have served as important guides to the steam engine designer as explained in Art. 65.

The ideal or perfect engine and its efficiency. The important theorem concerning the maximum possible efficiency of a steam engine is established by an argument based on the assumption that the operation of the engine involves no sweeping processes of any kind. The ordinary engine does involve such processes, but if the engine were frictionless, if it were run slowly, if the cylinder were prevented from cooling the steam, and if the steam were expanded in the cylinder sufficiently to prevent puffing, then no sweeping processes would be involved. Such an ideal engine we will call a *perfect engine*.

The essential organs of the steam engine are shown in Fig. 35. The feed-water pump is arranged to take from the condenser not only water but also a certain amount of uncondensed steam, and the compression of this mixture of steam and water by the pump condenses the steam and raises the feed-water to boiler temperature. *With the feed-water pump acting in this way no outstanding change of any substance is involved in the action of the engine*, and, if we assume everything to be frictionless, etc., as specified above in the definition of a perfect engine, then no irreversible or sweeping processes are involved in the operation of the engine, and the only outstanding effect after the engine has been in operation for a while is that

a certain amount of heat H_1 has been taken from the boiler at temperature T_1 , a portion of this heat has been converted into mechanical work W , and the remainder of the heat H_2 has been delivered to the condenser with the exhaust steam at temperature T_2 .

According to the first law of thermodynamics the work

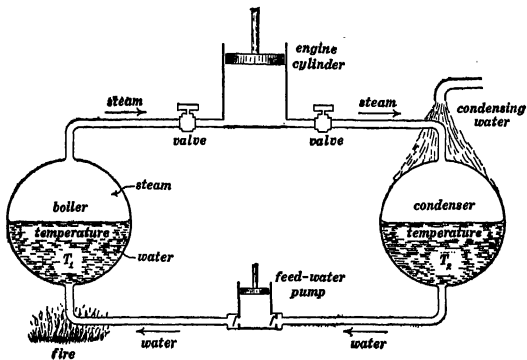


Fig. 35.

W must be equal to $H_1 - H_2$, heat being expressed in energy units. Therefore we have

$$W = H_1 - H_2 \dots\dots\dots(21)$$

For the sake of simplicity of argument the net result of the operation of the engine may be thought of as (a) The conversion into work of the whole of the heat H_1 which is taken from the boiler at temperature T_1 , and (b) The reconversion of a portion H_2 of this work back into heat at condenser temperature T_2 .

The *regeneration** associated with process (a) is equal to H_1/T_1 and the *degeneration* associated with process (b) is equal to H_2/T_2 . But since we have assumed that the engine operates without any sweeping processes, there can be no degeneration; that is the regeneration involved in process (a) must be equal to the degeneration involved in process (b). That is, we must have

$$\frac{H_1}{T_1} = \frac{H_2}{T_2} \dots \dots \dots (22)$$

Substitute the value of H_2 from equation (21) and solve for W , and we get

$$W = \frac{T_1 - T_2}{T_1} \cdot H_1 \dots \dots \dots (23)$$

That is to say, the fractional part $\left(\frac{T_1 - T_2}{T_1}\right) H_1$ of the heat H_1 is converted into work by the engine, and the fraction $\frac{T_1 - T_2}{T_1}$ is called the *efficiency* of the engine.

Efficiency of the imperfect engine. If the operation of a steam engine involves sweeping processes of any kind, then the thermodynamic degeneration which is associated with process (b) above mentioned must be greater than the regeneration which is associated with process (a). That is, we must have

$$\frac{H_1}{T_1} < \frac{H_2}{T_2}$$

* This argument may be given in a more concrete and convincing form by using the idea of entropy as developed in Art. 73, but for the present we must be content with this highly abstract form. To convert an amount of work W into heat at temperature T involves an amount of *degeneration*, and to convert the heat back into work would, if it were possible, involve the same amount of *regeneration*.

or, substituting the value of H_2 from equation (21) and solving for W , we get

$$W < \frac{T_1 - T_2}{T_1} \cdot H_1$$

Therefore, comparing this inequality with equation (23), we conclude that *any engine whose operation involves sweeping processes of any kind must be less efficient than our ideal or perfect engine, boiler and condenser temperatures being given.*

64. The Kelvin definition of the ratio of two temperatures. The definition of temperature value which is involved in equations (18) and (19) becomes explicit in equation (22), inasmuch as this equation may be written thus :

$$\frac{T_1}{T_2} = \frac{H_1}{H_2}$$

which is to say, the ratio of two temperatures is the ratio of the respective quantities of heat taken in and given out by a perfect engine working between those temperatures, as above explained. This definition is due to Lord Kelvin.

65. Conditions which affect the efficiency of a steam or gas engine in practice. A very important application of the law of entropy (the second law of thermodynamics) is its use as a guide in the design of highly efficient steam and gas engines.

A fraction, only, of the heat which is developed by the burning of gas or fuel is converted into work in an engine, and if this fraction is to be large, sweeping processes must be obviated in the operation of the engine, and the fraction T_1/T_2 must be large, where T_1 is the Kelvin temperature of the steam or gas at the start (temperature of the boiler or temperature of the exploded air and gas as it begins

doing work on the piston) and T_2 is the Kelvin temperature of the exhaust.

In steam engines (reciprocating engines or turbines) T_1 is limited to about 170°C . to 200°C . (443°K . to 473°K .) and the lowest feasible exhaust temperature is about 40°C . (313°K .) In gas engines T_2 may be 1500°C . (1773°K .) or higher, and this temperature is reduced by the expansion in the cylinder to six or eight hundred degrees centigrade (873°K . to 1073°K .)

The following discussion is given merely as an illustration of the application of the second law of thermodynamics, and the discussion is limited to steam engines, including reciprocating engines and steam turbines.

(a) **Furnace and boiler.** The most pronounced sweeping process between the completed combustion in the furnace and the final exhaust of the steam from an engine is *the flow of heat from the very high temperature of the fire in the furnace to the relatively low temperature of the steam boiler*, and the greatest waste in the operation of a steam engine **in the sense of loss of availability of the heat for conversion into mechanical energy** is involved in this sweeping process. This waste seems to be unavoidable because it is impracticable to operate a red-hot boiler, to say nothing of the difficulties of operating an engine with a supply of red-hot steam!

The greatest items of waste in the operation of a steam power plant in the ordinary sense of actual waste of heat are: (a) the incomplete combustion of the fuel in the furnace, and (b) the carrying away of great quantities of heat by the hot flue gases. The economic use of fuel for the production of mechanical energy depends very greatly, therefore, upon a properly designed furnace and *intelligent stoking* to insure complete combustion, and upon a large

exposure of boiler surface and frequent cleaning of same to facilitate the flow of heat from the furnace into the boiler.

(b) **Friction and eddies in steam flow.** When steam flows through a pipe and through the blades of a steam turbine the flow is opposed by friction (an irreversible effect), and eddies are produced after the passage of steam through a partly closed valve or port and during the passage of steam through the blades of a turbine (these eddies are an irreversible effect). Pipes of ample size must therefore be used, partly closed valves must be avoided, and the blades of a turbine must be designed so as to make the flow of the steam as smooth as possible.

(c) **Giving off of heat by pipes, etc., to the surrounding cool air.** It is a curious fact that the mere waste of heat by cooling of steam pipes and steam casings is not the whole story of the losses of engine efficiency involved, because if the steam is cooled by this loss the residue of heat in the steam is less available than before for the production of mechanical work!* Steam pipes and casings should be covered by heat-insulating coverings.

(d) **Puffing.** When a reciprocating engine does not expand the steam to condenser pressure the exhaust steam rushes into the condenser as a puff. An engine that puffs violently like a locomotive is an inefficient engine.

A large residual velocity of the exhaust steam in a

* This statement is apt to be misleading, and therefore it may be stated that the effect of loss of a given amount of heat depends on the temperature of the region which loses the heat. Thus in a multi-stage steam turbine the steam casings of the successive stages are at lower and lower temperatures, and the loss of a given amount of heat by the hottest casing is more serious than the loss of the same amount of heat by one of the cooler casings.

steam turbine corresponds very closely to puffing in a reciprocating engine. A turbine is designed to leave as small a residual steam velocity as possible.

