# PRINCIPLES

OF

# THERMODYNAMICS

BY

G. A. GOODENOUGH, M.E.

PROFESSOR OF THERMODYNAMICS IN THE UNIVERSITY
OF ILLINOIS

SECOND EDITION, REVISED

/

# PREFACE

THIS book is intended primarily for students of engineering. Its purpose is to provide a course in the principles of thermodynamics that may serve as an adequate foundation for the advanced study of heat engines. As indicated by the title, emphasis is placed on the principles rather than on the applications of thermodynamics. In the chapters on the technical applications the underlying theory of various heat engines is quite fully developed. The discussion, however, is restricted to ideal cases, and questions that involve the design, operation, or performance of heat engines are reserved for a second volume.

The arrangement of the subject matter and the method of presentation are the result of some twelve years' experience in teaching thermodynamics. Briefly, the arrangement is as follows: In the first six chapters, the fundamental laws are developed and the general equations of thermodynamics are derived. The laws of gases and gaseous mixtures are discussed in Chapters VII and VIII, and this discussion is followed immediately by the technical applications in which gaseous media play a part. A discussion of the properties of saturated and superheated vapors is likewise followed by the technical applications that involve vapor media.

Some of the features of the book to which attention may be directed are the following:

1. The method of presenting the fundamental laws. In this treatment I have followed very closely the development in Bryan's thermodynamics. The second law is made identical with the law of degradation of energy, the connection between irreversibility and loss of availability is pointed out, and by

entropy of a non-isolated system as the integral $\int \frac{dQ}{T}$ is easily derived. By this method of presentation, a definite conception of the meaning and scope of the second law is obtained, and the difficulties that usually surround the definition of entropy are removed.

2. The discussion of saturated and superheated vapors. The experiments in the Munich laboratory and the researches of Professor Marks and Dr. Davis have furnished new and accurate data on the thermal properties of saturated and superheated steam. In Chapters X and XI a concise but fairly complete account of these important researches is given. Knoblauch's experiments on specific volumes have been correlated with the experiments on specific heat by means of the Clausius relation $\left(\dfrac{\partial c_p}{\partial p}\right)_T = -AT\left(\dfrac{\partial^2 v}{\partial T^2}\right)_p$ and equations for the specific heat, entropy, energy, and heat content of superheated steam are thereby deduced. These results have not hitherto been published.

3. The discussion of the flow of fluids and of throttling processes. The applications of the throttling process are so important from all points of view that a separate chapter is devoted to them.

4. The treatment of gaseous mixtures, Chapter VIII. An attempt is made to present in concise form the principles and methods required in the accurate analysis of the internal combustion engine.

5. The note on the interpretation of differential expressions, Art. 23. This important topic should be discussed fully in calculus, but experience shows that students rarely have a grasp of it. In thermodynamics the exact differential has extensive applications; hence it seems desirable to include a rather complete explanation of exact and inexact differentials and their connection with thermodynamic magnitudes. A thorough understanding of this article should enable the student to pursue the subsequent mathematical discussions with intelligence and ease.

The text is illustrated by numerous solved problems, and exercises are given at the ends of the chapters and elsewhere. Many of the exercises require only routine numerical solutions, but others involve the development of principles.

References are given to the treatment of various topics in standard works and to original articles. It is not expected that undergraduate students will make extensive use of these references, but it is hoped that instructors and advanced students will find them helpful.

In writing this book I have consulted many of the standard works on thermodynamics, and have made free use of whatever material suited my purpose. I desire to acknowledge my special indebtedness to the works of Bryan, Preston, Griffiths, Zeuner, Chwolson, Weyrauch, and Lorenz, and to the papers of Dr. H. N. Davis. To Mr. John A. Dent I am indebted for assistance in the construction of the tables and in the revision of the proof sheets. Mr. A. L. Schaller also gave valuable assistance in getting the book through the press.

<div style="text-align: right">G. A. GOODENOUGH.</div>

# CONTENTS

## CHAPTER I

### ENERGY

## CHAPTER II

### CHANGE OF STATE. THERMAL CAPACITIES

## CHAPTER III

### THE FIRST LAW OF THERMODYNAMICS

## CHAPTER IV

### THE SECOND LAW OF THERMODYNAMICS

## CHAPTER V

### TEMPERATURE ENTROPY REPRESENTATION

## CHAPTER VI

### GENERAL EQUATIONS OF THERMODYNAMICS

# CHAPTER VII

## PROPERTIES OF GASES

# CHAPTER VIII

## GASEOUS COMPOUNDS AND MIXTURES. COMBUSTION

# CHAPTER IX

## TECHNICAL APPLICATIONS. GASEOUS MEDIA

## CHAPTER XII

### MIXTURES OF GASES AND VAPORS

## CHAPTER XIII

### THE FLOW OF FLUIDS

## CHAPTER XIV

### THROTTLING PROCESSES

## CHAPTER XV

### TECHNICAL APPLICATIONS, VAPOR MEDIA

#### The Steam Engine

#### The Steam Turbine

#### Refrigeration with Vapor Media

# SYMBOLS

NOTE. The following list gives the symbols used in this book. In a magnitude is dependent upon the weight of the substance, the small letter denotes the magnitude referred to unit weight, the capital letter same magnitude referred to $M$ units of weight. Thus $q$ denotes the h absorbed by one pound of a substance, $Q = Mq$, the heat absorbed by pounds.

$J$, Joule's equivalent.

$A$, reciprocal of Joule's equivalent.

$M$, weight of system under consideration.

$t$, temperature on the F. or the C. scale.

$T$, absolute temperature.

$p$, pressure.

$v$, $V$, volume.

$\gamma$, specific weight; also heat capacity.

$u$, $U$, intrinsic energy of a system.

$i$, $I$, heat content at constant pressure.

$s$, $S$, entropy.

$W$, external work.

$q$, $Q$, heat absorbed by a system from external sources.

$h$, $H$, heat generated within a system by irreversible transformation work into heat.

$c$, specific heat.

$c_v$, specific heat at constant volume.

$c_p$, specific heat at constant pressure.

$k$, ratio $c_p/c_v$.

$B$, constant in the gas equation $pv = BT$.

$R$, universal gas constant.

$n$, exponent in equation for polytropic change, $pV^n = C$.

$m$, molecular weight.

$a_1$, $a_2$..., atomic weights.

$H_m$, heating value of a fuel mixture.

$x$, quality of a vapor mixture (p. 165).

$q'$, heat of the liquid.

$q''$, total heat of saturated vapor.

$r$, latent heat of vaporization

$v'$, $v''$,   specific volume of liquid and of vapor, respectively.

$u'$, $u''$,   internal energy of liquid and of vapor, respectively.

$s'$, $s''$,   entropy of liquid and of vapor, respectively.

$i'$, $i''$,   heat content of liquid and of vapor, respectively.

$c'$, $c''$,   specific heat of liquid and of vapor, respectively.

$\phi$,   humidity.

$w$,   velocity of flow.

$w_s$,   acoustic velocity.

$F$,   area of cross-section of channel.

$z$,   work of overcoming friction in the flow of fluids.

$p_m$,   critical pressure (flow of fluids).

$\mu$,   Joule-Thomson coefficient.

$\eta$,   efficiency of a heat engine.

$N$,   steam consumption per h.p.-hour.

# PRINCIPLES OF THERMODYNAMICS

## CHAPTER I

### ENERGY

**1. Scope of Thermodynamics.** — In the most general sense, thermodynamics is the science that deals with energy. Since all natural phenomena, all physical processes, involve manifestations of energy, it follows that thermodynamics is one of the most fundamental and far-reaching of sciences. Thermodynamics lies at the foundation of a large region of physics and also of a large region of chemistry; and it stands in a more or less intimate relation with other sciences.

In a more restricted sense, thermodynamics is that branch of physics which deals specially with a form of energy called heat. It deals with transformations of heat energy into other forms of energy, develops the laws that govern such transformations, and investigates the properties of the media by which the transformations are effected. In technical thermodynamics the general principles thus developed are applied to the problems presented by the various heat motors.

In this volume the general principles of thermodynamics are developed so far as is essential to give a firm foundation for the technical applications in engineering practice. The scope of the book does not permit a discussion of the methods of investigation that are employed so fruitfully in physics and chemistry.

ing to rest, that is, in changing its state as regards velocity; a body in an elevated position can do work in changing its position; a heated metal rod is capable of doing mechanical work when it contracts in cooling. In each case some change in the state of the body results in the doing of work; hence, in each case the body in question possesses energy.

Energy, like motion, is purely relative. It is impossible to give a numerical value to the energy of a system without referring it to some standard system, whose energy we may arbitrarily assume to be zero. For example, the energy of the water in an elevated reservoir is considered with reference to the energy of an equal quantity at some chosen lower level. The kinetic energy of a body moving with a definite velocity is compared with that of a body at rest on the earth's surface, and having, therefore, zero velocity relative to the earth. The energy of a pound of steam is referred to that of a pound of water at the temperature of melting ice.

**3. Mechanical Energy** is that possessed by a body or system due to the motion or position of the body or system relative to some standard of reference. Mechanical kinetic energy is that due to the motion of a body and is measured by the product $\frac{1}{2} mv^2$, where $m$ denotes the mass of the body and $v$ its velocity relative to the reference system. It should be observed that $\frac{1}{2} mv^2$ is a scalar, not a vector, quantity and it must be considered positive in sign. Hence, if a system consists of a number of masses $m_1, m_2, \cdots, m_n$ moving with velocities $v_1, v_2, \cdots, v_n$, respectively, the total kinetic energy of the system is the sum

$$\frac{1}{2} (m_1 v_1^2 + m_2 v_2^2 + \cdots + m_n v_n^2) = \frac{1}{2} \Sigma m v^2,$$

independently of the directions of the several velocities.

The mechanical **potential** energy of a system is that due to

**4. Heat Energy.** — Heat is the name given to an active agent postulated to account for changes in temperature. It is observed that when two bodies are placed in communication, the temperature of the warmer falls, that of the colder rises, and the change continues until the two bodies attain the same temperature. To account for this phenomenon we say that heat flows from the hotter to the colder body. The fall of temperature of one body is due to the loss of heat, while the rise in temperature of the other is due to the heat received by it. It is to be noted that the change of temperature is the thing observed and that the idea of heat is introduced to account for the change, just as in dynamics the idea of force is introduced to account for the observed motion of bodies. Whatever may be the nature of heat, it is evidently something measurable, something possessing the characteristics of quantity.

In the old caloric theory, heat was assumed to be an imponderable, all-pervading fluid which could pass from one body to another and thus cause changes of temperature. The experiments of Rumford (1798), Davy (1812), and Joule (1840) shattered the caloric theory and established the modern mechanical theory, of which the following is a brief outline.

Heat may be generated by the expenditure of mechanical work. Familiar examples are shown in the heating of journals due to friction, the heating of air by compression, the development of heat by impact, etc. Conversely, work may be obtained by the expenditure of heat, as exemplified in the steam engine and other heat motors. Joule's experiments established the fact that a definite relation exists between the heat generated and the work expended; thus to produce a unit of heat a definite amount of work is required, no matter in what particular way the work is done. Heat and mechanical energy are therefore equivalent in a certain sense. Either may be produced at the expense of the other, and the ratio between the quantity of one produced and the quantity of the other expended is always the same. The conclusion is evident that heat is not a sub-

Heat energy, like mechanical energy, may be either of the kinetic or the potential form.  Denoting the mass of a molecule by $m$ and the velocity by $v$, the kinetic energy of the molecule is $\frac{1}{2} mv^2$.  In a given system the different molecules are moving with different velocities and in different directions; nevertheless, the summation

$$\Sigma \, \tfrac{1}{2} \, mv^2$$

extended to all the molecules of the system gives the thermal kinetic energy of the system.  If we denote by $c^2$ the mean square of the velocities of the molecules, we have

$$\Sigma \, \tfrac{1}{2} \, mv^2 = \tfrac{1}{2} Mc^2,$$

where $M$ denotes the mass of the system.  Considerations derived from the kinetic theory of gases show that the temperature of the system is a function of $c^2$; hence, since the kinetic energy is directly proportional to $c^2$, it follows that the temperature of a system is a measure of its thermal kinetic energy. Whenever the temperature of a body rises, we infer that the kinetic energy has increased, and that the mean velocity of the molecules is greater than before.

Potential thermal energy is due to the relative position of the molecules of the system.  The addition of heat to a body usually results in the expansion of the body.  The molecules are moving with higher speeds than before the addition of heat, and on the whole they are farther apart.  To separate them against their mutual attractions requires the expenditure of work; conversely, in coming back to the original configuration the molecules will do work.  Hence, the work expended in separating the molecules is stored in the system as potential energy.

As long as the body remains in the same state of aggregation, the potential energy it is capable of storing is small.  But if a body changes its state of aggregation, it may, during the process, store a large amount of potential energy.  Consider, for example, the melting of ice.  To change a unit weight of ice ...

structure of the solid ice and changing it to that of the liquid water. The heat is therefore stored as potential energy. In the same manner when water is transformed into steam, work is done in forcing apart the molecules against their cohesive forces, and this work is stored as potential energy.

**5. Other Forms of Energy.** — In addition to heat and mechanical energy, there are other forms of energy that require consideration. The energy stored in fuel or in explosives may be considered potential **chemical** energy. **Electrical** energy is exemplified in the electric current and in the electrostatic charge in a condenser. Other forms of energy are due to wave motions either in ordinary fluid media or in the ether. Sound, for example, is a wave motion usually in air. Light and radiant heat are wave motions in the ether.

The **vibratory** forms of energy are neither kinetic nor potential, but rather periodic alternations between the two. To illustrate this statement, let us consider the motion of a pendulum bob. In its lowest position the bob has zero potential energy and maximum kinetic energy ; as it rises its velocity decreases ; therefore, its kinetic energy also decreases, while its potential energy simultaneously increases and reaches a maximum at the end of the swing when the kinetic energy is zero. This same alternation from kinetic to potential and back occurs in vibrating strings, water waves, and, in fact, in all wave motions.

**6. Transformations of Energy.** — Attention has been called to the generation of heat energy by the expenditure of mechanical work. This is only one of a great number of energy changes that are continually occurring. We see everywhere in every-day life one kind of energy disappearing and another form simultaneously appearing. In a power station, for example, the potential energy stored in the coal is liberated and is used up in adding heat energy to the water in the boiler. Part of this heat energy disappears in the engine and its equivalent appears as mechanical work. Finally, this work is expended in driving a generator, and in place of it appears electric energy in the form of the current in the circuit. We say in such cases that

ing are a few familiar examples of energy transformations; many others will occur to the reader.

Mechanical to heat: Compression of gases; friction; impact.

Heat to mechanical: Steam engine; expansion and contraction of bodies.

Mechanical to electrical: Dynamo; electric machine.

Electrical to mechanical: Electric motor.

Heat to electrical: Thermopile.

Electrical to heat: Heating of conductors by current.

Chemical to electrical: Primary or secondary battery.

Electrical to chemical: Electrolysis.

Chemical to thermal: Combustion of fuel.

**7. Conservation of Energy.** — Experience points to a general principle underlying all transformations of energy.

*The total energy of an isolated system remains constant and cannot be increased or diminished by any physical processes whatever.*

In other words, energy, like matter, can be neither created nor destroyed; whenever it apparently disappears it has been transformed into energy of another kind.

This principle of the conservation of energy was first definitely stated by Dr. J. R. Meyer in 1842, and it soon received confirmation from the experiments of Joule on the mechanical equivalent of heat. The conservation law cannot be proved by mathematical methods. Like other general principles in physics, it is founded upon experience and experiment. So far, it has never been contradicted by experiment, and it may be regarded as established as an exact law of nature.

A perpetual motion *of the first class* is one that would supposedly give out energy continually without any corresponding expenditure of energy. That is, it would create energy from nothing. A perpetual-motion engine would, therefore, give out an unlimited amount of work without fuel or other external supply of energy. Evidently such a machine would violate the conservation law; and the statement that perpetual motion of

the first class is impossible is equivalent to the statement of the
conservation principle at the beginning of this article.

**8. Degradation of Energy.** — While one form of energy can
be transformed into any other form, all transformations are not
effected with equal ease. It is only too easy to transform
mechanical work into heat ; in fact, it is one duty of the
engineer to prevent this transformation as far as possible.
Furthermore, of a given amount of work *all* of it can be trans-
formed into heat. The reverse transformation, on the other
hand, is not easy of accomplishment. Heat is not transformed
into work without effort, and of a given quantity of heat only a
part can be thus transformed, the remainder being inevitably
thrown away. All other forms of energy can, like mechanical
energy, be completely converted into heat. Electrical energy,
for example, in the form of a current, can be thus completely
transformed. Comparing mechanical and electrical energy, we
see that they stand on the same footing as regards transforma-
tion. In a perfect apparatus mechanical work can be com-
pletely converted into electrical energy, and, conversely, electric
energy can be completely converted into mechanical work.

We are thus led to a classification of energy on the basis of
the possibility of complete conversion. Energy that is capable
of complete conversion, like mechanical and electrical energy,
we may call **high-grade** energy ; while heat, which is not capable
of complete conversion, we may call **low-grade** energy.

There seems to be in nature a universal tendency for energy
to degenerate into a form less available for transformation.
Heat will flow from a body of higher temperature to one of
lower temperature with the result that a smaller fraction of it
is available for transformation into work. High-grade energy
tends to degenerate into low-grade heat energy. Thus work is
degraded into heat through friction, and electrical energy is
rendered unavailable when transformed into heat in the con-
ducting system. Even when one form of high-grade energy is

substances, the difference being due to the heat developed during the reaction. As Griffiths aptly says: " Each time we alter our investment in energy, we have thus to pay a commission, and the tribute thus exacted can never be wholly recovered by us and must be regarded, *not* as destroyed, but as thrown on the waste-heap of the Universe."

The terms **degradation of energy, dissipation of energy,** and **thermodynamic degeneration** are applied by different writers to this phenomenon that we have just described. We may formally state the principle of degradation of energy as follows:

*Every natural process is accompanied by a certain degradation of energy or thermodynamic degeneration.*

The principle of the degradation of energy denies the possibility of perpetual motion *of the second class*, which may be described as follows : A mechanism with friction is inclosed in a case through which no energy passes. Let the mechanism be started in motion. Because of friction, work is converted into heat, which remains in the system, since no energy passes through the case. Suppose now that the heat thus produced can be transformed completely into work ; then the work may be used again to overcome friction and the heat thus produced can be again transformed into work. We then have a perpetual motion in a mechanism with friction without the addition of energy from an external source. Such a mechanism does not violate the conservation law, since no energy is created. It, however, is just as much of an absurdity as the perpetual motion of the first-class because it violates the principle of degradation.

We shall discuss the degradation principle more at length in a subsequent chapter.

## 9. Units of Energy.

— According to the conservation law, the quantity of energy remains unchanged through all transformations. Hence, a single unit is sufficient for the measurement of energy whatever its form may be. This unit is furnished by the **erg,** the absolute unit of work in the C. G. S. system, or by the **joule,** which is $10^7$ ergs. It would save much confusion

and annoyance if a single unit, as the joule, were used for all forms of energy. Unfortunately, however, the joule is ordinarily used in connection with electrical energy only, and other units are used for other forms of energy. The following are the units generally employed.

For mechanical energy:

1. The **foot-pound** (or in the metric system, the kilogram-meter). This is the unit ordinarily employed by engineers.

2. The **horsepower-hour,** which is equal to 1,980,000 foot-pounds. This unit is most convenient for expressing large quantities of work. It should be noted that although the word " hour " is included in the name, the time element is in reality lacking, and the horsepower-hour is a unit of work, not a unit of power.

For heat energy :

1. The **British thermal unit** (B. t. u.).
2. The **calorie.**

The accurate definition of these thermal units and the means employed in establishing them demand special consideration.

**10. Units of Heat.** — Obviously heat may be measured by observing the effects produced by it upon substances. Two of the most marked effects are : (1) rise of temperature ; (2) change of state of aggregation, as in the melting of ice or vaporization of water. Hence, we have two possible means of establishing a unit of heat:

1. The heat required to raise a given mass of a selected substance, through a chosen range of temperature may be taken as the unit.

2. The quantity of heat required to change the state of aggregation of some substance, as, for example, to melt a given weight of ice, may be taken as the unit.

20° C. *on the same scale.* This thermal unit is called the gram-calorie, or the small calorie. If the weight of water is taken as 1 kilogram, the resulting unit is the kilogram-calorie or large calorie. This is the unit employed by engineers.

The British thermal unit is defined as *the heat required to raise the temperature of* 1 *pound of water from* 63° *to* 64° *F.*

The method of establishing thermal units by the rise of temperature of water is open to one serious objection, namely: The energy required to raise the temperature of water one degree is quite different at different temperatures. Thus the number of joules required to raise a given mass of water from 0° to 1° C. or from 99° to 100° C. is considerably larger than the number of joules required to raise the same mass from 40° to 41° C. The curve, Fig. 1, shows graphically the energy required per degree rise of temperature from 0° to 100° C.
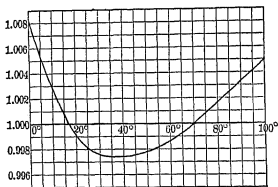


FIG. 1.

It follows that we may have a number of different thermal units depending upon the temperature adopted in the definition. By many physicists the 15°-calorie is used. This is the heat required to raise the temperature of a gram of water from $14\frac{1}{2}$° C. to $15\frac{1}{2}$° C. In recent years there has been a tendency to unite on the so-called **mean calorie**, which may be defined as the $\frac{1}{100}$ part of the heat required to raise a gram of water from 0° C. to 100° C. The $17\frac{1}{2}$°-calorie, as defined by Griffiths, is practically equal to the mean calorie. Corresponding to the mean calorie is the mean B. t. u., which is $\frac{1}{180}$ of the heat required to raise the temperature of one pound of water from 32° to 212° F. This is equal to the B. t. u. at $63\frac{1}{2}$°.

**11. Relations between Energy Units.** — The relation between the joule, the absolute unit of energy, and any of the gravita-

hour, is readily derived when the value of the constant $g$ is given. By international agreement $g$ is taken as

$$980.665 \frac{\text{cm.}}{\text{sec.}^2} = 32.174 \frac{\text{ft.}}{\text{sec.}^2}.$$

The second value is obtained by means of the conversion factor

$$1 \text{ cm.} = 0.3937 \text{ in.}$$

Bearing in mind the definition of the erg, we have

$$1 \text{ kilogram-meter} = 98066500 \text{ ergs}$$
$$= 9.80665 \text{ joules.}$$

Now making use of the relation $1$ kg. $= 2.204622$ lb. and the preceding relation between the units of length, we readily find the relation

$$1 \text{ foot-pound} = 1.3558 \text{ joules,}$$

or      $1$ joule      $= 0.73756$ foot-pound.

The numerical relation between the thermal unit and the joule, that is, the number of joules in one gram-calorie, is called the **mechanical equivalent** and is denoted by $J$. The determination of this constant has engaged the efforts of physicists since 1843.*

In this work two experimental methods have been chiefly employed: (1) The direct method, in which mechanical energy is transformed directly into heat. (2) The indirect method, in which heat is produced by the expenditure of energy in some form other than mechanical. Usually electrical energy is thus transformed.

The earliest experiments were those of Joule (1843), using the direct method. Work was expended in stirring water by means of a revolving paddle. From the rise of temperature of the known weight of water, the heat energy developed could be expressed in thermal units; and a comparison of this quantity with the measured quantity of work supplied gave immediately the desired value of $J$.

Professor Rowland (1878–1879) used the same method, but by driving the paddle wheel with a petroleum engine he was

to the water, and the influence of various corrections was correspondingly decreased. Rowland's results are justly given great weight in deducing the finally accepted value of $J$.

Another result of the highest value is that found by Reynolds and Moorby (1897). The work of a 100 horsepower engine was absorbed by a hydraulic brake. Water entered the brake at or near 0° C. and was run through it at a rate that caused it to emerge at a temperature of about 100° C. In this way the mechanical equivalent of the heat required to raise the temperature of one pound of water from 0° to 100° C. was determined.

Of the experiments by the indirect method those of Griffiths (1893), Schuster and Gannon (1894), and Callendar and Barnes (1899) deserve mention. In each set of experiments the heat developed by an electric current was measured and compared with the electrical energy expended.

From a careful comparison of the results of the most trustworthy experiments, Griffiths has decided that the most probable value of $J$ is 4.184. That is, taking the $17\frac{1}{2}°$ gram-calorie,

$$1 \text{ gram-calorie} = 4.184 \text{ joules.}$$

By the use of the necessary reduction factors, we obtain the following relations:

$$1 \text{ kg.-calorie} = 426.65 \text{ kilogram-meters.}$$
$$1 \text{ B. t. u.} = 777.64 \text{ foot-pounds.}$$

For ordinary calculations, the values 427 and 778, respectively, are sufficiently accurate.

In writing some of the general equations of thermodynamics it is frequently convenient to use the reciprocal of $J$. This is denoted by the symbol $A$; that is, $A \equiv \frac{1}{J}$. We may regard $A$ as the heat equivalent of work; thus

$$1 \text{ ft.-lb.} = A \text{ B. t. u.}$$

When the horsepower-hour is taken as the unit of work, we have

$$A \equiv \frac{1980000}{777.64} = 2546.2.$$

Hence,                    1 h.p.-hr. = 2546.2 B. t. u.,

a relation that is frequently useful.

## EXERCISES

**1.** If the thermal unit is taken as the heat required to raise the temperature of 1 pound of water from 17° to 18° C., what is the value of $J$ in foot-pounds?

**2.** In the combustion of a pound of coal 13,200 B. t. u. are liberated. If $7\frac{1}{2}$ per cent of this heat is transformed into work in an engine, what is the coal consumption per horsepower-hour?

**3.** A gas engine is supplied with 11,200 B. t. u. per horsepower-hour. Find the percentage of the heat supplied that is usefully employed.

**4.** In a steam engine 193 B. t. u. of the heat brought into the cylinder by each pound of steam is transformed into work. Find the steam consumption per horsepower-hour.

**5.** The metric horsepower is defined as 75 kilogram-meters of work per second. Find the equivalent in kilogram-calories of a metric horsepower-hour.

**6.** Find the numerical relations between the following energy units:

> (*a*) Joule and B. t. u.
> (*b*) Joule and metric h.p.-hr.
> (*c*) B. t. u. and kg.-meter
> (*d*) h.p.-minute and B. t. u.

**7.** A unit of power is the watt, which is defined as 1 joule per second. 1 kilowatt (kw.) is 1000 watts. Find the number of B. t. u. in a kw.-hr.; the number of foot-pounds in a watt-hour.

**8.** A Diesel oil engine may under advantageous conditions transform as high as 38 per cent of the heat supplied into work. If the combustion of a pound of oil develops 18,000 B. t. u., what weight of oil is required per h.p.-hr.?

## REFERENCES

### The Mechanical Theory of Heat

Rumford: Phil. Trans., 1798, 1799.

Davy: Complete works **2**, 11.

Black: Lectures on the Elements of Chemistry **1**, 33.

Verdet: Lectures before the Chemical Society of Paris, 1862. (See Röntgen's Thermodynamics, 3, 29.)

## CONSERVATION AND DEGRADATION OF ENERGY

Helmholtz: Über die Erhaltung der Kraft. Berlin, 1847.
Thomson (Lord Kelvin): Edinb. Trans. **20**, 261, 289 (1851); Phil. Mag. (4) **4** (1852).
Griffiths: Thermal Measurement of Energy, Lecture I.
Preston: Theory of Heat, 86, 630.
Planck: Treatise on Thermodynamics (Ogg), 40.

### UNITS OF ENERGY. THE MECHANICAL EQUIVALENT

Rowland: Proc. Amer. Acad. **15**, 75. 1880.
Reynolds and Moorby: Phil. Trans. **190 A**, 301. 1898.
Schuster and Gannon: Phil. Trans. **186 A**, 415. 1895.
Barnes: Phil. Trans. **199 A**, 149. 1902. Proc. Royal Soc. **82 A**, 390. 1910.
Griffiths: Thermal Measurement of Energy.
Chwolson: Lehrbuch der Physik **3**, 414.
Winkelmann: Handbuch der Physik **2**, 537.
Marks and Davis: Steam Tables and Diagrams, 92.

# CHAPTER II

## CHANGE OF STATE. THERMAL CAPACITIES

**12. State of a System.** — A thermodynamic system may be defined as a body or system of bodies capable of receiving and giving out heat or other forms of energy. In general, we shall assume such a system at rest so that it has no appreciable kinetic energy due to velocity. As examples of thermodynamic systems, we may mention the media used in heat motors : water vapor, air, ammonia, etc.

We are frequently concerned with changes of state of systems, for it is by such changes that a system can receive or give out energy. We assume ordinarily that the system is a homogeneous substance of uniform density and temperature throughout ; also that it is subjected to a uniform pressure. Such being the case, the state of the substance is determined by the mass, temperature, density, and external pressure. If we direct our attention to some fixed quantity of the substance, say a unit mass, we may substitute for the density its reciprocal, the volume of the unit mass ; then the three determining quantities are the temperature, volume, and pressure. These physical quantities which serve to describe the state of a substance are called the coördinates of the substance.

In all cases, it is assumed that the pressure is uniform over the surface of the substance in question and is normal to the surface at every point ; in other words, hydrostatic pressure. We may consider this pressure in either of two aspects : it may be viewed as the pressure on the substance exerted by some external agent, or as the pressure exerted by the substance on whatever bounds it. For the purpose of the engineer, the latter view is the most convenient, and we shall always consider the pressure exerted by instead of on the substance. The pressure is always stated as a *specific* pressure, that is, pressure per unit

15

pound per square foot.

The volume of a unit weight of the substance is the *specific volume*. Ordinarily volumes will be expressed in cubic feet and specific volumes in cubic feet per pound. As it is frequently necessary to distinguish between the specific volume and the volume of any given weight of the substance, we shall use $v$ to denote the former and $V$ the latter. Thus, in general, $v$ will denote the volume of one pound of the substance, $V$ the volume of $M$ pounds; hence

$$V = Mv.$$

This convention of small letters for symbols denoting quantities per unit weight and capitals for quantities associated with any other weight $M$ will be followed throughout the book. Thus $q$ will denote the heat applied to one pound of gas and $Q$ the heat applied to $M$ pounds, $u$ the energy of a unit weight of substance, $U$ the energy of $M$ units, etc.

As regards the third coördinate, temperature, we shall accept for the present the scale of the air thermometer. Later the absolute or thermodynamic scale will be introduced. While the centigrade scale presents great advantages, the common use of the Fahrenheit scale in engineering practice compels the adoption of that scale in this book.

**13. Characteristic Equation.** — In general, we may assume the values of any two of the three coördinates $p$, $v$, $T$, and then the value of the third will depend upon values of these two. For example, let the system be one pound of air inclosed in a cylinder with a movable piston. By loading the piston we may keep the pressure at any desired value; then by the addition of heat we may raise the temperature to any predetermined value. Thus we may fix $p$ and $T$ independently. We cannot, however, at the same time give the volume $v$ any value we please; the volume will be uniquely determined by the assumed values of $p$ and $T$, or in other words, $v$ is a function of the independent variables $p$ and $T$. In a similar manner we may take $p$ and $v$ as independent variables, in which case $T$ will be the function, or we take $v$ and $T$ as independent and $p$ as the function depending on them.

$$\varphi\ (p,\ v,\ T) = 0, \tag{1}$$

or written in the explicit form

$$p = f\ (v,\ T). \tag{2}$$

The equation giving this relation is called the **characteristic equation** of the substance. The form of the equation must be determined by experiment.

For some substances more than one equation is required; thus for a mixture of saturated vapor and the liquid from which it is formed, the pressure is a function of the temperature alone, while the volume depends upon the temperature and a fourth variable expressing the relative proportions of vapor and liquid.

**14. Equation of a Perfect Gas.** — Experiments on the so-called permanent gases have given us the laws of Charles and Boyle. Assuming these to be followed strictly, we may readily derive the characteristic equation of a gas as follows.

According to the law of Charles, the increase of pressure when the gas is heated at constant volume is proportional to the increase of temperature; that is,



FIG. 2.

$$p - p_0 = k\ (t - t_0). \tag{1}$$

This equation defines, in fact, the scale of the constant volume gas thermometer. Charles' law is shown graphically in Fig. 2. Point $A$ represents the initial condition $(p_0, t_0)$, point $B$ the final condition $(p, t)$. Then

$$CB = p - p_0,\ AC = t - t_0,\ \text{and}\ \frac{CB}{AC} = \frac{p - p_0}{t - t_0} = k.$$

According to Charles' law, therefore, the points representing the successive values of $p$ and $t$, with $v$ constant, lie on a straight line through the initial point $A$, and the slope of this line is the

c
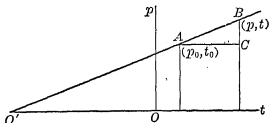
constant $k$. Evidently $k$ is independent of $p$ and $t$, but it may depend upon $v$; hence we may write

$$k = f(v).$$

Substituting this value of $k$ in (1), we get

$$p - p_0 = (t - t_0) f(v).$$

In this equation $t$ and $t_0$ are temperatures measured from the Fahrenheit zero; that is, from the origin $O$ (Fig. 2). Evidently the difference $t - t_0$ is independent of the position of the assumed zero; hence we may write

$$p - p_0 = (T - T_0) f(v), \tag{2}$$

where $T$ and $T_0$ denote temperatures measured from some new zero, assumed at pleasure. Let us choose this new zero such that $T = 0$ when $p = 0$. This is evidently equivalent to the selection of a new origin $O'$ (Fig. 2) at the intersection of the line $AB$ with the $t$-axis. If we now take the initial point $A$ at $O'$, we have $p_0 = 0$, $T_0 = 0$, and (2) takes the form

$$p = T f(v),$$

whence

$$pv = T v f(v). \tag{3}$$

By hypothesis, the substance follows Boyle's law; that is, the product $pv$ is constant when the temperature $T$ is constant. From (3), therefore, the factor $v f(v)$ is a constant; and denoting this constant by $B$ we have

$$pv = BT, \tag{4}$$

which is the characteristic equation desired.

The name **perfect gas** is applied to a hypothetical ideal gas which strictly obeys Boyle's law, and the internal energy of which is all of the kinetic form, and, therefore, dependent on the temperature only. No actual gas precisely fulfills these conditions; but at ordinary temperatures, air, nitrogen, hydrogen, and oxygen so nearly meet the requirements that they may be considered approximately perfect.

**15. Absolute Temperature.** — The zero of temperature defined in the preceding article is called the **absolute zero**, and temperatures measured from it are called **absolute temperatures**. The

molecules on the containing walls.  When this pressure is zero, we infer that molecular motion of translation has entirely ceased, and this is, therefore, the condition at absolute zero.

The position of the absolute zero relative to the centigrade zero may be determined approximately by experiments on a nearly perfect gas, such as air.  From Eq. (4), Art. 14, we have, assuming that the volume remains constant,

$$p_1 v = B T_1,$$
$$p_2 v = B T_2,$$

whence

$$\frac{p_2}{p_1} = \frac{T_2}{T_1}, \tag{1}$$

and

$$\frac{p_2 - p_1}{p_1} = \frac{T_2 - T_1}{T_1}. \tag{2}$$

Let us take $T_1$ as the temperature of melting ice, $T_2$ that of boiling water at atmospheric pressure.  Regnault's experiments on the increase of pressure of air when heated at constant volume gave the relation

$$\frac{p_2 \text{ (at } 100° \text{ C.)}}{p_1 \text{ (at } 0° \text{ C.)}} = 1.3665. \tag{3}$$

Since for the C. scale

$$T_2 - T_1 = 100,$$

we have

$$\frac{0.3665 \, p_1}{p_1} = \frac{100}{T_1}, \tag{4}$$

whence

$$T_1 = \frac{100}{0.3665} = 272.85. \tag{5}$$

That is, using air as the thermometric substance, the absolute zero is 272.85° C. below the temperature of melting ice.  Other approximately perfect gases, as nitrogen, hydrogen, etc., give slightly different values for $T_1$.  The experiments of Joule and Thomson indicate that for an ideal perfect gas, one strictly obeying the law expressed by the equation $pv = BT$, the value of $T_1$ would be between 273.1 and 273.14.  The corresponding value on the Fahrenheit scale may be taken as 491.6;

denote ordinary temperatures by $t$ and absolute temperatures
by $T$, we have

$$T = t + 273.1, \text{ for the C. scale.}$$
$$T = t + 459.6, \text{ for the F. scale.}$$

**16. Other Characteristic Equations.** — The equation $pv = BT$
gives a close approximation to the changes of state of the more
permanent gases. Other gases, as, for example, carbonic acid,
which are in reality only slightly superheated vapors, show
marked deviations from the behavior of the ideally perfect gas,
and this equation does not give even a rough approximation to
the actual facts.

On the basis of the kinetic theory of gases, van der Waals
has deduced a general characteristic equation applicable not
only to the gaseous but to the liquid state as well. It has the
following form:

$$p = \frac{BT}{v - b} - \frac{a}{v^2}, \tag{1}$$

in which $B$, $a$, and $b$ are constants which depend upon the
nature of the substance.