(e) **Cylinder condensation in the reciprocating engine.** As a charge of steam in the cylinder expands it cools and cools the cylinder and piston, so that when steam is next admitted it heats the cylinder and piston up again. This effect cannot be eliminated, but it can be largely reduced by providing separate passages for the ingress and egress of steam and by using a series of cylinders of increasing size, the smallest cylinder being arranged to take steam directly from the boiler and exhaust into the next larger cylinder, which in turn exhausts into a still larger cylinder, and so on. In this way the range of temperature in each cylinder is small and the effects of cylinder condensation are greatly reduced. A steam engine in which expansion of the steam takes place in two stages (in two cylinders) is called a compound engine. A steam engine in which the expansion of the steam takes place in three stages (in three cylinders) is called a triple expansion engine.

The loss of efficiency due to cylinder condensation is greatly reduced by the use of superheated steam, because the exchange of heat between the steam and the cylinder walls is very greatly reduced when the steam does not condense. Thus S. LeRoy Brown has found that heat is imparted to a cool metal surface about forty times as fast by condensing steam as by a gas at the same temperature.

The conversion of heat energy into mechanical energy in a steam jet. When high-pressure, high-temperature steam flows through a smoothly curved nozzle, the steam expands and cools, and the heat energy which is converted into mechanical energy (into the kinetic energy of the high velocity steam) is very nearly what would be converted

into mechanical energy by a perfect engine working between temperatures T_1 and T_2 , where T_1 is the original temperature of the steam and T_2 is the temperature of the steam in the jet. Therefore, in a certain sense, the simple steam jet is very nearly a perfect engine; and a steam turbine may be thought of as a device for the transformation of the kinetic energy (mechanical) of a steam jet with a minimum of dissipation, that is, with a minimum of reconversion of this kinetic energy into heat by the irreversible effects of friction and eddy action.

LEADING QUESTIONS.

L. Q. 71. Why is it necessary to think of a reversible process as taking place very slowly? What is a reversible process? Give an example.

L. Q. 72. Why is it helpful to call an irreversible process a sweeping process? Give examples of the three different kinds of sweeping processes.

L. Q. 73. What is the idea of thermodynamic degeneration?

L. Q. 74. What kind of sweeping process involves no progressive change of condition (or state) of any substance? Explain why this kind of process serves best as a basis on which to discuss thermodynamic degeneration?

L. Q. 75. Why is it impossible at the start to make any generalized quantitative statement as to the amount of thermodynamic degeneration which is associated with a simple sweep?

L. Q. 76. Prove that the thermodynamic degeneration which is associated with the conversion of work into heat at temperature T by a steady sweep must be proportional to the amount of work so converted, and prove that the proportionality factor here referred to is the larger the lower the temperature.

L. Q. 77. Explain the meaning of the term "direct repair"

in the general statement of the second law of thermodynamics. Give an example of direct repair.

L. Q. 78. Explain the meaning of the term "compensation" in the general statement of the second law of thermodynamics. Give an example illustrating the meaning of the term.

L. Q. 79. What is meant by an ideal perfect engine?

L. Q. 80. How does the efficiency of a perfect engine depend on the temperatures of boiler and of exhaust steam?

L. Q. 81. Give Kelvin's definition of the ratio of two temperatures.

L. Q. 82. If the perfect engine of Fig. 35 is driven backwards it becomes a refrigerating machine, and after running for a while an amount of heat H_2 will be taken in to the low-temperature container at temperature T_2 , an amount of heat H_1 will be given off by the high-temperature container at temperature T_1 , and an amount of work W will have been done in driving the machine. Find an expression for H_2 in terms of W , T_2 and T_1 .

PROBLEMS

76. The efficiency of a good steam engine is about $\frac{3}{4}$ of the efficiency of a perfect engine working between the same boiler and condenser temperatures. Find the efficiency of a good engine when the boiler temperature is 170° C. and the condenser temperature 65° C.

77. A refrigerating machine is said to have a refrigerating capacity of "one ton" when it will, every 24 hours, remove from a cold room the amount of heat which would melt one ton of ice, namely, 288,000 British thermal units. Find the power which would be required to drive a 50-ton refrigerating machine whose efficiency is $\frac{3}{4}$ of what it would be if it were a perfect engine, the temperature of the cold room being 10° below zero centigrade, and the warm region to which the heat is delivered being at 40° C. Take 1 British thermal unit equal to 778 foot-pounds. Ans. 56 horse-power.

78. Suppose the refrigerating machine of the previous problem to be a perfect engine; find the amount of work spent in driving the machine and find the amount of heat delivered to the warm region for every British thermal unit extracted from the cold room. Ans. (a) 148 foot-" pounds "; (b) 926 foot-" pounds " or 1.19 British thermal units.

79. How much power would be required to drive a perfect engine as a refrigerating machine to give an amount of refrigeration equivalent to 50 pounds of ice per day (7200 British thermal units to be taken out of the cold chest every 24 hours), the cold chest being at 41° F. and the warm region to which heat is delivered being at 86° F. Ans. 0.01 horse-power or $7\frac{1}{2}$ watts.

80. A windmill-driven refrigerating machine, erected complete, costs \$750 and the annual charge for interest, depreciation, attention, and repairs is \$100. The average power delivered by the windmill is 0.1 horse-power, the efficiency of the refrigerating machine is $\frac{1}{3}$ of the efficiency of a perfect engine, the cold region is kept at 23° F., and the heat is delivered to a region at 95° F. Find the refrigerating capacity of the installation in pounds of ice per day, and find the cost per 100-pounds-of-ice equivalent. Ans. 94 pounds of ice per day; 29 cents per hundred pounds of ice.

Note. This installation will not produce 94 pounds of ice per day it will give an amount of refrigeration equivalent to the melting of 94 pounds of ice per day.

CHAPTER VII

SOME CONSEQUENCES OF THE SECOND LAW OF THERMODYNAMICS

66. Clapeyron's relation. One of the most interesting of the consequences of the second law of thermodynamics is the relation which was pointed out in 1834 by the French physicist Clapeyron, and which is usually referred to as Clapeyron's relation. This relation is expressed by the equation in which c.g.s. units are used

$$\Delta T = \frac{T}{L}(s - w) \cdot \Delta p \dots\dots\dots(i)$$

where T is the boiling point of pure water at pressure p (the minimum temperature of steam at pressure p), $T + \Delta T$ is the boiling point of pure water at pressure $p + \Delta p$, L is the latent heat of vaporization of water in ergs per gram at temperature T and pressure p , s is the volume in cubic centimeters of one gram of steam at temperature T and pressure p , and w is the volume in cubic centimeters of one gram of water at temperature T and pressure p .

Equation (i) applies to the vaporization of any simple liquid, and with very slight modifications it applies to the freezing of any simple liquid and to such changes of state as are described in Art. 34. For the sake of intelligibility, however, the following discussion is applied explicitly to the vaporization of water.

Consider one gram of saturated steam at temperature

T and pressure p . The abscissa of the point a in Fig. 36 represents the volume s of this gram of steam and the ordinate of a represents the pressure p . We will speak

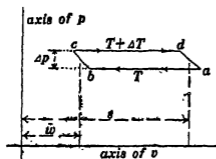


Fig. 36.

of this steam as our *working substance*, because sometimes the steam will be liquid water and sometimes it will be actual steam.

Imagine our gram of "working substance" to be carried *slowly* through four successive reversible processes, as described below, which bring the substance back to its initial condition as represented by the coordinates of the point a in Fig. 36.

Process 1. Compress the gram of substance from volume s to volume w and condense all but an infinitesimal residue of the steam to water, taking an amount of heat L from the substance, thus keeping the *temperature constant*. This process 1 is represented by the line ab in Fig. 36, and during this process an amount of work equal to $(s - w) \times p$ will be done **ON** the substance.

Process 2. Continue the compression by an infinitesimal amount *without taking heat from the substance*, thus condensing the residue of steam to water and causing temperature and pressure to rise to $T + \Delta T$ and $p + \Delta p$, respectively. This process 2 is represented by the infinitesimal line bc in Fig. 36.

Process 3. Expand the gram of substance from volume w to volume s and vaporize all but an infinitesimal residue of water by giving sufficient heat to the substance to keep the *temperature constant* at $T + \Delta T$. This process 3 is represented by the line cd in Fig. 36, and during this

process an amount of work equal to $(s - w) \times (p + \Delta p)$ will be done **BY** the substance.

Process 4. Continue the expansion by an infinitesimal amount *without giving heat to the substance*, thus vaporizing the residue of water and causing temperature and pressure to fall to the initial values T and p , respectively. This process 4 is represented by the infinitesimal line da in Fig. 36.

Application of the perfect engine argument to the above processes. The only outstanding result of the four processes is the doing of a net amount of work equal to $(s - w) \times \Delta p$ **BY** the working substance, the giving out of an amount of heat L at the lower temperature T , and the taking in of an amount of heat equal to $L + (s - w) \cdot \Delta p$ at the higher temperature $T + \Delta T$. Therefore, using $T + \Delta T$ for T_1 of Art. 63, using T for T_2 , using $L + (s - w) \cdot \Delta p$ for H_1 , using L for H_2 , and making use of equation (22) of Art. 63, we get

$$\frac{L + (s - w) \cdot \Delta p}{T + \Delta T} = \frac{L}{T}$$

which is easily transformed into Clapeyron's equation.

Numerical example. At standard atmospheric pressure ($p = 1,013,000$ dynes per square centimeter) the value of T is 373° K., the value of w is very nearly 1 cubic centimeter, the value of s is 1646 cubic centimeters, and L is $536 \times 4.18 \times 10^7$ ergs per gram. Using these values

in Clapeyron's equation we get the value of $\frac{dT}{dp}$, and if

we multiply this by any moderate increment of pressure Δp we get the corresponding rise of the boiling point of water. Thus for $\Delta p = 1$ mm. of mercury ($= 1,013,000/760$ dynes per square centimeter) we get $\Delta T = 0.0365$ of a centigrade degree.

67. **The Carnot Cycle and the Carnot Engine.** The four processes described in Art. 66 and represented by the lines ab , bc , cd and da in Fig. 36 bring the working substance back to its initial condition, and therefore the four processes constitute what is called a closed cycle. This particular cycle was first used by Sadi Carnot in 1824 as a basis for his celebrated theorem concerning the efficiency of a perfect engine (see equation (22) of Art. 63), and it is called the *Carnot cycle*, and an ideal arrangement in which a working substance could be carried through a Carnot cycle is called a *Carnot engine*.

The Carnot cycle is used in a variety of forms in the following articles, and the four reversible processes which go to make up the cycle are as follows :

Process 1 is an isothermal process at a low temperature T_2 , and during this process an amount of heat H_2 is taken from the working substance.

Process 2 is an adiabatic process during which the temperature is raised from T_1 to T_2 .

Process 3 is an isothermal process at high temperature T_1 , and during this process an amount of heat H_1 is given to the working substance.

Process 4 is an adiabatic process during which the temperature drops from T_1 to T_2 .

Let W be the net amount of work done **BY** the working substance during the whole cycle. Then from the first law of thermodynamics we have

$$W = H_1 - H_2 \dots \dots \dots (i)$$

and from the second law of thermodynamics we have

$$\frac{H_1}{T_1} = \frac{H_2}{T_2} \dots \dots \dots (ii)$$

exactly as in the discussion given in Art. 63.

Remark. No engine which brings the working substance back to its initial condition can convert heat into work if the engine is in a region which is everywhere at the same temperature. This is evident from the above equations (i) and (ii).

68. Discussion of the thermo-elastic properties of rubber. Take the ends of a rubber band in the hands, hold the band against the lips (which are very sensitive to changes of temperature), stretch the band and notice that its temperature rises, allow the stretched band to shorten and notice that the temperature of the band falls. Starting from these facts it can be shown that the tension of a stretched rubber band (length of band to remain unchanged) is increased if the temperature of the band is raised slightly.

Let $\lambda \cdot \Delta l$ be the heat energy in ergs which must be given to a stretched rubber band to keep the temperature of the band constant while it is being allowed to shorten by the amount Δl cm. (or the heat energy which must be taken from the band to keep its temperature from rising while its length is being increased by the amount Δl cm.) From the facts as stated above λ is a positive quantity.

Imagine the rubber band to be carried through a Carnot cycle as represented by $abcd$ in Fig. 37, as follows :

Process 1. The already stretched band is elongated by the amount Δl at constant temperature T and an amount of heat $\lambda \cdot \Delta l$ is taken from the band. During this isothermal elongation of the band the abscissas of the points on the line ab represent the increasing values of the length l

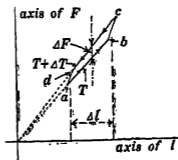


Fig. 37.

of the band, and the ordinates of the points on the line ab represent the increasing values of the tension F or stretching force acting on the band.

Process 2. The band is then stretched an infinitesimal amount adiabatically (no heat energy given to or taken from the band), thus causing the temperature of the band to rise from T to $T + \Delta T$. This process 2 is represented by the infinitesimal line bc in Fig. 37.

Process 3. The band is then allowed to shorten by a certain amount and heat is given to the band to keep its temperature constant. This process 3 is represented by the line cd in Fig. 37.

Process 4. The amount of shortening in 3 is such that a further infinitesimal adiabatic shortening brings the band back to its initial condition. This process 4 is represented by the infinitesimal line da in Fig. 37.

Application of the perfect engine argument. The outstanding results of the four processes above described is the doing of a net amount of work $\Delta F \times \Delta l$ **BY** the rubber band, the giving out by the band of the amount of heat $\lambda \Delta l$ at the lower temperature T , and the taking in by the band of the amount of heat $\lambda \Delta l + \Delta F \cdot \Delta l$ at the higher temperature so that, according to the perfect engine argument, we have

$$\frac{\lambda \Delta l + \Delta F \cdot \Delta l}{T + \Delta T} = \frac{\lambda \Delta l}{T}$$

which is easily reduced to

$$\Delta F = \frac{\lambda}{T} \Delta T$$

which shows that the tension of the stretched band is increased by a rise of temperature since λ/T is positive. This result is due to Lord Kelvin.

69. Helmholtz's relation. When no appreciable change of volume accompanies a chemical action the energy of the reaction is measured by the heat energy which must be taken from the reacting substances to keep the temperature constant. Under what conditions is all of the energy of the chemical action which takes place in a voltaic cell converted into electrical energy? This question was answered by Helmholtz on the basis of the second law of thermodynamics, using a Carnot cycle.

The electrical resistance of a voltaic cell involves the irreversible conversion of electrical* energy into heat, but this effect is negligible if the electric current is very small. Therefore in the following discussion the current is assumed to be extremely small.

What is called local action is assumed to be absent; then the amount of chemical action which takes place in the cell is proportional to the amount of electricity q which passes through the cell, and the chemical action is reversed if the passage of electricity is reversed.

Let $(E + e)q$ be the amount of energy in ergs developed by the chemical action which takes place when the voltaic cell delivers q abcoulombs of electricity, Eq being the part which is converted into electrical energy output, and eq being the part converted into heat so that the temperature of the cell will rise if an amount of heat energy eq is not taken from the cell. When q abcoulombs of electricity is sent backwards through the cell the chemical action is reversed, an amount of work Eq is done on the cell, an amount of heat eq disappears, because the amount of energy $(E + e)q$ is used up to bring about the chemical

* Electrical energy is to be classed as a form of mechanical energy as explained in the latter part of Art. 14.

action, and if an amount of heat energy equal to eq is not given to the cell its temperature will drop.

Imagine the voltaic cell to be carried through a Carnot cycle as follows :

Process 1. Let the voltaic cell deliver q abcoulombs and do Eq ergs of work, and let an amount of heat eq be taken from the cell so as to keep its temperature constant. This process is represented by the line ab in Fig. 38.

Process 2. Let the cell continue to deliver an infinitesimal amount of electricity adiabatically. This will cause the temperature of the cell to rise to $T + \Delta T$ and cause the electromotive force E of the cell to drop by the amount ΔE . This process is represented by the infinitesimal line bc in Fig. 38.