An empirical equation for superheated steam is

$$p(v + c) = BT - p(1 + ap)\frac{m}{T^n}. \tag{2}$$

It will be observed that for large values of $T$ and $v$, that is,
when the gas is extremely rarified, the last term of both equa-
tions becomes small and
the resulting equation ap-
proaches more nearly the
equation of the perfect gas.
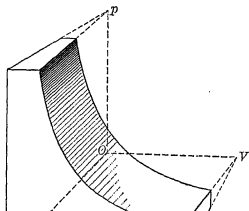
**17. Characteristic Sur-
faces.** — The characteristic
equation

$$\phi(p, v, T) = 0,$$

by its coördinates $p_1$, $v_1$, $T_1$, and this state is therefore represented by a point, on the surface. If the state changes, a second point with coördinates $p_2$, $v_2$, $T_2$, will represent the new state. The succession of states between the initial and final states will be represented by a succession of points on the surface. The point representing the state we will call the **state-point**. Hence, for any change of state there will be a corresponding movement of the state-point.

The surface representing the equation

$$pv = BT$$

is shown in Fig. 3. For other characteristic equations the surfaces are of a less simple form.

**18. Thermal Lines.**— If we impose the restriction that during a change of state the temperature of the substance shall remain constant, the state-point will evidently move on the characteristic surface parallel to the $pv$-plane. Such a change of state is called **isothermal**, and the curve described by the state-point is an isothermal curve or, briefly, an **isotherm**. By taking different constant values for the temperature, we get a complete representation of the characteristic equation. For the perfect gas, the isotherms consist of a system of equilateral hyperbolas having the general equation

$$pv = \text{const.} \tag{1}$$

The restriction may be imposed that the pressure of the substance shall remain constant during the change of state. The state-point will in this case move parallel to the $vT$-plane, and the projection of the path on the $pv$-plane will be a straight line parallel to $OV$, as $AB$ (Fig. 4). The relation between volume and temperature is found by combining the equation

Substituting this value of $p$ in the characteristic equation, we have

$$v = \frac{B}{C} T. \qquad (2)$$

If the substance changes its state at constant volume, the state-point moves parallel to the $pT$-plane, and the projection of the path on the $pv$-plane is a line parallel to the $p$-axis, as $CD$ (Fig. 4). In the case of a perfect gas, the relation between $p$ and $T$ for a change at constant volume is

$$p = \frac{B}{C} T = kT. \qquad (3)$$

Lines of constant pressure are called isopiestic lines; lines of constant volume, isometric lines.

Besides the cases just given, others are of frequent occurrence, and will be taken up in detail later. Thus we may have changes of state in which the energy of the system remains constant; such changes are called isodynamic. We may also have changes in which the system neither receives nor gives out heat; such are called adiabatic.

**19. Heat absorbed during a Change of State.** — A change of state of a system is generally accompanied by the absorption of heat from external sources. If we denote by $q$ heat thus absorbed per unit weight, we may by giving $q$ proper signs cover all possible cases; thus $+ q$ indicates heat absorbed, $- q$ heat rejected; while if $q = 0$, we have the limiting adiabatic change of state.
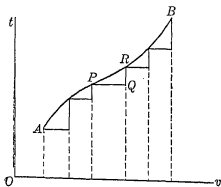


FIG. 5.

The heat absorbed may be determined from the changes in two of the three variables $p$, $v$, $t$ that define the state of the system. As we have seen, any pair may be selected as suits our convenience. For example, let $t$ and $v$ be taken as the independent variables, and let the curve $AB$ (Fig. 5) represent

this curve to be replaced by the broken line $PQR$, then the segment $PQ$ represents an increment of volume $\Delta v$ with $t$ constant and the segment $QR$ an increment of temperature $\Delta t$ with $v$ constant.  The *rate* of absorption of heat along $PQ$, that is, the heat absorbed per unit increase of volume, is given by the derivative $\left(\frac{\partial q}{\partial v}\right)_t$, the subscript $t$ indicating that $t$ is held constant during the process.  If the rate of absorption be multiplied by the change of volume $v$, the product $\left(\frac{\partial q}{\partial v}\right)_t \Delta v$ is evidently the heat absorbed during the change of state represented by $PQ$.  Similarly, the rate of absorption along $QR$ is $\left(\frac{\partial q}{\partial t}\right)_v$, and the heat absorbed is the product $\left(\frac{\partial q}{\partial t}\right)_v \Delta t$.  The heat absorbed during the change $PQR$ is, therefore,

$$\Delta q = \left(\frac{\partial q}{\partial v}\right)_t \Delta v + \left(\frac{\partial q}{\partial t}\right)_v \Delta t, \tag{1}$$

and the total heat absorbed along the broken path from $A$ to $B$ is given by the summation

$$\sum_{v_1, t_1}^{v_2, t_2} \left[ \left(\frac{\partial q}{\partial v}\right)_t \Delta v + \left(\frac{\partial q}{\partial t}\right)_v \Delta t \right]. \tag{2}$$

By taking the elements into which the curve is divided smaller and smaller, the broken path may be made to approach the actual path between $A$ and $B$.  Therefore, passing to the limit, we have instead of (1)

$$dq = \left(\frac{\partial q}{\partial v}\right)_t dv + \left(\frac{\partial q}{\partial t}\right)_v dt, \tag{3}$$

and for the heat absorbed during the change of state from $A$ to $B$

$$q = \int_{v_1, t_1}^{v_2, t_2} \left[ \left(\frac{\partial q}{\partial v}\right)_t dv + \left(\frac{\partial q}{\partial t}\right)_v dt \right]. \tag{4}$$

By choosing other pairs of variables as independent, other equations similar to (3) may be obtained.  Thus, taking $t$ and

or taking $p$ and $v$ as the independent variables, we have

$$dq = \left(\frac{\partial q}{\partial p}\right)_v dp + \left(\frac{\partial q}{\partial v}\right)_p dv. \qquad (6)$$

From (5) and (6) equations corresponding to (4) may be readily derived.

**20. Thermal Capacity. Specific Heat.** — Of the partial derivatives introduced in the preceding article, two are of special importance, namely, $\left(\frac{\partial q}{\partial t}\right)_v$ and $\left(\frac{\partial q}{\partial t}\right)_p$. In general, the heat required to raise the temperature of a body one degree under given external conditions is called the **thermal capacity** of the body for these conditions. Hence, if $Q$ denotes the heat absorbed by a body during a rise of temperature from $t_1$ to $t_2$, the quotient $\dfrac{Q}{t_2 - t_1}$ gives the mean thermal capacity of the body ; and the quotient $\dfrac{Q}{M(t_2 - t_1)} = \dfrac{q}{t_2 - t_1}$, the mean thermal capacity of a unit weight. If the thermal capacity varies with the temperature, then the limiting value of the quotient $\dfrac{q}{t_2 - t_1}$, that is, the derivative $\dfrac{dq}{dt}$, gives the instantaneous value of the thermal capacity. Accordingly, we recognize in the derivative $\left(\frac{\partial q}{\partial t}\right)_v$ the thermal capacity per unit weight of the body under the condition that the volume remains constant; and in the derivative $\left(\frac{\partial q}{\partial t}\right)_p$ the thermal capacity with the pressure constant.

According to the definition of the thermal units (Art. 10), the thermal capacity of 1 gram of water at 17.5° C. is 1 calorie, and that of one pound of water at 63.5° F. is 1 B. t. u.

The **specific heat** of a substance at a given temperature $t$ is the ratio of the thermal capacity of the substance at this temperature to the thermal capacity of an equal mass of water at some chosen standard temperature. If we take 17.5° C.

mal capacity per unit weight, then the specific heat $c$ is given
by the relation

$$c = \frac{\gamma_t (\text{of subtance})}{\gamma_{17\cdot5} (\text{of water})}.$$

But for water $\gamma_{17\cdot5} = 1$ cal.  It follows that the specific heat at
the temperature $t$ is numerically equal to the thermal capacity
of unit weight at the same temperature; thus at 100° C. the
thermal capacity of a gram of water is found to be 1.005 cal.,
and the specific heat is $\dfrac{\gamma_{100}}{\gamma_{17\cdot5}} = \dfrac{1.005 \text{ cal.}}{1 \text{ cal.}} = 1.005$.   On account
of this numerical equality, we may consider that the derivative
$\dfrac{dq}{dt}$ represents the specific heat, as well as the thermal capacity.
It is to be noted, however, that a specific heat is merely a ratio,
an abstract number, and it is determined by a comparison of
quantities of heat.  The deter-
mination of thermal capacity,
on the other hand, involves
energy measurements.

The specific heat of a sub-
stance may be represented geo-
metrically, as shown in Fig. 6.
Starting from some initial state,
let the rise of temperature be



Fig. 6.

taken as abscissa and the heat added to the substance as
ordinate.  The resulting curve $OM$ will represent the equation

$$q = f(t),$$

and the slope of the curve at any point, as $P$, will give the de-
rivative $\dfrac{dq}{dt}$, or the specific heat at the temperature correspond-
ing to $P$.  With constant specific heat the curve $OM$ is a
straight line; if the specific heat increases with the tempera-
ture, the curve is convex to the $t$-axis.

The heat applied to a substance, as will be shown presently,
may have other effects than raising the temperature.  The
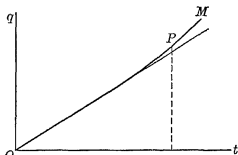
temperature; hence, the value of the specific heat will depend upon the conditions under which the heat is absorbed. If the substance is in the solid or in the liquid form, the specific heats are practically equal. For substances in the gaseous form, however, the specific heat may have any value from $-\infty$ to $+\infty$, depending upon the external conditions under which the heat is supplied.

**21. Latent Heat.** — If the heat added to a substance and the temperature be plotted as in Fig. 6, it may happen that at certain temperatures the curve has discontinuities. For example,
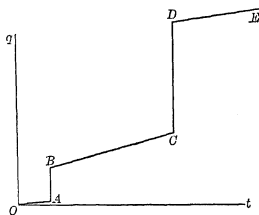


FIG. 7.

let heat be applied to ice at 0° F. The curve is practically a straight line until the temperature 32° is reached, but at this point considerable heat is added without any change in temperature. During this addition of heat, represented by the vertical segment $AB$ (Fig. 7), the state of aggregation changes from solid to liquid. As the water receives heat its temperature rises, as indicated by $BC$, until the temperature 212° F. is reached (assuming atmospheric pressure), where the temperature again remains constant during the addition of a considerable quantity of heat, and the state of aggregation again changes, this time from the liquid to the gaseous. The heat that is thus added to (or abstracted from) a substance during a change of state of aggregation is called latent heat. As pointed out in Art. 4, substantially all of the latent heat is stored in the system in the form of potential energy.

The specific heat $\dfrac{dq}{dt}$ becomes infinite during the changes indicated by $AB$ and $CD$, since $t =$ constant. The volume of the substance changes, however, and the rate at which heat is

is a thermal capacity called the **latent heat of expansion** and denoted by $l_v$. If the pressure also changes, we have in the derivative $\left(\dfrac{\partial q}{\partial p}\right)_t$ the heat added per unit change of pressure. This thermal capacity is called the **latent heat of pressure variation**, and is denoted by $l_p$.

**22. Relations between Thermal Capacities.** — Introducing the symbols $c_v$, $c_p$, $l_v$, and $l_p$ in equations (3) and (5) of Art. 19, we have

$$dq = l_v dv + c_v dT, \tag{1}$$

$$dq = l_p dp + c_p dT. \tag{2}$$

By means of the characteristic equation of the substance, namely,

$$v = f(T, p), \tag{3}$$

various relations between the thermal capacities may be derived. Some of the most useful are the following.

From (3) we obtain by differentiation,

$$dv = \frac{\partial v}{\partial T} dT + \frac{\partial v}{\partial p} dp, \tag{4}$$

which substituted in (1) gives

$$dq = l_v \frac{\partial v}{\partial p} dp + \left(c_v + l_v \frac{\partial v}{\partial T}\right) dT. \tag{5}$$

Comparing (2) and (5), we have

$$l_p = l_v \frac{\partial v}{\partial p}, \tag{6}$$

$$c_p - c_v = l_v \frac{\partial v}{\partial T}. \tag{7}$$

In the same way, substituting

$$dp = \frac{\partial p}{\partial T} dT + \frac{\partial p}{\partial v} dv$$

in (2), and comparing the resulting equation with (1), we obtain

$$l_v = l_p \frac{\partial p}{\partial v}, \tag{8}$$

ing thermal capacities when any one is given by direct experiment, provided the characteristic equation of the substance is known, so that the derivatives $\frac{\partial v}{\partial T}$, $\frac{\partial p}{\partial T}$ etc., can be determined.

For a perfect gas, as an example, $c_p$ is known from experiment and the ratio $\frac{c_p}{c_v}$ has also been determined. From the equation of the gas $pv = BT$, we have the partial derivatives

$$\frac{\partial v}{\partial T} = \frac{B}{p}, \quad \frac{\partial p}{\partial T} = \frac{B}{v};$$

hence from (7) and (9)

$$c_p - c_v = l_v \frac{B}{p}, \text{ or } l_v = \frac{p}{B}(c_p - c_v), \qquad (10)$$

and

$$l_p = -\frac{v}{B}(c_p - c_v). \qquad (11)$$

23. **Interpretation of Differential Expressions.** — In thermodynamics we frequently meet with expressions of the form

$$M dx + N dy$$

composed of two terms, of which each is the differential of a variable multiplied by a coefficient. The two coefficients may be constants or functions of the two variables involved. The proper interpretation of differentials of this form is likely to present difficulties to the student; we shall, therefore, devote this article to a discussion of such expressions, their properties, and their physical interpretations.

Let us consider first how such differential expressions may arise. Suppose we have given the characteristic equation of a substance in the form

$$p = f(v, t); \qquad (1)$$

by differentiation according to the well-known methods of calculus, we obtain the relation

$$dp = \frac{\partial p}{\partial v} dv + \frac{\partial p}{\partial t} dt, \qquad (2)$$

$$dp = Mdv + Ndt, \qquad (3)$$

where $M = \dfrac{\partial p}{\partial v}$, and $N = \dfrac{\partial p}{\partial t}$.

In Art. 19 we derived an equation of similar form, namely,

$$dq = \frac{\partial q}{\partial v}dv + \frac{\partial q}{\partial t}dt, \qquad (4)$$

which may likewise be written in the form

$$dq = M'dv + N'dt. \qquad (5)$$

The second members of (3) and (5) are differential expressions of the form $Mdx + Ndy$, which we have under consideration. Eq. (3) was produced from a known functional relation between $p$, $v$, and $t$, while Eq. (5) was derived directly from physical considerations by assuming increments $\Delta v$ and $\Delta t$ of the independent variables and deducing from them the quantity of heat $\Delta q$ that must necessarily be absorbed. No relation between $q$, $v$, and $t$ was given or assumed; in fact, it is known that no such relation exists; that is, $q$ cannot be expressed as a function of the variables $v$ and $t$.

Let us see what is implied by the existence or non-existence of a functional relation between $q$, $v$, and $t$. Referring to Fig. 5, let $A$ and $B$ denote the initial and final states of the system. Since $p$ is a function of $v$ and $t$ $[p = f(v, t)]$, the pressures at $A$ and $B$ are determined by the values of $T$ and $v$ at those points; thus for a perfect gas, $p_1 = \dfrac{BT_1}{v_1}$ and $p_2 = \dfrac{BT_2}{v_2}$. Hence, the change of pressure $p_2 - p_1$ in passing from $A$ to $B$ is fixed by the points $A$ and $B$ alone and is independent of the path between them. Similarly, if there is a functional relation between $q$, $v$, and $t$, that is, if $q = \phi(v, t)$, we shall have at $A$, $q_1 = \phi(v_1, t_1)$, at $B$, $q_2 = \phi(v_2, t_2)$. Therefore, the heat absorbed in passing from $A$ to $B$ will be

$$q_2 - q_1 = \phi(v_2, t_2) - \phi(v_1, t_1), \qquad (6)$$

and this will be determined by the points $A$ and $B$ alone. On the other hand, if the heat absorbed by the system depends upon the path between $A$ and $B$, there can be no relation

$q = \phi(v, t)$.    As a matter of fact, the heat absorbed is different for different paths between the same initial and final states; hence it is not possible to express $q$ in terms of $v$ and $t$.

The conclusions just given may be stated in general terms as follows.   Given an expression of the form

$$du = Mdx + Ndy, \qquad (7)$$

where the coefficients $M$ and $N$ are functions of $x$ and $y$, there may or may not exist a functional relation between $u$ and the variables $x$ and $y$. If $u$ is a function of $x$ and $y$, say $u = F(x, y)$, then the change in $u$ depends only on the initial and final values of $x$ and $y$ and is independent of the path.   This change is found from (7) by integration; thus

$$u_2 - u_1 = \int_{u_1}^{u_2} du = \int_{x_1, y_1}^{x_2, y_2} (Mdx + Ndy). \qquad (8)$$

In this integration no relation between $x$ and $y$ is required, for since $Mdx + Ndy$ arises from differentiating the function $\phi(x, y)$, the integral must be $\phi(x, y)$.   In this case $Mdx + Ndy$ is said to be an **exact differential**.

As an example, consider the equation

$$du = ydx + xdy.$$

Since $ydx + xdy$ is produced by the differentiation of the product $xy$, we have the relation

$$u = xy + C,$$

whence       $u_2 - u_1 = x_2 y_2 - x_1 y_1$.

The change of $u$ is represented by the shaded area (Fig. 8), and is evidently not dependent upon the path between the points $(x_1, y_1)$ and $(x_2, y_2)$.
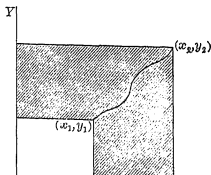
If, however, no functional relation exists between $u$ and the variables $x$ and $y$, then $Mdx + Ndy$ is said to be an **inexact differential**.   In this case a value

sumed; in other words, the value of $u$ depends upon the path between the initial and final points.   For example, let

$$du = y\,dx - 2\,x\,dy$$

and let the initial and final points be respectively $(0, 1)$ and $(2, 2)$.   No function of $x$ and $y$ can be found which upon differentiation will produce this differential.   If we choose as the path between the end points the straight line $y = \frac{1}{2}x + 1$, we have (since $dy = \frac{1}{2}dx$),

$$u = \int_0^2 \left[ (\tfrac{1}{2}x + 1)dx - x\,dx \right] = 1.$$

If we take as the path the parabola $y = \frac{1}{4}x^2 + 1$, we have

$$u = \int_0^2 \left[ (\tfrac{1}{4}x^2 + 1)dx - x^2 dx \right] = 0.$$

The dependence of the value of $u$ upon the path assumed is evident.