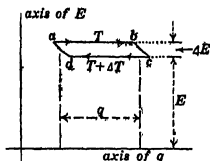


Fig. 38.

Process 3. Let q abcoulombs be pushed backwards through the cell; to do this requires the doing of $(E - \Delta E)q$ ergs of work ON the cell. During this process, which is represented by the line cd in Fig. 38, heat is given to the cell to keep its temperature constant at the value $T + \Delta T$.

Process 4. Let the backward flow of electricity through the cell be continued to an infinitesimal amount adiabatically, thus cooling the cell to the initial temperature. This process is represented by the infinitesimal line da in Fig. 38.

Application of the perfect engine argument. The net amount of work done by the voltaic cell during the cycle above described must be written $-q\Delta E$ because ΔE itself is negative in Fig. 38; the heat taken from the cell

at the lower temperature T is eq ergs, and the heat given to the cell at the higher temperature $T + \Delta T$ must be $eq - q \cdot \Delta E$. Therefore, using equation (22) of Art. 63, we get

$$\frac{eq}{T} = \frac{eq - q \cdot \Delta E}{T + \Delta T}$$

which is easily reduced to

$$e = -T \frac{\Delta E}{\Delta T}$$

This equation shows that e is positive (*less* than all of the energy of the chemical action in the cell is converted into electrical output) when $\Delta E/\Delta T$ is negative; and that e is negative (*more* than all of the energy of the chemical action in the cell is converted into electrical output) when $\Delta E/\Delta T$ is positive. In the former case the cell is slightly warmed when it delivers electrical energy, and in the latter case the cell is slightly cooled when it delivers electrical energy, current being extremely small and local action being non-existent as assumed at the beginning.

70. Boltzmann's derivation of Stefan's equation. In many cases the use of the second law of thermodynamics in an argument depends upon the assumption of highly idealized conditions, and Boltzmann's derivation of Stefan's equation of total radiation from an ideal black body (see Art. 46) is a good example of such. Boltzmann's argument is based on a theoretical result of Maxwell's which has been partially confirmed by experiment, namely that a region filled with radiant energy or radiant heat exerts a pressure p which is equal to $\frac{1}{3}E$ where E is the energy density in ergs per cubic centimeter, and p is the pressure in dynes per square centimeter. Boltzmann's argument leads to the conclusion that E is proportional

to T^4 where T is the Kelvin temperature of the radiation which is assumed to be normal radiation (see Art. 45).

To carry out Boltzmann's argument we must assume a cylinder in which radiation can be captured and held, and compressed and expanded like a gas. Such a cylinder would have to have perfectly reflecting walls so as to turn back the radiation completely. The walls of the cylinder must, of course, be assumed to be impervious to heat (this property is, perhaps, implied when it is stated that the walls are perfectly reflecting), and arrangements must be provided, by assumption, to take heat from or give heat to the captured radiation in the cylinder.

Imagine a batch of captured radiation to be carried through a Carnot cycle as follows :

Process 1. Let the volume of the captured radiation be reduced by the amount Δv at constant temperature T . Temperature being constant, the energy per unit volume

E is constant, and therefore the total energy of the captured radiation is reduced by $E \cdot \Delta v$ during this process 1, and an amount of work $p \cdot \Delta v$ ($= \frac{1}{3} E \cdot \Delta v$) is done ON the captured radiation. Therefore an amount of heat energy equal to $\frac{2}{3} E \cdot \Delta v$ must be taken

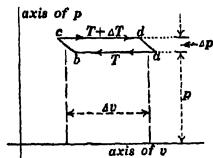


Fig. 39.

from the captured radiation during this process 1, which is represented by the line ab in Fig. 39.

Process 2. Let the volume of the captured radiation be reduced still further by an infinitesimal amount, adiabatically, so as to increase T , p and E to $T + \Delta T$, $p + \Delta p$, and $E + \Delta E$ respectively. This process 2 is represented by the infinitesimal line bc in Fig. 39.

Process 3. Let the volume of the captured radiation be increased by the amount Δv at constant temperature $T + \Delta T$. During this process, which is represented by the line cd in Fig. 39, an amount of work equal to $(\phi + \Delta\phi) \cdot \Delta v$ or to $\frac{1}{3}(E + \Delta E) \cdot \Delta v$ is done **BY** the captured radiation.

Process 4. Let the volume of the captured radiation be still further increased, adiabatically, by an infinitesimal amount, bringing temperature, pressure and energy per unit volume back to their initial values T , ϕ , and E .

Application of the perfect engine argument. The net amount of work done **BY** the captured radiation during the cycle is $\frac{1}{3}(E + \Delta E) \cdot \Delta v - \frac{1}{3}E \cdot \Delta v$ which is $\frac{1}{3}\Delta E \cdot \Delta v$. The amount of heat taken from the captured radiation at the lower temperature T (in process 1) is $\frac{1}{3}E \cdot \Delta v$, and therefore the amount of heat energy given to the captured radiation at the higher temperature $T + \Delta T$ (during process 3) is $\frac{1}{3}E \cdot \Delta v + \frac{1}{3}\Delta E \cdot \Delta v$. Therefore, using equation (22) of Art. 63, we have

$$\frac{\frac{1}{3}\Delta E \cdot \Delta v}{T} = \frac{\frac{1}{3}E \cdot \Delta v + \frac{1}{3}\Delta E \cdot \Delta v}{T + \Delta T}$$

which is easily reduced to

$$\frac{dE}{E} = 4 \frac{dT}{T}$$

where the d -notation has taken the place of the Δ -notation, and by integration this gives

$$E = \text{constant} \times T^4$$

71. Proposition. *An "air" thermometer, used as explained in Art. 5, would measure temperature ratios in accordance with Kelvin's definition as stated in Art. 64 if the gas used in the thermometer were a perfect gas as defined in Art. 49*

This proposition is a consequence of the second law of thermodynamics and its proof depends on an argument based on a Carnot cycle. Imagine a batch of perfect gas in a cylinder, and let us suppose the gas to be carried through a Carnot cycle as follows :

Process 1. The pressure and volume of the gas at the

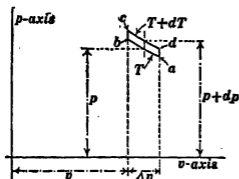


Fig. 40.

beginning are represented by ordinate and abscissa, respectively, of the point *a* in Fig. 40. The first process is to reduce the volume of the gas by the amount Δv at constant temperature T , and the heat energy which must be taken from the gas to keep its temperature

constant is equal to the work $p \cdot \Delta v$ done in compressing the gas.

Process 2. Continue the compression to an infinitesimal extent, adiabatically, as represented by the infinitesimal line *bc* in Fig. 40, thus raising the temperature of the gas to $T + \Delta T$.

Process 3. Allow the volume of the gas to increase by the amount Δv at temperature $T + \Delta T$, as represented by the line *cd* in Fig. 40.

Process 4. Continue the expansion of the gas, adiabatically, to an infinitesimal extent, thus bringing the gas back to its initial condition.

Application of the perfect engine argument. During process 3 the pressure of the gas is, on the average, Δp greater than during process 1, and therefore the work done by the gas during process 3 exceeds the work done on the gas in process 1 by the amount $\Delta p \cdot \Delta v$.

Therefore, using $p \cdot \Delta v$ for H_2 , using $p \cdot \Delta v + \Delta p \cdot \Delta v$ for H_1 , using T for T_2 , and using $T + \Delta T$ for T_1 , we get, from equation (22) of Art. 63

$$\frac{p \cdot \Delta v + \Delta p \cdot \Delta v}{T + \Delta T} = \frac{p \cdot \Delta v}{T}$$

which, using the d -notation instead of the Δ -notation, reduces to

$$\frac{dT}{T} = \frac{dp}{p}$$

whence, by integration, we get

$$\log T = \log p + \text{constant}$$

$$T = kp$$

where k is a constant. This equation shows that the Kelvin temperature T , as defined in Art. 64, is proportional to the pressure of a constant volume of an ideal gas.

72. The Washburn engine. The use of the Carnot cycle in a thermodynamic argument is more intelligible, especially to a beginner, than the purely algebraic kind of argument which is exemplified in Art. 78, but the Carnot cycle method is difficult to use when applied to a complicated chemical system. This difficulty is largely overcome, however, by a scheme which has been devised by E. W. Washburn,* and the more or less idealized arrangement used by Washburn to make his argument concrete may very properly be called the *Washburn engine*. Following are two examples showing the use of the Washburn engine.

Example 1. *Dependence of vapor pressure on total pressure when a saturated vapor is mixed with an inert gas.*

* "A simple system of thermodynamic chemistry based on a modification of the Carnot method," by E. W. Washburn, *Journal of the American Chemical Society*, Vol. XXXII, pages 467-502, 1910.

It is ordinarily considered that the pressure of a saturated vapor (at a given temperature) is the same whether the vapor occupies a region alone or is mixed with an inert gas at any pressure; but this is not exactly true as the following argument shows.

Two containers L and R , Fig. 41, contain water, water vapor, and air. The vapor pressure in L is P , the vapor pressure in R is $P + \Delta P$, the total pressure in L is p , and the total pressure in R is $p + \Delta p$, as indicated in the figure.

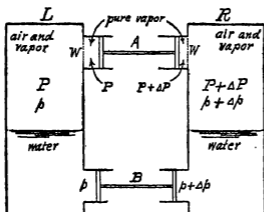


Fig. 41.

Temperature the same in L and R .

The dotted lines WW represent ideal semi-permeable* walls which allow water vapor to pass freely but which do not allow air to pass, so that the upper pair of pistons come against pure water vapor at pressure P and at pressure $P + \Delta P$ as indicated in Fig. 41, whereas the lower pair of pistons in Fig. 41 are acted on by the total pressure p and the total pressure $p + \Delta p$, respectively.

Suppose that one gram of water is vaporized in L ,

* The ideal semi-permeable wall is extensively used in thermodynamic arguments, and it seems to be a legitimate ideal. This question cannot, however, be discussed here. The idea of the semi-permeable wall, for it is an idea and not a fact, originated in the study of osmosis, and it was first used in careful thermodynamic arguments in 1888.

giving volume v of vapor at vapor pressure P . Suppose this newly formed vapor to be transferred to container R by moving pistons A to the right, doing work $v \cdot \Delta P$ ON the working substance. Suppose one gram of water to be condensed in R , and suppose this gram of water to be transferred to L by moving pistons B to the left during which movement work $w \cdot \Delta p$ will be done BY the working substance. The whole system has been brought back to its initial condition, and therefore, temperature being everywhere the same, the net work done by the engine is zero, so that $v \cdot \Delta P = w \cdot \Delta p$, which, using the d -notation instead of the Δ -notation, gives

$$\frac{dP}{dp} = \frac{w}{v} \dots \dots \dots (i)$$

To interpret this equation consider a closed vessel to contain water and water vapor (no air) at 373° K. Then the vapor pressure P and the total pressure p are the same and equal to 760 millimeters. Under these conditions w is very nearly 1 cubic centimeter, and v is about 1646 cubic centimeters. Let air be pumped into the vessel until the total pressure p is 10 atmospheres or 7600 millimeters, so that $\Delta p = 9 \times 760$ millimeters, then water will vaporize until the partial pressure of the water vapor becomes $760 + \Delta P$, where $\Delta P = \frac{w}{v} \cdot \Delta p = \frac{1}{1646} \times 9 \times 760$ millimeters = 4.06 millimeters.

Example 2. *The law of mass action.* Before carrying out a discussion of the law of mass action on the basis of the second law of thermodynamics it may be worth while to explain the meaning of the law in terms of the atomic theory. Hydrogen and chlorine gases when mixed combine very slowly at ordinary temperatures, and the

rate of combination (the rate at which the reaction takes place) is proportional to the number of collisions per second between hydrogen molecules and chlorine molecules, and this is in turn proportional to the product $n_h \times n_o$, where n_h is the number of hydrogen molecules in the containing vessel and n_o is the number of chlorine molecules in the vessel.

Consider four gases A , B , C , and D in two containers R and L as indicated in Fig. 42, and suppose that a mols

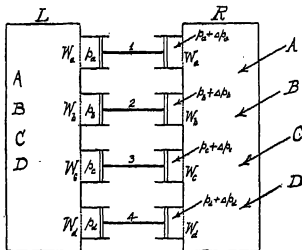
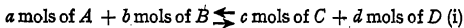


Fig. 42.

Temperature the same in L and R .

of A and b mols of B combine to form c mols of C and d mols of D , and that the opposite reaction is taking place at the same time (c mols of C and d mols of D combine to form a mols of A and b mols of B) in accordance with the reaction formula



one mol of any gas being m grams of the gas where m is the molecular weight of the gas.

Let p_a , p_b , p_c , and p_d , respectively, be the partial pressures of the gases in gases in L , and let $p_a + \Delta p_a$

$p_b + \Delta p_b$, $p_c + \Delta p_c$, and $p_d + \Delta p_d$ be the respective partial pressures of the gases in R ; also V_a , V_b , V_c and V_d be the volumes of one mol of the respective gases at the temperature T and at pressures p_a , p_b , p_c , and p_d .

Suppose the two walls W_a to be permeable only to gas A , the two walls W_b to be permeable only to gas B , the two walls W_c to be permeable only to gas C , and the two walls W_d to be permeable only to gas D .

Suppose volume cV_c of gas C and volume dV_d of gas D to be transferred from L to R by moving the two pairs of pistons 3 and 4 towards the right; and suppose volume aV_a of A and volume bV_b of B to be transferred from R to L by moving the two pairs of pistons 1 and 2 towards the left. These transferred volumes may be thought of as infinitesimal by supposing the containers and the exchange pistons to be very large.

Then the net work done by the working substance is $aV_a \cdot \Delta p_a + bV_b \cdot \Delta p_b - cV_c \cdot \Delta p_c - dV_d \cdot \Delta p_d$, and this work must be equal to zero because the temperature is everywhere the same and the initial and final states of the system are identical. Therefore

$$aV_a \cdot \Delta p_a + bV_b \cdot \Delta p_b - cV_c \cdot \Delta p_c - dV_d \cdot \Delta p_d = 0. \quad (\text{ii})$$

Let us suppose that each of the gases A , B , C , and D is a perfect gas in that each gas conforms to equation (8) of Art. 6. Then

$$V_a p_a = V_b p_b = V_c p_c = V_d p_d = KT \dots (\text{iii})$$

where K is a constant (the same for all gases, see L. Q. 6 on page 9). Therefore

$$V_a = \frac{KT}{p_a}, \quad V_b = \frac{KT}{p_b}, \quad V_c = \frac{KT}{p_c}, \quad \text{and} \quad V_d = \frac{KT}{p_d} \quad (\text{iv})$$

and if we substitute these values of $V_a \dots V_d$ in equation (ii) we get

$$a \frac{\Delta p_a}{p_a} + b \frac{\Delta p_b}{p_b} - c \frac{\Delta p_c}{p_c} - d \frac{\Delta p_d}{p_d} = 0 \dots\dots (v)$$

whence, by integration, we get

$$a \log p_a + b \log p_b - c \log p_c - d \log p_d = \text{a constant (vi)}$$

or

$$\frac{p_a^a p_b^b}{p_c^c p_d^d} = \text{a constant} \dots\dots\dots (vii)$$

This equation expresses the law of mass action as applied to the mixed gases, and it expresses the condition that the opposite reactions as expressed by formula (i) take place at equal rates so that the mixed gas is in equilibrium.

To understand equation (vii) let us consider its interpretation in terms of the atomic or molecular theory. The rate at which the gases A and B combine to form C and D (in container L for example) is proportional to the number of times per second that a molecules of A and b molecules of B come together in a single encounter or collision. This, at the given temperature, is proportional to $n_a^a \times n_b^b$, where n_a is the number of molecules of A in L , and n_b is the number of molecules of B in L . But n_a and n_b (at the given temperature) are proportional to p_a and to p_b respectively, so that the rate at which A and B combine to produce C and D is proportional to $p_a^a \times p_b^b$. Similarly, the rate at which C and D combine to produce A and B is proportional to $p_c^c \times p_d^d$. But when equilibrium is established (in container L , for example) these two rates are equal so that (a constant $\times p_a^a \times p_b^b = \text{a constant} \times p_c^c \times p_d^d$, and therefore, when the mixed gas is in equilibrium we have equation (vii).