The test for an exact differential is simple.   If the differential $du = M\,dx + N\,dy$ is exact, then $u$ must be a function of $x$ and $y$, say $f(x, y)$.   By differentiation, we have

$$du = \frac{\partial u}{\partial x}\,dx + \frac{\partial u}{\partial y}\,dy.$$

Hence $M$ and $N$ must be, respectively, the partial derivatives $\frac{\partial u}{\partial x}$ and $\frac{\partial u}{\partial y}$.   By a well-known theorem of calculus, we have

$$\frac{\partial}{\partial y}\left( \frac{\partial u}{\partial x} \right) = \frac{\partial}{\partial x}\left( \frac{\partial u}{\partial y} \right);$$

that is,

$$\frac{\partial M}{\partial y} = \frac{\partial N}{\partial x}. \qquad (9)$$

If relation (9) is satisfied, the differential is exact; otherwise, it is inexact.

As an example, we have from the differential $y\,dx - 2\,x\,dy$, $\frac{\partial M}{\partial y} = 1$, $\frac{\partial N}{\partial x} = -2$; therefore, the differential is inexact, as was shown in the preceding discussion.

In thermodynamics we meet with certain functions that depend only upon the coördinates $p$, $v$, $T$ of the substance under consideration.   From purely physical considerations the energy

(See Art. 26.) Hence if $u$ is expressed in terms of two of these coördinates as independent variables, thus,

$$du = Mdv + NdT,$$

we know at once that $du$ is exact and we can write

$$\int_1^2 du = u_2 - u_1 = f(v_2, T_2) - f(v_1, T_1).$$

Furthermore, from the test for an exact differential we must have the relation

$$\frac{\partial M}{\partial T} = \frac{\partial N}{\partial v}.$$

By making use of this test when the differential is known to be exact, many useful relations are deduced.

We have also magnitudes that depend upon the coördinates and also upon the method of variation; that is, upon the path. The heat $q$ absorbed by a system in changing state is one of these. If again we choose $v$ and $T$ as the independent variables, we may write

$$dq = M'dv + N'dT;$$

but since $dq$ is not exact, we cannot write

$$\int_1^2 dq = q_2 - q_1.$$

<center>EXERCISES</center>

**1.** Regnault's experiments on the heating of certain liquids are expressed by the following equations:

Ether         $q = 0.529\, t + 0.000296\, t^2,$   $-20°$ to $+30°$ C.
Chloroform    $q = 0.232\, t + 0.0000507\, t^2,$   $-30°$ to $+60°$ C.
Carbon disulphide $q = 0.235\, t + 0.0000815\, t^2,$   $-30°$ to $+40°$ C.
Alcohol       $q = 0.5476\, t + 0.001122\, t^2 + 0.00000022\, t^3,$   $-23°$ to $+66°$ C.

From these equations derive expressions for the specific heat, and for each liquid find the specific heat at 20° C.

**2.** From the data of Ex. 1, find the mean heat capacity of ether between 0° and 30° C. Also the mean heat capacity of alcohol between 0° and 50° C.

**3.** If the thermal capacity of a substance at temperature $t$ is given by the relation

$$\gamma = a + bt + ct^2,$$

**4.** In the investigation of the properties of gases, it is convenient to draw the isothermals ($T = $ const.) on a plane having the pressure $p$ as the axis of abscissas and the product $pv$ as the axis of ordinates. Show that the isothermals of a perfect gas are straight lines parallel to the $p$-axis.

**5.** Show on the $pv$-$p$ plane the general form of an isothermal of superheated steam, the characteristic equation being

$$p(v + c) = BT - p(1 + ap) \frac{m}{T^n}.$$

As an approximate equation for superheated steam, the form

$$p(v + c) = BT,$$

has been suggested by Tumlirtz. Show the form of the isothermal when this equation is used.

**6.** Derive relations between $c_p$, $c_v$, $l_p$, and $l_v$, similar to those given by Eq. (10) and (11) of Art. 22, using van der Waal's equation

$$p = \frac{BT}{v - b} - \frac{a}{v^2}$$

as the characteristic equation of the gas.

**7.** For a perfect gas, as will be shown subsequently, the thermal capacity $l_v$ is $Ap (A = \frac{1}{J})$. Show that $c_p - c_v = AB$; also that $l_p = -Av$.

**8.** Test the following differentials for exactness:

  (a) $v dp + np dv$.

  (b) $v^n dp + np v^{n-1} dv$.

  (c) $np(n + 1)\left(1 + \frac{a}{2}p\right)\dfrac{dT}{T^{n+1}} - \dfrac{(n+1)}{T^n}(1 + ap) dp$.

**9.** Find the function $u = f(p, T)$ which produces the differential (c) of Ex. 8.

**10.** The differential $[c'(1 - x) + c''x]\dfrac{dT}{T} + \dfrac{r}{T} dx$, which appears in the discussion of vapors, is known to be exact. $c'$ and $c''$ may be taken as constants, while $r$ is a function of $T$. Apply the test for exactness and thereby deduce the relation
$$c'' - c' = \frac{dr}{dT} - \frac{r}{T}.$$

**11.** For perfect gases, $dq = c_v dT + Ap dv$. (See Ex. 7, and Art. 22.) Making use of the characteristic equation $pv = BT$, show that while $dq$ is not an exact differential, $\dfrac{dq}{T}$ is an exact differential.

## REFERENCES

THERMAL CAPACITY. SPECIFIC HEAT

Weyrauch: Grundriss der Wärme-Theorie 1, 60.
Chwolson: Lehrbuch der Physik 3, 172.


### EXACT AND INEXACT DIFFERENTIALS IN THERMODYNAMICS

Chwolson: Lehrbuch der Physik 3, 434.
Clausius: Mechanical Theory of Heat, Introduction.
Preston: Theory of Heat, 597.
Weyrauch: Grundriss der Wärme-Theorie 1, 28.
Townsend and Goodenough: Essentials of Calculus, 245.

# CHAPTER III

## THE FIRST LAW OF THERMODYNAMICS

**24. Statement of the First Law.** — The first law of Thermo-dynamics relates to the conversion of heat into work, and merely applies the principle of conservation of energy to that process. It may be formally stated as follows : *When work is expended in producing heat, the quantity of heat generated is proportional to the work done, and conversely, when heat is employed to do work, a quantity of heat precisely equivalent to the work done disappears.*

If we denote by $Q$ the heat converted into work and by $W$ the work thus obtained, we have, therefore, as symbolic statements of the first law,

$$W = JQ, \text{ or } Q = AW.$$

**25. Effects of Heat.** — When a thermodynamic system, as a given weight of gas or a mixture of saturated vapor and liquid, undergoes a change of state, it in general receives or gives out energy either in the form of heat or in the form of mechanical work. These energy changes must, of course, conform to the conservation law. Suppose in the first place that the system is subjected to a uniform external pressure and that during the change of state the volume is decreased. Mechanical work is thereby done upon the system, or in other words, the system receives energy in the form of work. At the same time heat may be absorbed by the system from some external source. Denoting by $\Delta W$ the work received and by $\Delta Q$ the heat absorbed, the increment $\Delta U$ of the intrinsic energy of the system is given by the relation

$$\Delta U = J \Delta Q + \Delta W. \tag{1}$$

Ordinarily we take the work done by the system in expanding as positive ; hence the work done *on* the system during com-

that is, the increase of energy of the system is equal to the energy received in the form of heat less the energy given to the surrounding systems in the form of work. We may also write (2) in the form

$$J \Delta Q = \Delta U + \Delta W, \qquad (3)$$

and interpret the relation as follows. The heat absorbed by a substance is expended in two ways: (1) in increasing the intrinsic energy of the substance; (2) in the performance of external work.

Equation (3) is the **energy equation** in its most general form. Any one of the three terms may be positive or negative. We consider $\Delta Q$ positive when the system absorbs heat, negative when it gives out heat; as before stated, $\Delta W$ is positive when work is done *by* the system, negative when work is done *on* the system; $\Delta U$ is positive when the internal energy is increased, negative when the energy is decreased during the change of state.

**26. The Intrinsic Energy.** — The increase $\Delta U$ of the intrinsic energy is, in general, separable into two parts: (1) The increase of kinetic energy indicated by a rise of temperature of the system. As we have seen, this is due to an increase in the velocity of the molecules of the system. (2) The increase of potential energy arising from the increase of volume of the system. To separate the molecules against their mutual attractions, or to break up the molecular structure, as is done in changing the state of aggregation, requires work, and this work is stored in the system as potential energy.

The energy $U$ contained in a body depends upon the state of the body only, and the change of energy due to a change of state depends upon the initial and final states only. In Fig. 9, let $A$ represent the initial, and $B$ the final state. The point $B$ indicates a definite state of the body as regards pressure, volume, and temperature. Now the temperature indicated by $B$ fixes the kinetic energy and the volume at $B$ determines the potential energy. Hence the final total energy

to $B$. Whether we pass by the
path $m$ or the path $n$, we have the
same volume and temperature at $B$
and therefore the same total energy.
Since $U$ is thus a function of the
coördinates only, it follows that $dU$
is always an exact differential.

Fig. 9.

Choosing $T$ and $v$ as the inde-
pendent variables of the system,
we may express $U$ as a function of these variables. We have,
therefore,                    $$U = f(T, v),$$

whence                    $$dU = \frac{\partial U}{\partial T} dT + \frac{\partial U}{\partial v} dv.$$

The term $\frac{\partial U}{\partial T} dT$ is the increment of energy due to the in-

crease of temperature $dT$. The factor $\frac{\partial U}{\partial T}$ is the rate at which

the energy changes with the temperature when the volume

remains constant. Hence $\frac{\partial U}{\partial T} dT$ is the change of energy due

merely to the rise of temperature, that is, it is the change

of kinetic energy. The term $\frac{\partial U}{\partial v} dv$ is the change of energy

due merely to the change of volume with the temperature
constant; it is, therefore, the work done against molecular
attractions, the work that is stored as potential energy. For
a substance in which there are no internal forces between
the molecules, the energy is independent of the volume, that

is, $\frac{\partial U}{\partial v} = 0$, and therefore the term $\frac{\partial U}{\partial v} dv$ is zero.
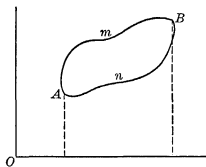
## 27. The External Work. — In nearly all cases dealt with in
applied thermodynamics, the external work $\Delta W$ is the work
done by the system in expanding against a uniform normal
pressure. A general expression for the external work may
be deduced as follows. Let $\Delta F$ denote an elementary area
on the surface inclosing the system and suppose that during

normal pressure per unit area, the work done against this pressure is for this one element

$$p \, \Delta F \cdot s. \qquad (1)$$

When all the elements of the surface are taken, the expression for the work is

$$\Delta W = p \Sigma s \, \Delta F. \qquad (2)$$

But evidently if $s$ be taken sufficiently small, $\Sigma s \, \Delta F$ is the increase of volume $\Delta V$; hence we may write

$$\Delta W = p \, \Delta V, \qquad (3)$$

from which we have

$$W = \sum p \, \Delta V = \int_{V_1}^{V_2} p \, dV \qquad (4)$$

for a change of volume from $V_1$ to $V_2$.

The external work for a given change of state is represented graphically by the area between the projection of the path of the state-point on the $pV$-plane and the $V$-axis. Thus in Fig. 10, let the variation of pressure and volume be represented by the curve $AB$; this is the projection on the $pV$-plane of the actual path of the state-point on the characteristic surface. The area $A_1ABB_1$ under $AB$ is clearly given by the integral

$$L \sum_{1}^{2} p \, \Delta V = \int_{V_1}^{V_2} p \, dV;$$

hence, it represents the work done by the system in passing from the initial to the final state according to the given law.
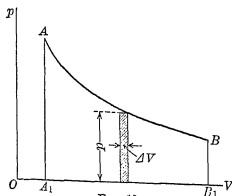


The general energy equation (3), Art. 25, may now be written in the form

$$J \Delta Q = \Delta U + p \, \Delta V, \qquad (5)$$

or using the differential notation, in the form

$$J dQ = dU + p \, dV \qquad (6)$$

For a unit weight of the substance, we have

$$J dq = du + p dv. \qquad (6\,a)$$

Fig. 10.

28.  Integration of the Eq.

by the subscripts 1 and 2, respectively, we have

$$\int_1^2 dU = U_2 - U_1,$$

whence
$$JQ = U_2 - U_1 + \int_1^2 p \, dV \qquad (1)$$

It should be noted carefully that since the energy $U$ depends only upon the state of the system and not upon the process of passing from the initial to the final state, the change of energy may be written at once as the difference $U_2 - U_1$. The external work

$$W = \int_1^2 p \, dV$$

is evidently dependent upon the path of the state-point between the initial and final states. See Fig. 10. Hence the sum of the change of energy and external work, that is, the heat added to the system, must also depend upon the path. It follows that $dQ$ is not an exact differential, and we cannot write

$$\int_1^2 dQ = Q_2 - Q_1.$$

In other words, we cannot properly speak of the heat *in* a a body in the state 1 or the state 2; we can speak only of the heat *imparted to* the body during the change of state with the reservation, stated or implied, that the quantity thus imparted depends upon the way in which the state is changed. For convenience we shall denote by $Q_{12}$ the heat imparted to the system in passing from state 1 to state 2; and likewise by $W_{12}$ the corresponding external work done by the system.

**29. Energy Equation applied to a Cycle Process.** — Let a system starting from an initial state pass through a series of processes and finally return to the initial state. The path of the state-point on the characteristic surface is a closed curve in space and the projection of the path on the $pV$-plane is a closed plane curve. See Fig. 11. Let $A$ represent the initial state; then in passing from $A$ to $B$ the external work done by the system is

$$\int_{V_a}^{V_b} p \, dV \text{ (along path } m),$$

which is represented by area $A_1AmBB_1$, while in passing from $B$ back to $A$ along path $n$ the external work is

$$\int_{V_b}^{V_a} p \, dV = -\int_{V_a}^{V_b} p \, dV \text{ (along path } n),$$

and this is represented by area $B_1BnAA_1$. Hence the net external work done by the system is represented by the area inclosed by the curve of the cycle.



Fig. 11.

Since the energy $U$ of the system depends upon the state only, the change of energy for the cycle is

$$U_A - U_A = 0,$$

and the energy equation reduces to

$$JQ = W.$$

That is, *for a closed cycle of processes, the heat imparted to the system is the equivalent of the external work*, and both are represented graphically by the area of the cycle on the $pV$-plane.

**30. Adiabatic Processes.** — When a system in changing its state has no thermal communication with other bodies and therefore neither absorbs nor gives out heat, the change of state is said to be **adiabatic**. In general, adiabatic changes are possible only when the system is inclosed in a non-conducting envelope. Rapid changes of state are approximately adiabatic, since time is required for conduction or radiation of heat; thus the alternate expansion and contraction of air during the passage of sound waves is nearly adiabatic; the flow of a gas or vapor through an orifice is practically an adiabatic process.

For an adiabatic change, the term $JQ$ of the energy equation reduces to zero, and we have, consequently,

$$0 = U_2 - U_1 + W_{12},$$

or

$$W_{12} = U_1 - U_2. \tag{1}$$

During an adiabatic change, therefore, the external work done
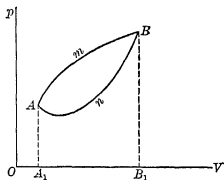
The projection on the $pV$-plane of the path of the state-point during an adiabatic change gives the adiabatic curve. See Fig. 12. The area $A_1ABB_1$ represents the work $W_{12}$ of the system nd from (1) it represents also the decrease of the intrinsic energy in passing from state 1 epresented by $A$ to state 2 epresented by $B$. Making se of this principle, we can rrive at a graphical represen- ation of the intrinsic energy f a system. Suppose the diabatic expansion to be con- inued indefinitely; the adia- atic curve $AB$ will then pproach the $V$-axis as an

symptote, and the work of the expanding system will be epresented by the area $A_1A\infty$ between the ordinate $A_1A$, the xis $OV$, and the curve extended indefinitely. The area $A_1A\infty$ epresents also the change of energy resulting from the expan- ion. Hence if we assume that the final energy is zero, we have
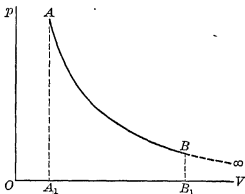
$$U_1 - 0 = \text{area } A_1A\infty,$$

$$\text{or} \quad U_1 = \text{area } A_1A\infty = \int_{V_1}^{\infty} p\,dV.$$
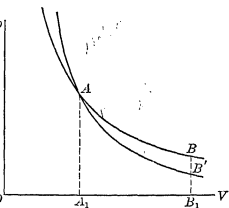
It is instructive to compare the adiabatic curve with the isothermal. When the two curves are projected on the $pV$-plane, the adiabatic is the steeper. See Fig. 13. This follows from the fact that dur- ing adiabatic expansion the

nergy decreases and as a result the temperature falls; hence

On the other hand, the area under the indefinitely extended isothermal *is* infinite.

**31. Isodynamic Changes.** — If the intrinsic energy of the system remains unchanged during a change of state, the change is called **isodynamic** or **isoenergic**. In this case the energy equation reduces to the form

$$JQ_{12} = W_{12} = \int_{V_1}^{V_2} p \, dV.$$

For perfect gases, the isodynamic curve is also the isothermal, but for other substances this is not the case.
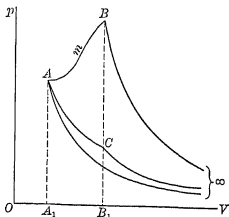
**32. Graphical Representations.** — The three magnitudes $JQ_{12}$, $U_2 - U_1$, and $W_{12}$ entering into the energy equation can be represented graphically by areas on the $pV$-plane. Suppose the change of state to be represented by the curve $m$ between the initial point $A$ and final point $B$ (Fig. 14). Let adiabatic lines be drawn through $A$ and $B$ and extended indefinitely; then from preceding considerations we have



FIG. 14.

$$W_{12} = \text{area } A_1ABB_1,$$
$$U_1 = \text{area } A_1A\infty,$$
$$U_2 = \text{area } B_1B\infty.$$

Hence, $JQ_{12} = U_2 - U_1 + W_{12}$
$$= \text{area } A_1ABB_1 + \text{area } B_1B\infty - \text{area } A_1A\infty$$
$$= \text{area } AB\infty.$$

That is, *the heat imparted is represented on the $pV$-plane by the area included between the path and two indefinitely extended adiabatics drawn through the initial and final points, respectively.*

Through the initial point $A$ let an isodynamic line be drawn, cutting $BB_1$ in the point $C$, and through $C$ let the indefinitely extended adiabatic $C\infty$ be drawn. Then the energy $U_3$ of the system in state $C$ is equal to $U_1$, and, therefore,

It should be noted that the area representing $U_2 - U_1$ is not influenced by the path $m$.