CHAPTER VIII

ENTROPY AND THERMODYNAMIC POTENTIALS

73. Entropy as a measurable property of a substance.

The idea of thermodynamic degeneration which is developed in Art. 61 and used in the perfect-engine argument in Art. 63 would be greatly strengthened if we could develop the idea further so as to be able to say concerning the explosion of a batch of gunpowder, for example, that the thermodynamic degeneration due to the explosion is ϕ units *because a measurable property of the substance has increased ϕ units in value*. It is the purpose of the following discussion to show that such a measurable property of a substance does exist. This measurable property of the substance is called the *entropy* of the substance, and we speak of the entropy of a substance just as we speak of its temperature, or its pressure, or its volume. Every sweeping process causes an increase of entropy of one or more substances, and the thermodynamic degeneration which is associated with a sweeping process is equal to or measured by this increase of entropy. The existence of the "entropy function" (of entropy as a measurable property of a substance) is established by Clausius' theorem and its corollary as set forth below, and the entropy function so established is related to thermodynamic degeneration as explained in the example given below.

Clausius' theorem. Consider any slow (reversible)

change of state of a substance which brings the substance back to its initial condition. Such a process is called a reversible cyclic process and may be represented by a closed curve CC in the p, v diagram as shown in Fig. 43.

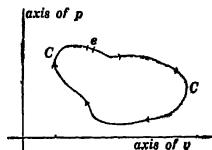


Fig. 43.

Consider a very small element or stage e of such a cyclic process, let T be the Kelvin temperature of the working substance during this infinitesimal stage e , and let ΔH be the heat energy that is given to the substance during

the stage e (ΔH is to be considered as negative if it represents heat energy taken from the working substance). Then, according to Clausius, the algebraic sum of all such quotients as $\Delta H/T$ for the entire cycle CC is zero.

Proof. Let the dotted lines ϕ_1 and ϕ_2 in Fig. 44 be two very closely adjacent adiabatic lines, lines which show the relation between pressure and volume during adiabatic expansion or compression of the working substance. Then the infinitesimal portions of the curve CC which lie between ϕ_1 and ϕ_2 may be taken as equivalent to two infinitesimal portions ab and cd of two isothermal lines at temperatures T_1 and

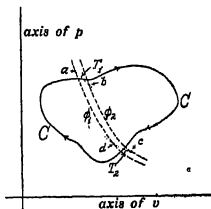


Fig. 44.

T_2 so that $abcd$ represents a Carnot cycle. Let ΔH_1 be the heat energy given to the working substance during the isothermal expansion ab , and let $-\Delta H_2$ be the heat energy taken from the working substance during the isothermal

compression *cd*. Then, according to the perfect-engine argument of Art. 63, we have $\Delta H_1/T_1 = -\Delta H_2/T_2$, or

$$\frac{\Delta H_1}{T_1} + \frac{\Delta H_2}{T_2} = 0 \dots\dots\dots(i)$$

Now the curve *CC* may be cut across by an infinite number of closely adjacent adiabatic lines, thus dividing the process curve *CC* into pairs of elements like *ab* and *cd* in Fig. 44, and for each pair of elements an equation like (i) is true. Therefore the quotients $\Delta H/T$ annul each other in pairs so that the sum of all such quotients is zero. Q.E.D.

Note. The sum of all such quotients as $\Delta H/T$ along any given portion of the process curve *CC* is reversed in sign, if the process is carried out in a reverse direction. This is evident when we consider that if heat is *given* to the working substance during any stage of the process, then an equal amount of heat must be *taken from* the substance during this stage if the process is carried out in a reverse direction.

Corollary of Clausius' theorem. Consider any two states *A* and *B* of a substance. The sum of such quotients as $\Delta H/T$ is the same for any two and therefore for all reversible processes that lead from *A* to *B*. Let the two chosen states *A* and *B* be represented by the points *A* and *B* in Fig. 45. Let ϕ be the value of $\Sigma\Delta H/T$ for path *APB*, and let ψ be the value of $\Sigma\Delta H/T$ for path

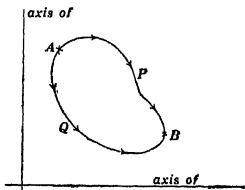


Fig. 45.

AQB. Then $-\psi$ is the value of $\Sigma\Delta H/T$ for path *BQA*, and $\phi - \psi$ is the value of $\Sigma\Delta H/T$ for the closed cycle from *A* to *B* and back from *B* to *A*. But the value of

$\int dQ/T$ for a closed cycle is zero, according to Clausius' theorem. Therefore $\phi - \psi = 0$ or $\phi = \psi$. Q.E.D.

Definition of the entropy of a substance in any given state

If we take state A of the working substance arbitrarily as a standard or zero state of the substance in which the entropy is arbitrarily taken as zero, then the value of $\int \Delta H/T$ for any reversible process leading from

A to state B is called the entropy of the substance in state B .

The definition of the entropy of a substance in a given state B may be expressed by the equation

$$\phi = \int \frac{dH}{T} \dots\dots\dots(24)$$

The integration being extended over any reversible process which brings the substance from an arbitrarily chosen state to the given state, and this equation may be written in the entirely equivalent differential form

$$\left. \begin{aligned} d\phi &= \frac{dH}{T} \\ dH &= T \cdot d\phi \end{aligned} \right\} \dots\dots\dots(25)$$

This definition of the entropy of a substance in a given state is based solely upon a consideration of reversible processes, whereas the physical significance of entropy is only apparent in any sweeping process whatever must involve an increase of the entropy of one or more substances; it is therefore, in a sense, unfortunate that one is unable to understand the physical meaning of entropy from the above definition! To understand the meaning of entropy, and especially to understand the important rôle that reversible processes play in connection with the notion of entropy, it is best to consider an actual example as follows:

In any sweeping process that takes place in a substance and pro-

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duces a certain amount of thermodynamic degeneration ϕ ; (b) The substance is then brought back to its initial condition by a reversible process so that the degeneration ϕ must be handed on to some other substance, and it is found that the entropy of the other substance, as defined above, is thereby increased by the amount ϕ .

Example showing the physical meaning of entropy.

(a) A volume v of perfect gas* at pressure p and Kelvin temperature T is allowed to increase to volume $v + \Delta v$ by *free expansion*, and the expanded gas is allowed to settle to thermal equilibrium. Its temperature is then the same as at first, namely, T . (b) The expanded gas is then compressed slowly to its initial volume v , and sufficient heat ΔH is taken from the gas (and given to an adjacent substance) to keep its temperature constant during the compression. This heat ΔH is equal to the work $p \cdot \Delta v$ done on the gas in compressing it.

Process (a) is a sweeping process and it involves a certain amount of thermodynamic degeneration ϕ ; but process (b) is a reversible process involving no thermodynamic degeneration, this process merely hands the degeneration ϕ to the adjacent substance. Therefore it is important to consider two things, namely, (1) how much thermodynamic degeneration is associated with process (a), and (2) what is the entropy increase of the adjacent substance due to process (b). The first question is to be answered from the point of view of Art. 61, and the second question is to be answered on the basis of the above definition of entropy.

Question 1. Process (b), being reversible, involves no

* The only reason for assuming a perfect gas is to make the example simple.

thermodynamic degeneration, and therefore the thermodynamic degeneration ϕ which is due to process (a) may be thought of as due to (a) and (b) together. But the *only* result of (a) and (b) together is the conversion of an amount of work $p \cdot \Delta v$ into heat at temperature T , and therefore the value of ϕ is $p \cdot \Delta v / T$ or $\Delta H / T$ according to equations (19) and (20) of Art. 6r.

Question 2. During process (b) an amount of heat ΔH is given to the adjacent substance at temperature T , and the increase of entropy of the adjacent substance is therefore equal to $\Delta H / T$ according to the above definition.

Conclusion. Therefore when the havoc wrought by the sweeping process (a) is repaired by the reversible process (b), the thermodynamic degeneration due to (a) is equal to (or measured by) the increase of entropy of the adjacent substance.

Remark. Process (b) decreases the entropy of the working substance by the amount $\Delta H / T$, according to the above definition, and, of course, process (b) must bring the entropy of the working substance back to its initial value because it brings the working substance back to its initial condition or state. Therefore the sweeping process (a) increases the entropy of the working substance by an amount equal to the thermodynamic degeneration involved in (a).

74. Entropy of M grams of a perfect gas expressed in terms of its pressure and volume. According to equation (8) of Art. 6, we have

$$pv = MRT \dots\dots\dots (i)$$

so that the change of temperature dT corresponding to a given change of volume dv at constant pressure is

$$dT = \frac{p \cdot dv}{MR} \dots\dots\dots (ii)$$

and the change of temperature dT corresponding to a given change of pressure dp at constant volume is

$$dT = \frac{v \cdot dp}{MR} \dots\dots\dots (iii)$$

Change of entropy due to change of volume at constant pressure. Equation (ii) gives the rise of temperature involved in the increase of volume dv at constant pressure, and if we multiply this rise of temperature by the mass M of the gas and by its specific heat at constant pressure, C_p , we get the amount of heat ΔH which must be given to the gas, and if we divide this by T we get the increase of entropy $d\phi$, according to equation (25) of Art. 73. Therefore, using pv/MR for T , according to equation (i), we get

$$d\phi = C_p M \frac{dv}{v} \dots\dots\dots (iv)$$

Change of entropy due to change of pressure at constant volume. Equation (iii) gives the rise of temperature involved in the increase of pressure dp at constant volume, and if we multiply this rise of temperature by the mass M of the gas and by its specific heat at constant volume, C_v , we get the amount of heat which must be given to the gas, and if we divide this by $T (= pv/MR)$ we get the increase of entropy, namely,

$$d\phi = C_v M \frac{dp}{p} \dots\dots\dots (v)$$

Complete differential of entropy. Equation (iv) expresses the differential of entropy with respect to volume and equation (v) expresses the differential of entropy with respect to pressure. Therefore the complete differential of entropy is given by the equation

$$d\phi = C_p M \frac{dv}{v} + C_v M \frac{dp}{p} \dots\dots\dots (vi)$$

which, by integration, gives

$$\phi = C_p M \log_e v + C_v M \log_e p + \text{a constant} \dots (vii)$$

If we choose our zero state as $v = 1$ and $p = 1$ (for which state ϕ is taken, arbitrarily, as zero), then the constant of integration is zero, and equation (vii) becomes

$$\phi = M(C_v \log_e v + C_p \log_e p) \dots\dots\dots(\text{viii})$$

LEADING QUESTIONS

L. Q. 83. Let i be the volume of a gram of ice at 0°C. , let w be the volume of a gram of ice water, and let L be the latent heat of fusion of ice in ergs per gram. Using an argument similar to that of Art. 66, show that

$$dT = -\frac{T}{L}(i - w) \cdot dp$$

where T is 273°K. , and dT is the lowering of the freezing point of water due to an increase of pressure amounting to dp dynes per square centimeter.

L. Q. 84. State, in general terms, what four reversible processes or changes constitute a Carnot cycle.

L. Q. 85. Follow a particular portion of the working substance as it passes through the engine in Fig. 35 to the condenser, thence through the feed-water pump to the boiler, and thence to the engine again, and show that this portion of working substance passes through a Carnot cycle.

L. Q. 86. Using equation (24) of Art. 73, show that the entropy of a substance in a given state is proportional to the mass of the substance. That is to say, the entropy of 100 grams of boiling water is 100 times as great as the entropy of one gram of boiling water.

L. Q. 87. If the thermodynamic degeneration involved in the explosion of one gram of gunpowder is ϕ , how much thermodynamic degeneration is involved in the explosion of 10 grams of gunpowder? How does this fact tie up with the matter referred to in L. Q. 86?

L. Q. 88. To convert one gram of water at 100°C. into steam at the same temperature requires 536 calories, or

2240 joules, or 2.24×10^{10} ergs of heat energy, and if we divide this amount of heat by the Kelvin temperature corresponding to 100°C . we get $\Delta\phi$, where $\Delta\phi$ is the amount by which the entropy of one gram of steam at 100°C . and normal atmospheric pressure exceeds the entropy of one gram of water at the same temperature and pressure. State in terms of what unit or units entropy may be expressed.

L. Q. 89. Let us assume that heat is given to the boiler in Fig. 35 by a large amount of substance S_1 which is only infinitesimally warmer than the boiler, and that heat is taken from the condenser by a large amount of substance S_2 which is only infinitesimally cooler than the condenser, so that not only all changes undergone by the working substance in the engine are reversible but also the exchanges of heat are reversible. Write down expressions for the changes of entropy of S_1 and S_2 while an amount of heat H_1 is given to the boiler by S_1 and an amount of heat H_2 is taken from the condenser by S_2 . After long-continued operation of the engine the working substance is in the same state as at the beginning, and therefore there can be no change of entropy of the working substance. Also, since there is no sweeping process involved anywhere, there can be no increase of entropy, on the whole. What, therefore, is the relation between the entropy changes of S_1 and S_2 ?

Write this relation as an equation involving T_1 , T_2 , H_1 and H_2 .

L. Q. 90. Consider two substances A and B in contact, A being at 100°C . and B being at 0°C . What is the entropy change of each and what is the total entropy change of both together when 1000 calories of heat energy has passed from A to B ? What would the total entropy change of both together be if the temperature difference were infinitesimal?

L. Q. 91. Suppose that a certain physical change involving only a specified group of substances were to cause a net decrease of entropy. What would this mean? See Art. 6r.

L. Q. 92. State, in terms of entropy, the meaning of the term *compensation* as used in Art. 6z.

L. Q. 93. One thousand units of heat energy is taken from a boiler at 100°C . ; what amount of this heat would have to be delivered to a region at 50 degrees below zero centigrade to compensate for the conversion of the remainder into mechanical energy ?

PROBLEMS

81. Find the entropy in ft.-lbs. per Fahrenheit degree of one pound of water at 212°F ., taking ice water as the zero state and assuming the specific heat of water to be constant and equal to 1 British thermal unit per pound per Fahrenheit degree. One British thermal unit equals 778 ft.-lbs.

82. Find the entropy in ergs per centigrade degree of 10 grams of water at 100°C ., taking ice water as the zero state and assuming the specific heat of water to be constant and equal to 4.18×10^7 ergs per gram per centigrade degree.

83. Find the entropy in ergs per centigrade degree of 10 grams of steam at 100°C . and at standard atmospheric pressure.

84. Find the entropy of 10 grams of water at 50°C . Find the entropy of 10 grams of water at 30°C . Find the entropy of 20 grams of water at 30°C . Find the increase of entropy when 10 grams of water at 50°C . is mixed with 10 grams of water at 30°C . Take ice water as the zero state and assume specific heat of water to be constant.

75. Formulation of the first and second laws of thermodynamics as a differential equation. Imagine a substance to undergo, reversibly, a minute change which involves the doing of an amount of work dW on the substance and the giving of an amount of heat dH to the substance. Let E be the total heat-energy of the substance (the internal energy of the substance, as it is called). Then, according to the principle of the conservation of energy (the first law of thermodynamics), we have

$$dE = dH + dW \dots\dots\dots(i)$$

The second law of thermodynamics is completely, though not very explicitly, expressed by the mere existence of entropy as a measurable property of a substance, and, according to equation (25) of Art. 73, we have

$$dH = T \cdot d\phi \dots\dots\dots(ii)$$

so that equation (i) becomes

$$dE = T \cdot d\phi + dW \dots\dots\dots(26)$$

This differential equation is applicable to any infinitesimal, reversible process whatever and it completely expresses both the first and the second laws of thermodynamics.