A second graphical representation is shown in Fig. 15. Through the initial point $A$ an isodynamic line is drawn, and through the final point $B$ an adiabatic is drawn, the two lines intersecting at point $C$. We have then, denoting the energy in the state $C$ by $U_3$,
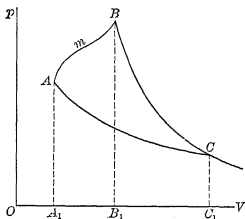


FIG. 15.

$$U_3 = U_1,$$
$$U_2 - U_1 = U_2 - U_3 = \text{area } B_1BCC_1,$$
$$W_{12} = \text{area } A_1ABB_1,$$
$$JQ_{12} = W_{12} + U_2 - U_1 = \text{area } A_1ABCC_1.$$

As before, the change of energy is independent of the path $m$, while both the external work and the heat imparted depend upon the form of $m$.

### EXERCISES

**1.** Show that the energy equation may be written in the form

$$Jdq = \left(\frac{\partial u}{\partial T}\right)_v dT + \left[\left(\frac{\partial u}{\partial v}\right)_t + p\right] dv,$$

and that consequently the derivative $\left(\frac{\partial u}{\partial T}\right)_v$ must be equal to $Jc_v$.

**2.** If the energy of a substance is independent of the volume, show that the energy equation reduces to the form

$$Jdq = Jc_v dT + pdv.$$

**3.** Using the method of graphical representation, show by areas $Q_{12}$, $U_2 - U_1$, and $W_{12}$ (*a*) for a change at constant pressure, (*b*) for a change at

**7.** Apply the general energy equation to the process of changing ice at 32° F. to water. What is the effect of greatly increasing the pressure on the ice during the process?

## REFERENCES

Preston: Theory of Heat, 596.

Zeuner: Technical Thermodynamics (Klein) **1**, 28.

Planck: Treatise on Thermodynamics (Ogg), 38.

# CHAPTER IV

## THE SECOND LAW OF THERMODYNAMICS

**33. Introductory Statement.** — While the first law of thermodynamics gives a relation that must be satisfied during any change of state of a system, and of itself leads to many useful results, it is not sufficient to set at rest all questions that may arise in connection with energy transformations. It gives no indications of the *direction* of a physical process ; it imposes no conditions upon the transformations of energy from one form to another except that there shall be no loss, and thus gives no indication of the possibilities of complete transformation of different forms; it furnishes no clue to the availability of energy or transformation under given circumstances. To settle these questions a second principle is required. This principle, called the **second law of thermodynamics**, has been stated in many ways. In effect, however, it is the principle of degradation of energy, just as the first law is the principle of the conservation of energy.

There are conceivable processes which, while satisfying the requirements of the first law, are declared to be impossible because of the restrictions of the second law. As a single example, it is conceivable that an engine might be devised that could deliver work without the expenditure of fuel, merely by using the heat stored in the atmosphere; in fact, such a device has been several times proposed. The first law would not be violated by such a process, for there would be transformation, not creation of energy; in other words, such an engine would not be a perpetual motion of the first class. Experience shows, however, that a process of this character, while not violating the conservation law, is nevertheless impossible. The statement

**34. Availability of Energy.** In Art. 8 was noted the distinction between various forms of energy with respect to the possibility of complete conversion. We shall now consider the point somewhat in detail.

Mechanical and electrical energy stand on the same footing as regards possibility of conversion; either can be completely transformed into the other in theory, and nearly so in practice. Either mechanical or electrical energy can be completely transformed into heat. On the other hand, experience shows that heat energy is not capable of complete conversion into mechanical work, and to get even a part of heat energy transformed into mechanical energy, certain conditions must be satisfied. As a first condition, there must be two bodies of different temperature; it is impossible to derive work from the heat of a body unless there is available a second body of lower temperature. Suppose we have then a source $S$ at temperature $T_1$ and a refrigerator $R$ at lower temperature $T_2$; how is it possible to derive mechanical work from a quantity of heat energy $Q_1$ stored in $S$? If the bodies $S$ and $R$ are placed in contact, the heat $Q_1$ will simply flow from $S$ to $R$ and no work will be obtained. Hence, as a second condition, the systems $S$ and $R$ must be kept apart and a third system $M$ must be used to convey energy. This third system is the **working fluid** or **medium**. In the steam plant, for example, the boiler furnace is the source $S$, the condenser is the refrigerator $R$ at a lower temperature, and the steam is the medium or working fluid $M$. The medium $M$ is placed in contact with $S$ and receives from it heat $Q_1$; it then by an appropriate change of state (expansion) gives up energy in the form of work, and delivers to $R$ a quantity of heat $Q_2$, smaller than $Q_1$, the difference $Q_1 - Q_2$ being the heat transformed into work. The details of this process will be given in following articles, where it will be shown that in no other way can a larger fraction of the heat be transformed into work.

The part of the heat $Q_1$ that can be thus transformed into work, that is, $Q_1 - Q_2$, is the **available** part of $Q_1$; and the part $Q_2$ that must be rejected to the refrigerator $R$, and which is of no further

cal work. In general, the term availability signifies the fraction of the energy of a given system in a given state that can be transformed into mechanical work.

In Art. 8 attention was called to the apparent tendency of energy to degenerate into less available forms. We have now to investigate this point somewhat closely in connection with reversible and irreversible changes of state.

**35. Reversibility.** — The processes described in thermodynamics are either reversible or irreversible. A process is said to be **reversible** when the following conditions are fulfilled:

1. When the direction of the process is reversed, the system taking part in the process can assume in inverse order the states traversed in the direct process.

2. The external actions are the same for the direct and reversed processes or differ by an infinitesimal amount only.

3. Not only the system undergoing the change but all connected systems can be restored to initial conditions.

A process which fails to meet these requirements in any particular is an **irreversible** process. The following examples illustrate the above definitions.

(1) Suppose a confined gas to act on a piston, as in the steam or gas engine. See Fig. 16. If $A$ is the piston area, the pressure acting on the face of the piston is $pA$, and for equilibrium
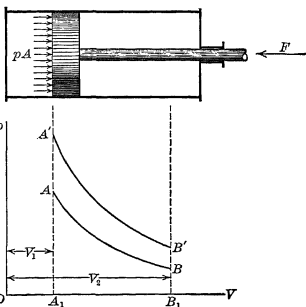


FIG. 16.

this pressure must be equal to the force $F$. If now we assume the force $pA$ slightly greater than $F$, the piston will move slowly to the right and the confined gas will assume a succes-

sion of states indicated by the curve $AB$. If at the state $B$ the motion is arrested and $F$ is made infinitesimally greater than $pA$ for all positions of the piston, the series of states from $B$ to $A$ will be retraced and the system (the confined gas in this case) will be brought back to its original state without leaving changes in outside bodies. The reversed process is accomplished by an infinitely small modification of the external force $F$. The process is therefore reversible.

(2) Let the force $F$ be removed entirely. Then the piston will move suddenly and the confined gas will be thrown into commotion. When the gas finally attains a state of thermal equilibrium with the volume $V_2$, that state will be represented by some point as $B'$. No path can be drawn between $A$ and $B'$ because during the passage from $A$ to $B'$ the gas is not in thermal equilibrium, and its state at any instant cannot, therefore, be determined. Evidently, therefore, the gas cannot be returned to state $A$ by reversing in all particulars the direct change from $A$ to $B'$. It can be returned to state $A$, however, in the following manner : A force $F$, slightly greater than $pA$, is applied to the piston and the gas is thus compressed slowly, the successive states being indicated by the curve $B'A'$, say. Then the gas in the state $A'$ is cooled at the constant volume $V_1$ until the original state $A$ is attained. The restoration of the gas to its initial state has, however, left changes in other bodies or systems. Thus the work of compression from $B'$ to $A'$ must be furnished from one external body, and the heat given up by the cooling from $A'$ to $A$ must be absorbed by another external body. The free expansion of the gas is, therefore, an irreversible process.

It is easy to see that the flow of a fluid through an orifice from a region of high pressure to a region of low pressure is essentially equivalent to the irreversible expansion just described. Such cases are of frequent occurrence in technical applications of thermodynamics. The flow of liquid ammonia through the expansion valve of the refrigerating machine may be cited as an example.

and bearing due to the conversion into heat of the work of overcoming friction. A complete reversal of this process would involve turning the shaft in the opposite direction by cooling the bearing.

(4) The conduction of heat from one body to another is an irreversible process. There must be a temperature difference to produce the flow of heat, and heat of itself will not flow in the reverse direction; that is, from the colder to the hotter body. If, however, we take the temperature difference $\Delta T$ indefinitely small and let the transfer take place very slowly, the process can be reversed by changing the sign of $\Delta T$. Hence we can conceive of reversible flow as the ideal limiting condition of the actual irreversible flow.

Strictly speaking, there are no reversible changes in nature. We must consider reversibility as an ideal limiting condition that may be approached but not actually attained when the processes are conducted very slowly.

**36. General Statement of the Second Law.** — According to the first law, the total quantity of energy in a system of bodies cannot be increased or decreased by any change, reversible or irreversible, that may occur within the system. It is not, however, the *total* energy, but the *available* energy of the system that is of importance ; and experience shows that a change within the system usually results in a change in the availability of the energy of the system.

It may be considered as almost self-evident that no change of a system which will take place of itself can increase the available energy of the system. On the other hand, experience teaches that all actual changes involve loss of availability. Consider, for example, the flow of heat from a body of temperature $T_1$, to another at temperature $T_2$. For the flow to occur of itself we must have $T_1 > T_2$, and as a result of the process there is a loss of availability. To produce an increase of availability would require $T_2$ to be greater than $T_1$ ; in that case, however, the process would not be possible. In the limiting reversible

of energy, are based entirely on experience:

I. *No change in a system of bodies that can take place of itself can increase the available energy of the system.*

II. *An irreversible change causes a loss of availability.*

III. *A reversible change does not affect the availability.*

These statements may be regarded as fundamental natural laws underlying all physical and chemical changes. The second and third together constitute the law of degradation of energy. The first may be taken as a general statement of the second law of thermodynamics.

By considering special processes the general statement of the second law here given may be thrown into special forms. Thus if heat could of itself pass from a body of lower to a body of higher temperature, the result of the process would be an increase of available energy, a result that is impossible according to our first statement. We have, therefore, Clausius' form of the second law, viz:

*It is impossible for a self-acting machine unaided by any external agency to convey heat from one body to another at higher temperature.*

Again, if we consider the increase of available energy that would result from deriving work directly from the heat of the atmosphere, we are led to Kelvin's statement, namely:

*It is impossible by means of inanimate material agency to derive mechanical effect from any portion of matter by cooling it below the temperature of surrounding objects.*

In order to estimate the available energy of a system in a given state, or the loss of available energy when the system undergoes an irreversible change, it is necessary to know the most efficient means of transforming heat into mechanical work under given conditions. This knowledge is furnished by a study of the ideal processes first described by Carnot in 1824.

**37. Carnot's Cycle.** — Suppose that the conditions stated in Art. 34 are furnished; that is, let there be a source of heat $S$ at temperature $T_1$, a refrigerator $R$ at a lower temperature $T_2$,

and an intermediate system, the working fluid or medium $M$. The medium we may assume to be inclosed in a cylinder provided with a piston (Fig. 18).

Let the medium initially in a state represented by $B$ (Fig. 17), at the temperature $T_1$ of the reservoir $S$, expand adiabatically until its temperature falls to $T_2$, the temperature of body $R$. By this expansion the second state $C$ is reached, and the work done by the medium is represented by the area $B_1BCC_1$. The expansion is assumed to proceed slowly so that the pressures on the two faces of the piston are sensibly equal, and the process is, therefore, reversible. The cylinder is now
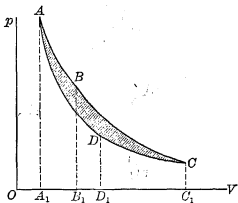


Fig. 17.

placed in contact with $R$ so that heat can flow from $M$ to $R$, and the medium is compressed. The work represented by the area $C_1CDD_1$ is done on the medium, and heat $Q_2$ passes from the medium to the refrigerator. The process is again assumed to be so slow as to be reversible. From the state $D$ the medium is now compressed adiabatically, the cylinder being removed from $R$ until its temperature again becomes $T_1$, that of the source $S$. During this third process work represented by the area $D_1DAA_1$ is done on the fluid. Finally, the cylinder is placed in contact with $S$ and the fluid is allowed to expand at the constant temperature $T_1$
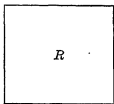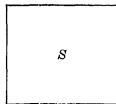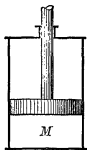


Fig. 18.

temperature is kept constant by the flow of heat $Q_1$ from $S$ to $M$.

The area $ABCD$ inclosed by the four curves of the cycle represents the mechanical work gained; that is, the excess of work done by the medium over that done on the medium. Denoting this by $W$, we have from the first law,

$$(Q_1 - Q_2) = A W.$$

The efficiency of the cycle is the ratio of the work gained to the heat supplied from the source $S$. Denoting the efficiency by $\eta$, we have

$$\eta = \frac{Q_1 - Q_2}{Q_1} = \frac{A W}{Q_1}.$$

Since all the processes of the Carnot cycle are reversible, it is evident that they may be traversed in reverse order. Thus starting from $B$, the fluid is compressed isothermally from $B$ to $A$ and gives up heat $Q_1$ to $S$; from $A$ to $D$ it expands adiabatically, from $D$ to $C$ it expands at the constant temperature $T_2$ and in so doing receives heat $Q_2$ from $R$; finally it is compressed adiabatically from $C$ to the initial state $B$. In this case the work $W$ represented by area $ABCD$ is done on the fluid $M$, heat $Q_2$ is taken from the refrigerator $R$, and the sum $Q_2 + A W$ $= Q_1$ is delivered to the source $S$. This ideal reversed engine is the basis of our modern refrigerating machines.

**38. Carnot's Principle.** — The efficiency of Carnot's ideal engine evidently depends upon the temperatures $T_1$ and $T_2$ of the source and refrigerator, respectively. The question at once arises whether the efficiency depends also upon the properties of the substance $M$ used as a working fluid. The answer is contained in Carnot's principle, namely :

*Of all engines working between the same source and the same refrigerator, no engine can have an efficiency greater than that of a reversible engine.*

In other words, all reversible engines working between the same temperature limits $T_1$ and $T_2$ have the same efficiency; that is, *the efficiency is independent of the working fluid.*

efficient than a reversible engine $B$ working between the same temperatures, then $A$ and $B$ can be coupled together in such a way as to produce available energy without a compensating loss of availability.

Suppose the two engines $A$ and $B$ (Fig. 19) to take equal quantities of heat $Q_1$ from the source when running direct. Then, since by hypothesis $A$ is the more efficient,

$$W_A > W_B$$

and

$$Q_2{}^A < Q_2{}^B.$$

Now let engine $B$ be run reversed. It will take heat $Q_2{}^B$ from $R$ and deliver $Q_1$ to $S$. If $A$ and $B$ are coupled together, $A$ will run $B$ reversed and deliver in addition the work $W_A - W_B$. The source is unaffected since it simultaneously receives heat $Q_1$ and gives up heat $Q_1$. The refrigerator, however, loses the heat $Q_2{}^B - Q_2{}^A$, which is the equivalent of the work $W_A - W_B$ gained. We have, therefore, an arrangement by which unavailable energy in the form of heat in the reservoir is transformed into mechanical work. In other
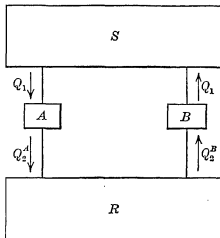


Fig. 19.

words, by a self-acting process the available energy of the system of bodies $S$, $R$, $A$, and $B$ is increased. According to the second law (Art. 36), such a result is impossible; if such a result were possible, power in any quantity could be obtained from the heat stored in the atmosphere without consumption of fuel.

The assumption that engine $A$ is more efficient than the reversible engine $B$ leads to a result that experience has shown to be impossible. We conclude, therefore, that the assumption is not admissible and that engine $A$ cannot be more efficient than engine $B$. But if engine $A$ is also reversible, $B$ cannot be more efficient than $A$, and it follows that all reversible

engines between the same source and the same refrigerator are
equally efficient.

**39. Determination of the Efficiency.** — Since the efficiency of
the reversible Carnot engine is independent of the properties of
the medium and depends upon the temperatures of source and
refrigerator only, we have

$$\eta = \frac{AW}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = f(T_1, T_2), \tag{1}$$

whence

$$\frac{Q_2}{Q_1} = 1 - \eta = F(T_1, T_2); \tag{2}$$

that is, the quotient $\frac{Q_2}{Q_1}$ is some function of the temperatures
$T_1$ and $T_2$. The form of this function is required.

So far, we have considered temperatures as given by a mer-
cury or air thermometer. The different temperatures of a
series of bodies are indicated by sets of numbers which may
denote (1) the different lengths of a column of mercury or
(2) the different pressures of a mass of confined gas. These
sets may or may not precisely agree. Now there are other
ways in which such a set of numbers may be chosen. Suppose
we take several sources of heat $S_1, S_2, S_3, \cdots, S_n$, whose tem-
peratures are $t_1, t_2, t_3, \cdots, t_n$ as defined by the mercury or gas
scale, and let

$$t_1 > t_2 > t_3 > \cdots > t_n.$$

If we use $S_1$ as a source and $S_2$ as a refrigerator, a reversible
engine will take $Q_1$ from $S_1$ and deliver $Q_2$ to $S_2$. Since the
bodies $S_1$ and $S_2$ have definite temperatures $T_1$ and $T_2$, what-
ever the scale adopted, the function $F(T_1, T_2)$ has some defi-
nite value; therefore, from (2) the fraction $\frac{Q_2}{Q_1}$ must have a
definite value, and consequently $Q_2$ has one and only one value.
If $S_2$ is used as a source and $S_3$ as a refrigerator, a second
engine taking $Q_2$ from $S_2$ will give up $Q_3$ to $S_3$, and so on.
Starting with $Q_1$, we thus obtain a determinate set of values
$Q_2, Q_3, Q_4$, etc., which must fulfil the condition

Here we have a set of numbers suitable to define a scale of temperature. Starting with the heat $Q_1$ taken from the source $S_1$, to each source there corresponds a number indicating the heat that would be rejected to it if it were used as a refrigerator in connection with $S_1$. If we choose these numbers to define a new scale, then denoting the new temperatures by

$$T_1, \ T_2, \ T_3, \ \cdots, \ T_n,$$

we have

$$T_1 = kQ_1, \quad T_2 = kQ_2, \quad T_3 = kQ_3, \quad \cdots, \quad T_n = kQ_n,$$

whence follows

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2} = \cdots = \frac{Q_n}{T_n}. \tag{4}$$

Returning now to the quotient $\dfrac{Q_2}{Q_1}$, we have at once

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

hence, using this new scale, the efficiency of the Carnot engine is

$$\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1}, \tag{5}$$

and the form of the function is determined.

The scale of temperatures arrived at from the investigation of Carnot's cycle was first proposed by Lord Kelvin in 1848, and is known as the **absolute scale** because it is independent of the property of any substance. The scale is simply such that any two temperatures on it are proportional to the quantities of heat absorbed and rejected by a reversible Carnot engine working between these temperatures.

If in (5) we make $Q_2 = 0$, $\eta = 1$ and $T_2 = 0$. If we conceive a temperature lower than the zero on the absolute scale, that is, if we assume a negative value for $T_2$, then $\dfrac{T_1 - T_2}{T_1} > 1$,

be shown subsequently that this absolute zero is precisely the same as that derived from the reduction in pressure of a perfect gas, and that the new scale coincides with that of a thermometer using a perfect gas as a fluid.

**40. Available Energy and Waste.** — Carnot's ideal cycle gives us a means of measuring the available energy of a system and the waste due to an irreversible change of state. Suppose that a quantity of heat $\Delta Q$ is absorbed by the system at a temperature $T$, and that we wish to find the part of this heat that can possibly be transformed into work. As we have seen, no device can transform a larger portion of $\Delta Q$ into work than the ideal Carnot engine. If $T_0$ is the lowest temperature that can be obtained for a refrigerator, the fraction $\dfrac{T - T_0}{T}$ of $\Delta Q$ can be transformed into work by a Carnot engine, and this is, therefore, the availability of $\Delta Q$ under the given conditions. The available part of $\Delta Q$ is, therefore,

$$\Delta Q \frac{T - T_0}{T} = \Delta Q \left( 1 - \frac{T_0}{T} \right),$$

and the waste is $\quad \Delta Q \dfrac{T_0}{T}.$

The temperature $T_0$ cannot be lower than that of surrounding objects, *i.e.* the atmosphere; * for even if a refrigerator could be found with a temperature lower than that of the atmosphere, it could not be maintained in that state. Hence, the temperature of the atmosphere imposes a natural limitation on the availability of heat in the performance of work.

EXAMPLE. If the absolute temperature of a source is 1000° F. and that of the atmosphere is 520°, the available energy is

$$\frac{1000 - 520}{1000} = 0.48 \text{ of the total energy.}$$

Therefore, for every 1000 B. t. u. received from the source, not more than 480 B. t. u. can by any means whatever be transformed into work, and at least 520 B. t. u. must be rendered unavailable.

* Possibly under special conditions a refrigerator whose temperature is permanently below that of the atmosphere may exist ; *e.g.* the water of the ocean or of one of the great lakes.

associated with certain important irreversible processes.

(1) *Conduction of Heat.* — Suppose a quantity of heat $Q$ to pass by conduction from a source at a temperature $T_1$ to another at lower temperature $T_2$. At the original temperature the available energy was

$$\left(1 - \frac{T_0}{T_1}\right)Q.$$

The same quantity of heat in the second source has the available energy

$$\left(1 - \frac{T_0}{T_2}\right)Q.$$

The available energy is, therefore, decreased by the quantity

$$Q\left[\frac{T_0}{T_2} - \frac{T_0}{T_1}\right] = T_0\left[\frac{Q}{T_2} - \frac{Q}{T_1}\right];$$

and the unavailable energy is increased by an equal amount.

(2) *Irreversible Conversion of Work into Heat.* — A common irreversible process is the conversion of work into heat in the interior of a system through the agency of friction. Examples are found in the flow of steam through nozzles and blades, and in the frictional losses due to internal whirls and eddies in fluids. Heat thus produced we shall denote by the symbol $H$, reserving $Q$ to denote heat brought into the system from outside.

If now within the system the small quantity of heat $\Delta H$ is generated while the system remains at the temperature $T$, the part of $\Delta H$ that is available is

$$\Delta H \frac{T - T_0}{T} = \Delta H\left(1 - \frac{T_0}{T}\right),$$

where, as usual, $T_0$ denotes the lowest available temperature. Of the work $J\Delta H$ expended in producing the heat $\Delta H$, the part

$$J\Delta H\left(1 - \frac{T_0}{T}\right)$$

may therefore be recovered in the form of work. The remainder

$$J\Delta H - J\Delta H\left(1 - \frac{T_0}{T}\right) = J\Delta H \frac{T_0}{T} = JT_0 \frac{\Delta H}{T}$$

is rendered unavailable.

To obtain the total increase of unavailable energy, when the quantity of heat $H$ is generated, the temperature of the system varying in the meantime, we sum the element of the type just obtained. Thus if the temperature rises from $T_1$ to $T_2$ during the process, we have for the total waste

$$JT_0 \lim \sum_{T_1}^{T_2} \frac{\Delta H}{T} = JT_0 \int_{T_1}^{T_2} \frac{dH}{T}.$$

(8) *Free expansion of a gas.* — The waste due to free expansion, as described in Art. 35, may be determined by returning the gas to its initial state and observing the changes left in outside bodies.

The compression indicated by $B'A'$ (Fig. 16) requires that work $W$, represented by area $B'A'$ $A_1B_1$, be supplied from an outside body $S_2$. Another outside body $S_3$ must receive from the gas heat $Q$ equivalent to the work $W$. The gas, the the system $S_1$, has the same available energy as at first, being restored to its initial condition; system $S_2$ has lost available energy $W = JQ$; and system $S_3$ has received energy $JQ$ of which only part is available. On the whole, therefore, there is an increase of unavailable energy. The loss of availability due to the original irreversible expansion of the gas (system $S_1$) is repaired in this system, but an equal loss is brought about in systems $S_2$ and $S_3$. It can be shown that the waste thus incurred is given by an expression of the form $T_0 \int \frac{dQ}{T}$.

**41. Entropy.** — The expressions for the increase of unavailable energy derived under various conditions are alike in having $T_0$, the lowest temperature available for a refrigerator, as a factor. It appears, therefore, that the unavailable energy changes with $T_0$; the lower $T_0$ can be taken, the smaller the waste and the larger the fraction of the heat supplied that can be transformed into work.

The other factor in the expression must necessarily, for the sake of consistent units, have the form $\frac{Q}{T}$ or $\int \frac{dQ}{T}$. To this

measure of the change in the unavailable energy of the system; an increase of entropy involves an increase of unavailable energy, and *vice versa*. We may formally define entropy as follows:

*If, from any cause whatever, the unavailable energy of a system is increased and if the increase be divided by $T_0$, the lowest temperature available for a cold body, the quotient is the increase of entropy of the system.*

This definition requires close examination to obviate possible misconception. The "system" spoken of may be either a single substance, as the medium employed in a heat motor, or it may be all the bodies taking part in the process. Now, according as we take one or the other of these viewpoints we get a particular notion of the significance of the term entropy.

To illustrate this point, let us consider a simple example. Suppose we have a fluid medium $M$ and a source of heat $S$, as described in connection with the Carnot engine. We may direct our attention either to the system $M$ alone or to the system $M + S$ composed of the medium and source. Let both $M$ and $S$ be at the temperature $T$ and suppose that at this temperature heat $Q$ is transferred from $S$ to $M$. This is the ideal reversible transfer assumed in the description of the Carnot engine. In receiving $Q$ the system $M$ has its available energy increased by $Q\left(1 - \dfrac{T_0}{T}\right)$ and its unavailable energy increased by $Q\dfrac{T_0}{T} = T_0\dfrac{Q}{T}$; hence by the definition just given the entropy of system $M$ is increased by $\dfrac{Q}{T}$. At the same time system $S$ has lost the energy $Q$ and, therefore, the unavailable energy $Q\dfrac{T_0}{T}$; hence the entropy of $S$ is decreased by $\dfrac{Q}{T}$. It follows that the change of entropy of the system $M + S$ is zero. As the result of the reversible transfer of heat from $S$ to $M$ there is no change in the unavailable energy of the large system $S + M$ and no change in the entropy of this system. Suppose now that system $M$ is again at temperature $T$, but that system $S$ has a higher temperature $T'$, as must be the case in any actual transfer

of heat. If now heat $Q$ passes from $S$ to $M$, the unavailable energy of $M$ is increased by $Q\dfrac{T_0}{T'}$, as before, and the increase of entropy of system $M$ is $\dfrac{Q}{T'}$. The system $S$ has, however, lost the unavailable energy $Q\dfrac{T_0}{T''}$, and its entropy has decreased by $\dfrac{Q}{T''}$. The system $S + M$ has had its unavailable energy increased by the amount $Q\dfrac{T_0}{T'} - Q\dfrac{T_0}{T''} = T_0\left(\dfrac{Q}{T'} - \dfrac{Q}{T''}\right)$. The irreversible transfer has therefore resulted in a net loss of available energy of this amount, and this degradation is accompanied by an increase of entropy $\dfrac{Q}{T'} - \dfrac{Q}{T''}$. The result here obtained for two systems may be applied to any number of systems.

When we apply the notion of increase of entropy to the system composed of *all* the bodies involved in a process, in other words, *an isolated system*, we are led to the conception that the increase of entropy measures the degradation of energy incident to the process. If we combine this notion with that expressed by the second law, we arrive at the following important principles :

1. *Any process that can proceed of itself is accompanied by an increase of the entropy of the system of bodies involved in the process.*

2. *The direction of a process, physical or chemical, that occurs of itself is such as will bring about an increase of entropy in the system.*

These principles lie at the foundation of the application of thermodynamics to chemistry.

**42. Second Definition of Entropy.** — While the conception of entropy as the factor that measures degradation is the funda-

unavailable energy of this single system involves an increase in the entropy of the system, but, as we have seen, degradation does not necessarily follow, for the increase of unavailable energy of $M$ may be compensated by an equal loss in some other system taking part in the process.

We now inquire by what means the unavailable energy of the single system under consideration can be increased. There are at least three ways that are suggested from the previous discussion of available energy (Art. 40).

(1) If energy is added to the system in the form of heat, the total energy of the system is increased, and consequently the unavailable energy is increased. If the heat $\Delta Q$ is thus added when the temperature of the system is $T$, the resulting increase of unavailable energy is

$$\Delta Q \frac{T_0}{T} = T_0 \frac{\Delta Q}{T}.$$

If, as is generally the case, the temperature rises as heat is added, we shall have for the increase

$$\int_{T_1}^{T_2} dQ \frac{T_0}{T} = T_0 \int_{T_1}^{T_2} \frac{dQ}{T}.$$

(2) The unavailable energy may be increased by the conversion of work into heat through internal friction. As shown in Art. 40 (2), the increase of unavailable energy from this cause is

$$T_0 \int_{T_1}^{T_2} \frac{dH}{T}.$$

(3) If the parts of the system are not at the same temperature, there will be an irreversible flow of heat from one part of the system to another, and this will increase the unavailable energy. We may remove this source of unavailable energy by assuming that the system is at all times of uniform temperature throughout, an assumption that is usually justifiable.

Neglecting this third effect, we have for the increase of unavailable energy from state 1 to state 2,

whence by definition, the increase of entropy is

$$\int_{T_1}^{T_2} \frac{dQ}{T} + \int_{T_1}^{T_2} \frac{dH}{T}.$$

Now while the actual change of the system from state 1 to state 2 may, and usually does, involve frictional effects, we can conceive of a *hypothetical* change in which these internal irreversible effects are entirely absent and in which the increase of unavailable energy is due entirely to the addition to the system of heat from some external source. Denoting by $Q_r$ the heat thus added, we have for the increase of entropy involved in this particular process the integral

$$\int_{T_1}^{T_2} \frac{dQ_r}{T}.$$

The important question now arises: Does the increase of entropy of the single system under consideration depend only upon the initial and final states or upon the path connecting the states? It is easily shown that the increase of entropy, like the increase of energy, depends upon the initial and final states only. For the change of energy is independent of the path; therefore, the change of the unavailable part of the energy, as determined by the constant temperature $T_0$ and the temperatures $T_1$ and $T_2$ at the initial and final states, is also independent of the path; therefore the change of entropy, which is the change of unavailable energy divided by $T_0$, is also independent of the path. It follows that the integral $\int_{T_1}^{T_2} \frac{dQ}{T}$ has the same value whether taken along the path $r$ (Fig. 20) or any other reversible path $r'$. We may write, therefore,

$$\int_{T_1}^{T_2} \frac{dQ}{T} = S_2 - S_1,$$

where $S$ denotes a function of the coördinates of the system which may be termed the **entropy** of the system. We have, then, the following definition:

*The change of entropy of a system corresponding to a change of the system from state 1 to state 2 is the definite integral* $\int_{T_1}^{T_2} \frac{dQ}{T}$

According to this more restricted conception, the entropy of a system, like the energy, pressure, or temperature, is a magnitude determined by the state of the system, and change of entropy has no necessary connection with degradation of energy.

It should be noted that entropy as thus defined is like energy purely relative. We are never concerned with the absolute value of the entropy of a system in a given state; what is desired is the *change of entropy* associated with a given change of state. For convenience of calculation we assume the zero of entropy to be the entropy of a system in some specified state. Thus, in dealing with vapors we assume the zero of entropy to be the entropy of a unit weight of liquid at 0° C.

**43. The Inequality of Clausius.** — If an actual irreversible change be represented by the path $i$, Fig. 20 (assuming it to be possible to give such a representation), a correct value of the change cannot be obtained from the integral $\int_{T_1}^{T_2} \frac{dQ_i}{T}$ taken along the path $i$. For as we have seen

$$S_2 - S_1 = \int_{T_1}^{T_2} \frac{dQ_i}{T} + \Sigma,$$

where $\Sigma$ is the increase of entropy due to the internal irreversible changes. For the actual irreversible change we have, therefore,

$$S_2 - S_1 > \int_{T_1}^{T_2} \frac{dQ}{T}.$$

This is the inequality of Clausius.

FIG. 20.

**44. Summary.** — To present the important principles of this chapter in concise form and in logical order the following summary is added.

1. Experience shows that heat energy is not completely transformable into mechanical work. The ratio of the energy
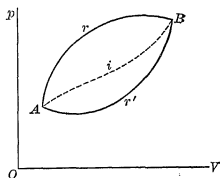
2. Experience further shows that an irreversible process always decreases the availability of a system.

3. The second law of thermodynamics asserts that the available energy of an isolated system cannot be increased by any process that takes place of itself.

4. To gain a means of measuring availability the ideal Carnot engine is introduced. By the aid of the second law it is shown that no engine working between the same temperature limits can have an efficiency greater than the Carnot engine, and as a consequence, that the efficiency of this engine is a function of the temperature limits only.

5. By the introduction of Kelvin's absolute scale of temperature the efficiency of the Carnot engine is found to be given by the fraction $\dfrac{T_1 - T_2}{T_1}$.

6. Having the efficiency fraction $\dfrac{T_1 - T_2}{T_1}$, the available part of a given quantity of heat $Q$ at temperature $T$ is found to be $Q\left(1 - \dfrac{T_0}{T}\right)$ and the unavailable part, $Q\dfrac{T_0}{T}$.

7. By special examples of irreversible processes it is found that the expression for the loss of available energy in such processes has the general form $T_0 \sum \dfrac{Q}{T}$ or $T_0 \int \dfrac{dQ}{T}$.

8. The factor $\sum \dfrac{Q}{T}$ or $\int \dfrac{dQ}{T}$ which multiplied by $T_0$ gives the increase of unavailable energy is called the *increase of entropy* of the system.

9. Two conceptions of entropy are possible: (*a*) If attention be directed to all the bodies involved in a process, the increase of entropy of the whole system of bodies measures the degradation of energy resulting from the process. (*b*) If attention be directed to a single body, as a medium used in a heat motor, the entropy of this simple system is merely a function of the coördinates of the system.

10. The change of entropy of a simple system is given by the integral $\int^{T_2} dQ$

the initial and final states.   The value of this integral is independent of the path.

11.  For an irreversible change of state the change of entropy is greater than $\int_{T_1}^{T_2} \frac{dQ}{T}$.

## 45. Boltzmann's Interpretation of the Second Law.— A very clear insight into the real physical meaning of natural irreversible processes and of the second law of thermodynamics is afforded by the researches of Boltzmann and Planck.  In this article it is possible to give merely a brief outline of Boltzmann's contribution; for a complete exposition the reader is referred to Professor Klein's admirable book, *The Physical Significance of Entropy.** 

According to the molecular theory, the ultimate particles of matter are in a state of incessant motion, the character of the motion depending upon the state of aggregation, — solid, liquid, or gaseous.   In a gas it is assumed that a particle has a free path and moves along a straight line until it collides with another particle or with a restraining surface, as the wall of the containing vessel.   To the motion of particles as to the motion of masses we may apply the conception of constraint or control.   Thus, in the wave motions that characterize sound, the motion of the particles that constitute the mediums is in some degree controlled or ordered.   The molecular motion that constitutes heat is, on the other hand, wholly uncontrolled and disordered.   For any given particle of a gas all directions of motion are equally possible and, therefore, equally probable; and the direction of motion and velocity of any particle is independent of the motions of other particles.   In a volume of gas particles will be moving in all directions with all possible velocities.   However, because of the great number of particles even in a small volume, the values of magnitudes that depend upon the molecular motion, such as pressure and temperature, remain constant notwithstanding the haphazard character of the molecular motion.

According to Boltzmann, there is apparently a universal tendency toward the disordered motion that characterizes heat.   A motion that is in any degree ordered or controlled tends to become disordered.   Thus, as sound waves die out the uniform motion of the particles in the wave changes to disordered motion, and the energy of sound is transformed into heat energy.   The relative motion of two bodies in contact is retarded by friction, and the work of overcoming friction is transformed into heat; that is, the constrained motion of the particles in the mass gradually changes to the disordered motion of heat.   Since the energy of disordered molecular motion is necessarily less available for direction into any required channel than the energy of constrained or controlled motion, it follows that a change from a less probable state of controlled motion to a more probable state of

to a condition of less available energy. Hence, the statement of the natural tendency toward disordered motion is in reality a broad statement of the second law of thermodynamics.

From the preceding considerations a physical interpretation of entropy is readily deduced. A system of itself passes from a less probable to a more probable state; that is, to a state of more disordered molecular motion. The entropy of the system during the change must increase. Therefore, the entropy of the system may be associated with the probability of the state of the system. From the laws of probability, Planck has shown that the entropy is proportional to the logarithm of the probability of the state.

The following quotations from Prof. Klein's book indicate in some degree the significance of this conception of entropy.

"Growth of entropy is a passage from a somewhat regulated to a less regulated state."

"Entropy is a universal measure of the *disorder* in the mass points of a system."

"Entropy is a universal measure of the spontaneity with which a system acts when it is free to change."