Let us consider a case in which work is done on or by the substance because of change of volume. Then the work done on the substance is equal to $p \cdot dv$ where dv is a decrement of volume, and being a decrement of volume dv should be thought of as negative. Therefore we have

$$dW = -p \cdot dv \dots\dots\dots(iii)$$

so that equation (26) becomes

$$dE = T \cdot d\phi - p \cdot dv \dots\dots\dots(27)$$

This equation completely expresses the first and second laws of thermodynamics for all cases in which work is done on or by a substance because of compression or expansion—not by electrical or magnetic or any other kind of change which may involve the doing of work on or by the substance.

76. Free-energy functions. The two important free-energy functions derive their significance from the following propositions 1 and 2.

Proposition 1. The function $B = T\phi - E$ is a function (having a definite value for each equilibrium state of a

substance) whose increase during any *reversible, isothermal* change of the substance from state a to state b is equal to the external work done by the substance during the change from a to b .

Proof. Let us call the substance under consideration the "working" substance, to distinguish it from the surrounding substance; T is the temperature of the working substance (and of the surrounding substance), ϕ is the entropy of the working substance, and E is the internal energy of the working substance.

It is evident that $dE = dH - dW$, where dE is the increase of internal energy from a to b , dH is the heat energy given to the working substance, and dW is the work done by the working substance. But, the change being reversible, we have $dH = T \cdot d\phi$ according to equation (25) of Art. 73. Therefore $dE = T \cdot d\phi - dW$, or $dW = T \cdot d\phi - dE$, or $dW = d(T\phi - E)$ since T is constant. Q.E.D.

Proposition 2. The amount of work dW done by the working substance as it changes *reversibly* from a to b is definite in amount, as explained above, but, if the change from a to b takes place *irreversibly*, then the work dW' done by the working substance will be less than dW .

Proof. The increase of entropy, $d\phi$, of the working substance from a to b is perfectly definite in amount whether the change from a to b is reversible or irreversible; this is evident when we consider that the working substance has a definite entropy in state a and a definite entropy in state b .

When the working substance changes from a to b *reversibly* the surrounding substance decreases in entropy by an amount equal to an increase of entropy of the

working substance, because during a reversible process there can be, on the whole, no increase of entropy (no thermodynamic degeneration); but when the change of the working substance from a to b is *irreversible*, a part of its increase of entropy $d\phi$ must be due to this irreversibility (equal to the degeneration involved), and the remainder is compensated by and equal to the decrease of entropy of the surrounding substance. Therefore the decrease of entropy $d\phi'$ of the surrounding substance is less than $d\phi$, and the heat dH' ($= T \cdot d\phi'$) taken from the surrounding substance (and given to the working substance) is less than dH in the above discussion. But $dE = dH' - dW'$ and dE has a perfectly definite value for the change from a to b whether the change be reversible or irreversible. Therefore $dE = dH - dW = dH' - dW'$, and therefore if dH' is less than dH it is evident that dW' must be less than dW . Q.E.D.

The **Helmholtz free-energy function** is usually defined as

$$A = E - T\phi \dots\dots\dots(28)$$

or equal to $-B$ in the above discussion, and therefore the Helmholtz free-energy is a function whose *decrease* during any isothermal change of the working substance from state a to state b is the maximum possible work that can be gotten out of the change. This maximum work is obtained if the change from a to b is reversible, and less than this maximum amount of work is obtained if the change from a to b is irreversible.

The Lewis free-energy function. The work dW done by the working substance in the above discussion may be work done by expansion of the substance ($p \cdot dv$), or it may be work done electrically (*see* Art. 69), or it may be work done magnetically, or it may be work done because of surface tension (in the case of a liquid), etc

It is sometimes desirable to ignore the work done by expansion ($p \cdot dv$) and consider only the work done electrically or otherwise; and the function whose *decrease* gives the maximum amount of work (other than $p \cdot dv$) obtainable from an isothermal change is

$$F = E - T\phi - pv \dots\dots\dots(29)$$

This function F is called the Lewis free-energy function

Thermodynamic potentials. The functions A and F are sometimes called *thermodynamic potentials* "because of rough analogies to mechanics" which are of no special significance. The use of these functions for expressing the conditions of thermal equilibrium of a substance is discussed in Lewis and Randall's *Thermodynamics*, pages 155-166.

77. The Maxwell thermodynamic relations.* The Maxwell thermodynamic relations are algebraic expressions for the necessary consequences (physical) of the second law of thermodynamics. There are four important relations, but we will discuss only two of them here.

First relation. Consider equation (27) of Art. 75. This equation expresses dE as a complete differential [the right-hand member of (27) is conceivably obtainable by differentiating a definite function of ϕ and v] and therefore the coefficient of $d\phi$ in equation (27) is the value of $\frac{dE}{d\phi}$, and the coefficient of dv in equation (27) is

the value of $\frac{dE}{dv}$. That is to say

$$\frac{dE}{d\phi} = T \dots\dots\dots(i)$$

and

$$\frac{dE}{dv} = -p \dots\dots\dots(ii)$$

* These relations are discussed on pages 737-743 of Preston's *Theory of Heat*.

Therefore, differentiating (i) with respect to v and differentiating (ii) with respect to ϕ , we get

$$\frac{d^2E}{dv \cdot d\phi} = \frac{dT}{dv} \dots\dots\dots (iii)$$

and
$$\frac{d^2E}{d\phi \cdot dv} = - \frac{dp}{d\phi} \dots\dots\dots (iv)$$

But $\frac{d^2E}{dv \cdot d\phi} = \frac{d^2E}{d\phi \cdot dv}^*$, so that from (iii) and (iv) we have

$$\left(\frac{dT}{dv}\right)_{\phi \text{ constant}} = - \left(\frac{dp}{d\phi}\right)_{v \text{ constant}} \dots\dots (30)$$

This is the first Maxwell relation.

Second relation. Consider the Helmholtz free-energy function

$$A = E - T\phi \dots\dots\dots (28)$$

differentiating we get

$$dA = dE - T \cdot d\phi - \phi \cdot dT$$

and, substituting the value of $T \cdot d\phi$ from this equation into equation (27), we get

$$dA = - \phi \cdot dT - p \cdot dv \dots\dots\dots (31)$$

Whence, using the same line of argument as in equations (i) to (iv), we get

$$\left(\frac{d\phi}{dT}\right)_{T \text{ constant}} = \left(\frac{dp}{dV}\right)_{v \text{ constant}} \dots\dots (32)$$

78. Algebraic derivation of Clapeyron's equation (See Art. 66). Clapeyron's equation may be written in the form

$$\left(\frac{dp}{dT}\right)_{v \text{ constant}} = \frac{L}{T(s-w)} \dots\dots\dots (i)$$

* The proof of this relation is given in any good treatise on calculus. See, for example, Franklin, McNutt and Charles' *Calculus*, pages 249-251.

Consider water and water vapor in a closed vessel at temperature T and pressure p . Let an infinitesimal amount of the water, dm grams, be vaporized (temperature and pressure constant, volume allowed to increase). Then the amount of heat required is $dH = L \cdot dm$, and this heat must be given to the substance in the closed vessel. Therefore, according to equation (25) of Art. 73, we have

$$d\phi = \frac{L \cdot dm}{T} \dots\dots\dots(ii)$$

and the increase of volume of water and vapor is

$$dv = (s - w) \cdot dm \dots\dots\dots(iii)$$

Using the value of dm from (iii) in (ii), we get

$$\left(\frac{d\phi}{dv}\right)_{T \text{ constant}} = \frac{L}{T(s - w)} \dots\dots\dots(iv)$$

whence, using equation (32), we get

$$\left(\frac{d\phi}{dT}\right)_{v \text{ constant}} = \frac{L}{T(s - w)} \dots\dots\dots(v)$$

LEADING QUESTIONS

L. Q. 94. Look up specific volumes of water and ice at 0°C and 760 mm., take latent heat of fusion of ice as 80 calories per gram, and, using Clapeyron's equation, calculate the change in the temperature of melting ice due to an increase of pressure from one atmosphere to 1.1 atmosphere.

L. Q. 95. Substitute dH/T for $d\phi$ in equation (30) and give a verbal statement of the meaning of the resulting equation.

L. Q. 96. Substitute dH/T for $d\phi$ in equation (32) and give a verbal statement of the meaning of the resulting equation.

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