"Growth of entropy is a passage from a concentrated to a distributed condition of energy; energy originally concentrated variously in the system is finally scattered uniformly in said system. In this aggregate aspect it is a passage from variety to uniformity."

## EXERCISES

1. If a source of heat has an absolute temperature of 1400° F. and the lowest available temperature is 525° F., what fraction of the heat drawn from the source is available?

2. In a boiler 10,000 B. t. u. pass from the hot gases of the furnace, the temperature of which is 2500° F., through the boiler shell into water at a temperature of 330° F. If the lowest available temperature is 80° F., find the loss of available energy.

3. Show how the result of Ex. 2 suggests the superior efficiency of the gas engine compared with the steam engine.

4. Point out the loss of available energy when heat flows from steam in a radiator at a temperature of 225° into a room at 70°. Devise a system of heating that would obviate this loss.

5. A mass of water weighing 60 lb. at a temperature of 70° F. is churned by a paddle wheel until the temperature rises to 120°. Find the increase of entropy, and the loss of available energy. Take the specific heat of water as 1.

6. In the demonstration of Carnot's principle, Art. 38, assume the two engines A and B to do the same work W. Then show that if engine A

REFERENCES

REVERSIBLE AND IRREVERSIBLE PROCESSES

Planck: Treatise on Thermodynamics, Ogg's trans., 82.
Bryan: Thermodynamics, 34, 40.
Klein: Physical Significance of Entropy, 29.
Chwolson: Lehrbuch der Physik 3, 443.
Parker: Elementary Thermodynamics, 105.


THE SECOND LAW.   ENTROPY

Sadi Carnot: Reflections on the Motive Power of Heat.  Translated by
    Thurston.
Clausius: Mechanical Theory of Heat.
Rankine: Phil. Mag. (4) 4.  1852.
Thomson: Phil. Mag. (4) 4.  1852.
Franklin: Phys. Rev. 30, 776.  1910.
Lorenz: Technische Wärmelehre, 164.
Chwolson: Lehrbuch der Physik 3, 485, 497.
Bryan: Thermodynamics, 43, 57.
Preston: Theory of Heat, 625.
Klein: Physical Significance of Entropy.
Magie: The Second Law of Thermodynamics (contains Carnot's " Reflec-
    tions " and the discussions of Clausius and Thomson).
Planck: Treatise on Thermodynamics (Ogg), 86.
Parker: Elementary Thermodynamics, 104.

# CHAPTER V

## TEMPERATURE ENTROPY REPRESENTATION

**46. Entropy as a Coördinate.** — It was shown in Art. 42 that the entropy of a system measured from an arbitrary zero is dependent only upon the state of the system; that is, the entropy is a function of the coördinates of the system. It follows that the entropy itself may be included among the coördinates used to define a system. We have, therefore, five coördinates, namely, $p$, $v$, $T$, $u$, and $s$, that may be thus used. From these five, ten pairs may be selected, and the change of state of a system may be represented by ten different curves on ten different planes. Of these possible graphical representations two are of special importance: (1) representation on the $pV$-plane, because the area between the curve and $V$-axis represents the external work done by the system; (2) representation on the $TS$-plane, because with certain restrictions the area under the curve represents the heat absorbed by the system from external sources. Graphical representations on the $pV$-plane have been considered in Art. 32. This chapter will be devoted chiefly to representations on the $TS$-plane.

From the second definition of entropy, we have

$$S - S_1 = \int_{T_1}^{T} \frac{dQ}{T},\qquad(1)$$

from which relation we obtain at once the differential forms

$$dS = \frac{dQ}{T},\qquad(2)$$

and

$$T dS = dQ.\qquad(3)$$

Let the curve $AB$ (Fig. 31) be the path of the state point

But from (3) this integral is the heat $Q_{12}$ absorbed by the system from external sources during the change of state. It follows that the area between the curve $AB$ and the axis $OS$ represents graphically the heat absorbed along the path $AB$.

One most important restriction must, however, be observed. In defining entropy by means of equation (1) it was expressly stated that the change of state must not involve any internal irreversible effects. If such effects are present, the equation for the change of entropy is
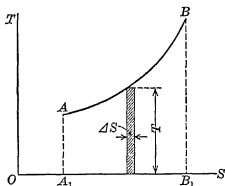
$$S_2 - S_1 = \int_{T_1}^{T_2} \frac{dQ}{T} + \Sigma, \qquad (4)$$

where $\Sigma$ denotes the increase of entropy due to internal processes, conduction between the parts of the system, transformation of work into heat through friction, etc., and $\int_{T_1}^{T_2} \frac{dQ}{T}$ is the increase of entropy due to the absorption of heat from external bodies. From (4) it follows that in this case

$$\int_{T_1}^{T_2} \frac{dQ}{T} < S_2 - S_1,$$

whence

$$dQ < T dS, \qquad (5)$$

or the heat absorbed from outside *is less than* the area between the $TS$-curve and the $S$-axis. *This area therefore may be taken as representing the heat absorbed by the system when, and only when, the change of state involves no irreversible effects.* Neglect of this restriction has led to many errors.

**47. Isothermals and Adiabatics.** — If the temperature of the system remains constant during the change of state, the

$AB$ (Fig. 22). The change of entropy is simply

$$S_B - S_A = \frac{1}{T}\int_A^B dQ = \frac{Q_{AB}}{T}.$$

In this case we have merely to divide the heat added to the system (assuming, of course, that the change of state is reversible) by the constant temperature $T$, and the quotient is the change of entropy.


Fig. 22.

If the state point passes from $B$ to $A$, that is, so as to decrease the entropy, the area $A_1ABB_1$ represents heat rejected by the system to outside bodies.
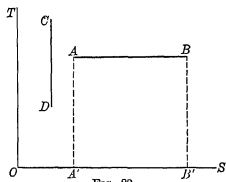
For an adiabatic change of state, $dQ = 0$; hence from (1) $S_2 = S_1$ and the adiabatic line on the $TS$-plane, if the change of state involves no irreversible effects, is a straight line parallel to the $T$-axis, as $CD$ (Fig. 22). If the state-point moves from $C$ to $D$, indicating a decrease of temperature, external work is done by the system, and the change of state is an adiabatic expansion. If the point moves upward from $D$ to $C$ the change of state is an adiabatic compression.

**48. The Curve of Heating and Cooling.** — From the equation

$$c = \frac{dq}{dT},$$

which defines the specific heat of a substance, we have

$$dq = c\,dT. \tag{1}$$

Substituting this expression for $dq$ in (1), Art. 46, we get for a reversible process

$$s - s_1 = \int_{T_1}^T \frac{c\,dT}{T}. \tag{2}$$

If the specific heat $c$ is constant during the change of state, we have for the change of entropy of unit weight of the substance

$$s - s_1 = c\int_{T_1}^T \frac{dT}{T} = c\log_e \frac{T}{T_1}. \tag{3}$$

For the weight $M$,

$$S - S_1 = Mc \log_e \frac{T}{T_1}. \tag{3 a}$$

If, however, $c$ is variable, it can usually be expressed as a function of the temperature; that is, we can write

$$c = f(T),$$

whence

$$s - s_1 = \int_{T_1}^{T} \frac{f(T) dT}{T}. \tag{4}$$

The integration can be effected when the function $f(T)$ is known.

EXAMPLE. Let the specific heat of a substance be given by the relation

$$c = a + bt = a + b(T - 459.6);$$

we have then

$$s_2 - s_1 = (a - 459.6 \, b) \int_{T_1}^{T_2} \frac{dT}{T} + b \int_{T_1}^{T_2} dT$$

$$= (a - 459.6 \, b) \log_e \frac{T_2}{T_1} + b(T_2 - T_1).$$

The general form of the curve that represents Eq. (3) is shown in Fig. 23. This curve represents the ordinary process of heating a body or substance, as the heating of water in a boiler or metal in a furnace. It is called by some writers the **polytropic** curve. The subtangent of the curve is constant and numerically equal to the specific heat. Thus from the figure we have
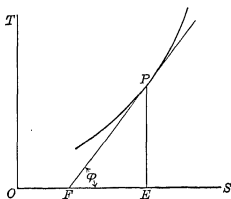


FIG. 23.

$$EF = EP \cot \phi$$

$$= T \frac{ds}{dT} = \frac{dq}{dT} = c.$$

It follows that the smaller the value of $c$, the greater the slope of the curve.

The isothermal and adiabatic curves (Fig. 22) may be con-

Fig. 24.
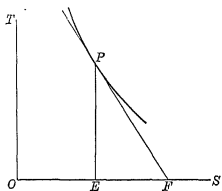
Cases may arise in which the slope of the $TS$-curve is negative, as shown in Fig. 24. In such cases abstraction of heat is accompanied by a rise in temperature or *vice versa*. Evidently the specific heat $\dfrac{dq}{dT}$ must be negative, as is indicated geometrically by the negative subtangent. Examples will be shown in the compression of air in the ordinary air compressor, and in the expansion of dry saturated steam with the provision that it remains dry during the expansion.

**49. Cycle Processes.** — Since any reversible process may be shown by a curve in $TS$-coördinates, it follows that a series of such processes forming a closed cycle may be represented by a closed figure on the $TS$-plane. In Fig. 25 is shown such a cycle composed of two polytropics $AB$ and $DE$, an isothermal $BC$, and two adiabatics $CD$ and $EA$.

In any such cycle the area included by the cycle represents the net heat added to (or abstracted from) the working fluid during the cycle process. Assuming the cycle to be traversed in the clockwise sense, we have
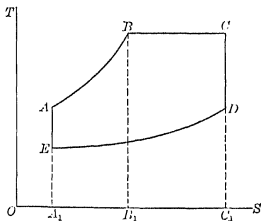


Fig. 25.

$$Q_{ab} = \text{area } A_1ABB_1,$$
$$Q_{bc} = \text{area } B_1BCC_1,$$
$$Q_{cd} = 0,$$

$$= Q_{ab} + Q_{bc} + Q_{cd} + Q_{de} + Q_{ea} = A_1ABB_1 + B_1BCC_1 - C_1DEA_1$$
$$= ABCDE.$$

the cycle is traversed in the counterclockwise sense, we have idently

$$Q = - \text{ area } ABCDE.$$

it from the first law, $Q$ is the heat transformed into work; nce for the direct cycle

$$\text{area } ABCDE = Q = AW,$$

d for the reversed cycle

$$\text{area } ABCDE = - Q = - AW.$$

This reasoning evidently holds for any number of processes, d therefore for a reversible sed cycle of any form. Thus the cycle shown in Fig. 26, have

$$\text{area } F = Q = AW,$$
$$\text{area } F = - Q = - AW,$$

cording as the cycle is traversed the clockwise or counter clock- se sense.



FIG. 26.

In later developments it will quently be necessary to show cycle processes on the $TS$-plane.

**50. The Rectangular Cycle.** When the curves representing four processes of the Carnot cycle are transferred to the



FIG. 27.

$TS$-plane, the cycle becomes the simple rectangle $ABCD$, Fig. 27. The area $A_1ABB_1$ represents the heat $Q_1$ absorbed by the medium from the source during the isothermal expansion $AB$, and the area $B_1CDA_1$, the heat $Q_2$ rejected to the refrigerator during the isothermal compression $CD$. The lines $BC$ and $DA$ represent, respectively, the adiabatic expansion and the adiabatic compression.
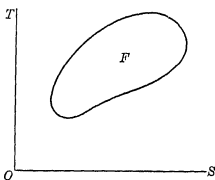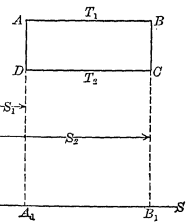
From the geometry of the figure, we have

$$Q_1 = T_1(S_2 - S_1),$$
$$Q_2 = T_2(S_2 - S_1),$$
$$AW = Q_1 - Q_2 = (T_1 - T_2)(S_2 - S_1),$$

whence        $\eta = \dfrac{AW}{Q_1} = \dfrac{T_1 - T_2}{T_1},$

as already deduced in Art. 39.

When the cycle is traversed in the counterclockwise sense, the heat $Q_2$ is received by the medium from the cold body during the isothermal expansion $DC$, and the larger amount of heat $Q_1$ is rejected to the hot body during isothermal compression $BA$. The difference $Q_2 - Q_1 = -AW$ represented by the cycle area is the work that must be done *on* the medium, and must therefore be furnished from external sources.

The reversed heat engine may be used either as a refrigerating machine or as a warming machine. In the first case the space to be cooled acts as the source and delivers the heat $Q_2 = $ area $A_1DCB_1$ to the medium. In the second case the space to be warmed receives the heat $Q_1 = $ area $B_1BAA_1$ from the medium.

**51. Internal Frictional Processes.** — Referring to Art. 42, the increase of entropy when heat is generated in the interior of a system is seen to be

$$S_2 - S_1 = \int_{T_1}^{T_2} \frac{dQ}{T} + \int_{T_1}^{T_2} \frac{dH}{T}. \tag{1}$$

If $Q = 0$, that is, if no heat enters the system from outside sources, the increase of entropy is

$$S_2 - S_1 = \int_{T_1}^{T_2} \frac{dH}{T}, \tag{2}$$

and is due entirely to the generation of heat in the interior of the system. If it be assumed that this process is steady, so that the system at every instant is approximately in thermal equilibrium, the usual graphical representation may be applied to (2), and the area under the $TS$-curve will in this case represent not the heat brought into the system but the heat $H$

int $A$ (Fig. 28) has its pressure decreased in passing along the
zzle, and as a result the temperature likewise falls. The
ocess is adiabatic, that is, no heat
received from external bodies;
nce, if there were no internal
ction, the drop in temperature
uld be indicated by a motion of
e state-point along $AA_1$. But
rk is expended in overcoming
e friction between the fluid and
zzle wall. This work is neces-
rily transformed into heat, which
retained by the fluid. It follows



Fig. 28.

at there is an increase of entropy, as indicated by the curve $AB$.
om (2) the heat generated is represented by the area $A_1ABB_1$.
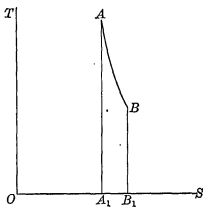
## 52. Cycles with Irreversible Adiabatics. — In certain cases the
osed cycle of operations of a heat motor may contain an adia-
tic irreversible process, the irreversibility arising either from
ternal generation of heat or from the free expansion or wire-
awing of the working fluid. Even if it is possible to draw



Fig. 29.

a $TS$-curve representing such
a process, the area under that
curve does not represent the
heat entering the system from
an external source. Hence
some care is required to inter-
pret properly the graphical
representations of cycles with
such irreversible parts.
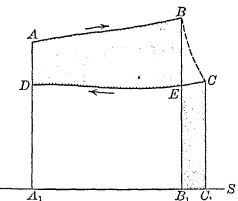
In the cycle shown in Fig. 29,
suppose the process $BC$ to be
an irreversible adiabatic, the

her parts of the cycle being reversible. Since $AB$ is revers-
e, the heat absorbed in passing from $A$ to $B$ is represented by
e area $A_1ABB_1$. Likewise area $C_1CDA_1$ represents the heat
ected by the system in changing state from $C$ to $D$. The

process $DA$ is adiabatic, hence $Q_{da} = 0$; and by hypothesis $Q_{bc} = 0$. The value of $\Sigma Q$ for the cycle is, therefore,

$$Q_{ab} + Q_{cd} = \text{area } A_1 A B B_1 - \text{area } C_1 C D A_1$$
$$= \text{area } A B E D - \text{area } B_1 E C C_1.$$

The energy equation applies to any process, reversible or irreversible. Therefore for this cycle, as for those previously considered, we have

$$W = JQ = J(Q_{ab} + Q_{cd}).$$

It appears, therefore, that the work derived is less by the area $B_1 E C C_1$ than it would have been if the reversible adiabatic $B E$ had been followed.

For the reversed cycle (Fig. 30) we have as the work required from external sources
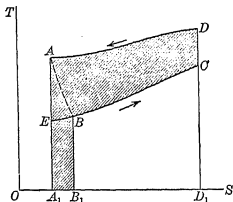
$$W = J(Q_{da} + Q_{bc}) = -\text{area } D_1 D A A_1 + \text{area } B_1 B C D_1$$
$$= -\text{area } B_1 B C D A A_1.$$

Comparing this cycle with the cycle $AECD$ having the reversible adiabatic $AE$, it is seen that the heat absorbed from the cold body is smaller by the heat represented by the area $A_1 E B B_1$, while the work required to drive the machine is greater by an equal amount. In every case the irreversible process results in a reduction of the useful effect.

**53. Heat Content.** — Since the quantities $p$, $v$, $T$, $u$, and $s$ are function of the state of a system only, it follows that any combination of these quantities is likewise a function of the state only. For example, let

$$i = A(u + pv); \tag{1}$$
$$I = A(U + pV); \tag{1 a}$$
$$F = Au - Ts; \tag{2}$$
$$\Phi = Au - Ts + Apv. \tag{3}$$

Then $i$, $F$, and $\Phi$ are magnitudes...

tentials, and are used in certain applications of thermo-
namics to physics and chemistry. The function $I$ has use-
l applications in technical thermodynamics.

To gain a physical meaning for the function $I$, let us consider
e process of heating a substance at constant pressure. If $U_1$,
, and $p_1$ denote the initial energy, volume, and pressure,
spectively, and $U_2$, $V_2$, and $p_2$ the final values of the same
rdinates, we have from the energy equation

$$Q_{12} = A(U_2 - U_1 + W)$$
$$= A[U_2 - U_1 + p(V_2 - V_1)]$$
$$= A[U_2 - U_1 + (p_2 V_2 - p_1 V_1)], \text{ since } p_2 = p_1$$
$$= [A(U_2 + p_2 V_2) - A(U_1 + p_1 V_1)]$$
$$= I_2 - I_1.$$

at is, the change in $I$ is equal to the heat added to the sys-
n during a change of state at constant pressure. For this
ason $I$ is called the **heat con-
t of the system** *at constant
essure*, or, more briefly, the
eat content."

In some subsequent investiga-
ns, especially those relating to
e flow of fluids, it will be con-
nient to use $I$ and $S$ as the in-
pendent variables and to repre-
t changes of state by curves on
e $IS$-plane. The great advantage
the $IS$-representation over the



FIG. 31.

-representation lies in the fact that in the former quantities
heat are represented by linear segments, while in the latter,
we have seen, they are represented by areas. A reversible
abatic on the $IS$-plane is a vertical line, as $BC$ (Fig. 31).
t in this diagram segment $BC$ represents a quantity of heat
tead of a change of temperature.
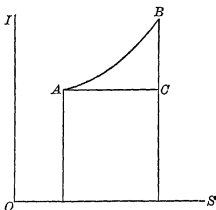
**2.** Assuming that the specific heat of water is constant, $c = 1$, plot on cross-section paper the $TS$-curve representing the heating of water from 32° to 212°.

**3.** Langen's formula for the specific heat of $CO_2$ at constant pressure is $c_p = 0.195 + 0.000066\ t$. Find the increase of entropy when $CO_2$ is heated at constant pressure from 500° to 2000° F.; also the heat absorbed.

**4.** A direct motor operates on a rectangular cycle between temperature limits $T_1 = 840°$ and $T_2 = 600°$ and receives from the source 200 B. t. u. per minute. Find the efficiency, and the work done per minute.

**5.** A reversed motor, rectangular cycle, operates between temperature limits of 10° and 130°, and receives 600 B. t. u. per minute from the cold body. Find the heat rejected to the hot body, and the horsepower required to drive the motor.

**6.** A direct motor, rectangular cycle, operating between temperatures $T_1 = 900°$ and $T_2 = 680$, takes 1000 B. t. u. from a boiler. The heat rejected is delivered to a building for heating purposes. This direct motor drives a reversed motor which operates on a rectangular cycle between temperatures $T_4 = 460°$ (temperature of outside atmosphere) and $T_3 = 600$. The reversed motor takes heat from the atmosphere and rejects heat to the building. Find the total heat delivered to the building per 1000 B. t. u. taken from the boiler.

**7.** In the vaporization of water at atmospheric pressure, the temperature remains constant at 212° F., and 970.4 B. t. u. are required for the process. Find the increase of entropy.

**8.** The expression for the energy $U$ for a given weight of a permanent gas is $\dfrac{pV}{k-1} + U_0$, where $k$ and $U_0$ are constants. Derive an expression for the heat content $I$ for the gas.

**9.** Combine the energy equation $dQ = AdU + ApdV$ with the defining equation $I = A(U + pV)$ and show that $dI = dQ + AVdp$.

## REFERENCES

### USE OF TEMPERATURE-ENTROPY COÖRDINATES

Berry: The Temperature-Entropy Diagram.
Sankey: The Energy Diagram.
Boulvin: The Entropy Diagram.
Swinburne: Entropy.

### USE OF HEAT CONTENT AND ENTROPY AS COÖRDINATES

Berry: The Temperature-Entropy Diagram, 127.
Mollier: Zeit. des Verein. deutscher Ing. **48**, 271.

## GENERAL EQUATIONS OF THERMODYNAMICS

**54. Fundamental Differentials.** — The introduction of the entropy $s$ and the functions $i$, $F$, and $\Phi$ (Art. 52) permits the derivation of a large number of relations between various thermodynamic magnitudes. While the number of formulas that can be thus derived is almost unlimited, we shall introduce in the present chapter only those that will prove useful in the subsequent study of the properties of various heat media. In this article we shall by simple transformations express the differentials of $u$, $i$, $F$, and $\Phi$ in terms of the differentials of the variables $p$, $v$, $T$, and $s$.

We have to start with the fundamental energy equation

$$dq = A(du + pdv), \tag{1}$$

and for a reversible process the relation

$$dq = Tds. \tag{2}$$

Combining (1) and (2), we obtain

$$du = \frac{T}{A} ds - pdv, \tag{3}$$

an equation that gives $u$ as a function of the independent variables $s$ and $v$.

From the defining equation

$$i = A(u + pv)$$

we have

$$di = Adu + Ad(pv)$$
$$= Adu + Apdv + Avdp.$$

Introducing the expression for $Adu$ given by (3), we get

Here $i$ is given as a function of $s$ and $p$ as independent variables.

Likewise, from the relation

$$F = Au - Ts,$$
$$dF = Adu - Tds - sdT;$$

whence from (3)

$$-dF = sdT + Apdv. \tag{5}$$

Finally, from the defining relation

$$\Phi = Au + Apv - Ts,$$
$$d\Phi = Adu + Ad(pv) - d(Ts)$$
$$= Tds - Apdv + Apdv + Avdp - Tds - sdT;$$

or $\qquad d\Phi = Avdp - sdT. \tag{6}$

Now since the functions $u$, $i$, $F$, and $\Phi$ depend on the state only, their differentials are exact; hence the second members of (3), (4), (5), and (6) are all exact differentials.

Certain results can be deduced at once from the differential equations (3)–(6). For example, from (6), if a system changes state reversibly under constant pressure and at constant temperature, the function $\Phi$ remains constant. Again from (5), if a change of state occurs at constant temperature, the external work done is equal to the decrease of the function $F$. These results are important in the application of thermodynamics to chemistry.

**55. The Thermodynamic Relations.** — The fact that the differentials in (3), (4), (5), and (6) of the last article are exact gives a means of deriving four important relations. In (3) we have $u$ expressed as a function of the variables $s$ and $v$; that is,

$$u = f(s, v),$$

whence $\qquad du = \dfrac{\partial u}{\partial s}\, ds + \dfrac{\partial u}{\partial v}\, dv.$

Comparing this symbolic equation with (3), it appears that

$$\frac{\partial}{\partial v}\left(\frac{\partial}{\partial s}\right) = \frac{\partial}{\partial s}\left(\frac{\partial}{\partial v}\right);$$

that is,

$$\frac{1}{A}\frac{\partial}{\partial v}(T) = \frac{\partial}{\partial s}(-p),$$

or

$$\left(\frac{\partial T}{\partial v}\right)_s = -A\left(\frac{\partial p}{\partial s}\right)_v. \tag{A}$$

The subscripts denote the variables held constant during the differentiations indicated.

Relation (A) may be expressed in words as follows: The rate of increase of temperature with respect to the volume along an isentropic is equal to $A$ times the rate of decrease of the pressure with respect to the entropy along a constant volume curve. That is, if the reversible change of state be represented by curves, — one on the $Tv$-plane, another on the $ps$-plane, — the slope of the second curve at a point representing a given state is $-A$ times the slope of the first curve at the point that represents the same state.

In (4) we have $s$ and $p$ as the independent variables; and since $di$ is exact, the necessary condition of exactness gives

$$\frac{\partial}{\partial p}(T) = \frac{\partial}{\partial s}(Av),$$

or

$$\left(\frac{\partial T}{\partial p}\right)_s = A\left(\frac{\partial v}{\partial s}\right)_p. \tag{B}$$

That is, the rate of increase of temperature with respect to the pressure in adiabatic change is $A$ times the rate of increase of volume with respect to the entropy in a constant-pressure change.

Since in (5) $dF$ is an exact differential, we have

$$\left(\frac{\partial s}{\partial v}\right)_T = A\left(\frac{\partial p}{\partial T}\right)_v. \tag{C}$$

From (6), likewise, we obtain

$$\left(\frac{\partial s}{\partial p}\right)_T = -A\left(\frac{\partial v}{\partial T}\right)_p. \tag{D}$$

The relations given by (A), (B), (C), and (D) are known as Maxwell's thermodynamic relations. They hold for all

(C) and (D) by means of the relation $ds = \dfrac{dq}{T}$, are useful:

$$\left(\frac{\partial q}{\partial v}\right)_T = A T \left(\frac{\partial p}{\partial T}\right)_v, \qquad (C')$$

$$\left(\frac{\partial q}{\partial p}\right)_T = - A T \left(\frac{\partial v}{\partial T}\right)_p. \qquad (D')$$

**56. General Differential Equations.** — From the thermo-dynamic relations certain useful general equations are at once deduced. As in Art. 19, we may write

$$dq = \left(\frac{\partial q}{\partial T}\right)_v dT + \left(\frac{\partial q}{\partial v}\right)_T dv,$$

$$dq = \left(\frac{\partial q}{\partial T}\right)_p dT + \left(\frac{\partial q}{\partial p}\right)_T dp,$$

according as $T$ and $v$ or $T$ and $p$ are taken as the independent variables. Now replacing $\left(\dfrac{\partial q}{\partial T}\right)_v$ and $\left(\dfrac{\partial q}{\partial T}\right)_p$ by $c_v$ and $c_p$, respectively, and $\left(\dfrac{\partial q}{\partial v}\right)_T$ and $\left(\dfrac{\partial q}{\partial p}\right)_T$ by the expressions given in $(C')$ and $(D')$, these equations become, respectively,

$$dq = c_v dT + A T \left(\frac{\partial p}{\partial T}\right)_v dv, \qquad (I)$$

$$dq = c_p dT - A T \left(\frac{\partial v}{\partial T}\right)_p dp. \qquad (II)$$

Eliminating $dT$ between (I) and (II), a third equation having $p$ and $v$ as the variables is obtained. Thus

$$dq = \frac{A T}{c_p - c_v} \left[ c_p \left(\frac{\partial p}{\partial T}\right)_v dv + c_v \left(\frac{\partial v}{\partial T}\right)_p dp \right]. \qquad (III)$$

Two other important equations may be derived from (I) and (II). Since from the energy equation

$$du = Jdq - pdv,$$

we have from (I)

$$du = Jc_v dT + \left[ T \left(\frac{\partial p}{\partial T}\right)_v - p \right] dv; \qquad (IV)$$

$$di = c_p dT - A\left[T\left(\frac{\partial v}{\partial T}\right)_p - v\right]dp. \qquad \text{(V)}$$

The general equations (I)–(V) hold for reversible changes of state. The partial derivatives involved may be found from the characteristic equation of the substance under investigation.

As an application of (IV), we may derive expressions for the change of energy (a) of a gas that follows the law $pv = BT$; (b) of a gas that obeys van der Waals' equation

$$\left(p + \frac{a}{v^2}\right)(v - b) = BT.$$

(a) From the characteristic equation $pv = BT$, we have

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{B}{v};$$

hence

$$du = Jc_v dT + \left(\frac{BT}{v} - p\right)dv$$
$$= Jc_v dT,$$

and

$$u_2 - u_1 = J\int c_v dT$$
$$= Jc_v(T_2 - T_1),$$

assuming $c_v$ to be a constant.

(b) From van der Waals' equation, we have

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{B}{v - b},$$

whence

$$\left[T\left(\frac{\partial p}{\partial T}\right)_v - p\right] = \frac{BT}{v - b} - p = \frac{a}{v^2}.$$

From (IV), we have, therefore,

$$du = Jc_v dT + \frac{a}{v^2}dv,$$

whence, assuming again that $c_v$ is constant,

$$u_2 - u_1 = Jc_v(T_2 - T_1) + a\left(\frac{1}{v_1} - \frac{1}{v_2}\right).$$

It appears, therefore, that if a gas follows the law $pv = BT$, the energy is a function of the temperature only, while if it follows van der Waals' law, the energy depends upon the temperature and volume; in other words, the gas possesses both kinetic and potential energy.

**57. Additional Thermodynamic Formulas.** — For certain investigations of imperfect gases, especially the superheated vapors, certain formulas involving the specific heats $c_p$ and $c_v$ are useful. The most important of these are (VI), (VII), and (VIII) following.

Since $du$ is an exact differential, we obtain, upon applying the criterion of exactness to (IV),

$$\frac{\partial}{\partial v}(Jc_v) = \frac{\partial}{\partial T}\left[T\left(\frac{\partial p}{\partial T}\right)_v - p\right],$$

or

$$J\left(\frac{\partial c_v}{\partial v}\right) = T\left(\frac{\partial^2 p}{\partial T^2}\right)_v + \left(\frac{\partial p}{\partial T}\right)_v - \left(\frac{\partial p}{\partial T}\right)_v;$$

whence

$$\left(\frac{\partial c_v}{\partial v}\right)_T = AT\left(\frac{\partial^2 p}{\partial T^2}\right)_v. \qquad (VI)$$

In a similar manner, since $di$ is exact, we have from (V)

$$\left(\frac{\partial c_p}{\partial p}\right)_T = -AT\left(\frac{\partial^2 v}{\partial T^2}\right)_p. \qquad (VII)$$

Equations (VI) and (VII) may be used to show the dependence of the specific heats $c_v$ and $c_p$ upon the pressure and volume. For example, if a gas follows the equation $pv = BT$ we find $\frac{\partial^2 v}{\partial T^2} = 0$, whence from (VII) $\left(\frac{\partial c_p}{\partial p}\right)_T = 0$, and it follows that $c_p$ does not depend upon the pressure, though it may vary with the temperature. Also $\frac{\partial^2 p}{\partial T^2} = 0$, whence it follows that $c_v$ does not vary with the volume. The student may show that the second result follows from van der Waals' equation or from any equation in which $p$ and $T$ appear in the first degree only. If, however, we take the characteristic equation

which applies to superheated steam, we obtain

$$\frac{\partial^2 v}{\partial T^2} = -\frac{mn(n+1)}{T^{n+2}}(1+ap),$$

hence

$$\left(\frac{\partial c_p}{\partial p}\right)_T = \frac{Amn(n+1)(1+ap)}{T^{n+1}}.$$

Integrating this with $T$ constant, we have

$$c_p = \frac{Amn(n+1)}{T^{n+1}}\, p\left(1+\frac{a}{2}p\right) + \phi(T),$$

where $\phi(T)$, an arbitrary function of $T$, is the constant of integration. In this case it is seen that $c_p$ is a function of both $T$ and $p$.

An expression for $c_p - c_v$ is obtained as follows: Writing the entropy $s$ as a function of $p$ and $v$, we have

$$ds = \frac{\partial s}{\partial p}\, dp + \frac{\partial s}{\partial v}\, dv.$$

This, combined with the familiar equation

$$Adu = Tds - Apdv,$$

gives the equation

$$Adu = T\frac{\partial s}{\partial p}\, dp + \left(T\frac{\partial s}{\partial v} - Ap\right)dv.$$

Since $du$ is an exact differential, we have

$$\frac{\partial}{\partial v}\left(T\frac{\partial s}{\partial p}\right) = \frac{\partial}{\partial p}\left(T\frac{\partial s}{\partial v} - Ap\right);$$

that is,

$$\frac{\partial T}{\partial v}\frac{\partial s}{\partial p} + T\frac{\partial^2 s}{\partial v \partial p} = \frac{\partial T}{\partial p}\frac{\partial s}{\partial v} + T\frac{\partial^2 s}{\partial p \partial v} - A,$$

hence

$$\frac{\partial T}{\partial v}\frac{\partial s}{\partial p} - \frac{\partial T}{\partial p}\frac{\partial s}{\partial v} = -A. \qquad (1)$$

From the definition of specific heat, we have

$$c = \frac{dq}{dT} = T\frac{ds}{dT},$$

and if we express both $s$ and $T$ as functions of $p$ and $v$, this relation becomes

$$c = T\frac{\dfrac{\partial s}{\partial p}\, dp + \dfrac{\partial s}{\partial v}\, dv}{\dfrac{\partial T}{\partial p}\, dp + \dfrac{\partial T}{\partial v}\, dv}. \qquad (2)$$

If $p$ is constant, $c = c_p$ and $dp = 0$; hence we have from (2)

$$c_p = T \frac{\frac{\partial s}{\partial v}}{\frac{\partial T}{\partial v}}. \tag{3}$$

Likewise, when $v$ is constant we have

$$c_v = T \frac{\frac{\partial s}{\partial p}}{\frac{\partial T}{\partial p}}. \tag{4}$$

Combining (3) and (4), we obtain

$$c_p - c_v = T \left[ \frac{\frac{\partial s}{\partial v}}{\frac{\partial T}{\partial v}} - \frac{\frac{\partial s}{\partial p}}{\frac{\partial T}{\partial p}} \right] = T \frac{\left( \frac{\partial T}{\partial p} \frac{\partial s}{\partial v} - \frac{\partial T}{\partial v} \frac{\partial s}{\partial p} \right)}{\frac{\partial T}{\partial v} \cdot \frac{\partial T}{\partial p}}. \tag{5}$$

Making use of (1), we get finally

$$c_p - c_v = A T \frac{\partial v}{\partial T} \frac{\partial p}{\partial T}. \tag{VIII}$$

EXAMPLE. For the characteristic equation $pv = BT$, we have

$$\frac{\partial v}{\partial T} = \frac{B}{p}, \quad \frac{\partial p}{\partial T} = \frac{B}{v}.$$

Therefore, from (8),

$$c_p - c_v = \frac{AB^2 T}{pv} = AB \frac{BT}{pv} = AB.$$

That is, the difference $c_p - c_v$ is constant even if $c_p$ and $c_v$ vary with the temperature.

Taking Zeuner's equation for superheated steam, viz:

$$pv = BT - Cp^n,$$

we have

$$\frac{\partial v}{\partial T} = \frac{B}{p}, \quad \frac{\partial p}{\partial T} = \frac{B}{nCp^{n-1} + v};$$

whence

$$c_p - c_v = AB \frac{BT}{nCp^n + pv} = AB \frac{BT}{(n-1)Cp^n + BT}.$$

In this case, therefore, the difference $c_p - c_v$ varies with $T$ and $p$.

By various substitutions and transformations we could add almost indefinitely to this list of thermodynamic formulas. However, the eight formulas (I)–(VIII) are sufficient for the investigation of nearly all problems

apter $T$ must necessarily denote the temperature defined by
e Kelvin absolute scale. The coincidence of this scale with
e perfect gas scale will be shown in the next chapter.

**58. Equilibrium.** — For irreversible processes the equations of Art. 54
ist be replaced by inequalities. Since for an irreversible process,

$$dq < Tds, \qquad (1)$$

. (3), (4), (5), and (6) of Art. 54 become, respectively,

$$Adu < Tds - Apdv, \qquad (2)$$
$$di < Tds + Avdp, \qquad (3)$$
$$- dF > sdT + Apdv, \qquad (4)$$
$$d\Phi < Avdp - sdT. \qquad (5)$$

From the inequalities (4), (5), and (1) the following conclusions are at
ce apparent :

1. If the temperature and volume of a system remain constant, then from
), $dF < 0$. That is, $dF$ must be negative, and any change in the system
ist result in a decrease of the function $F$.

2. If the temperature and pressure remain constant, as in fusion and
porization, then from (5), $d\Phi < 0$. Hence any change in the system must
 such as to decrease the function $\Phi$.

3. If the system be isolated, $q = 0$, and from (1), $ds > 0$. Hence an
lated system any change must result in an increase of entropy.

The conditions of equilibrium are readily deduced from these conclusions.
ider the condition of constant $T$ and $v$, change is possible so long as $F$
n decrease. When $F$ becomes a minimum, no further change is possible
d the system is in stable equilibrium. Likewise, with $T$ and $p$ constant,
ible equilibrium is attained when the function $\Phi$ is a minimum.

The functions $F$ and $\Phi$ are evidently analogous to the potential function
 in mechanics. A mechanical system is in a state of equilibrium when
e potential energy is a minimum, and similarly a thermodynamic system
in equilibrium when either the function $F$ or the function $\Phi$ is a minimum.
r this reason $F$ and $\Phi$ are called thermodynamic potentials.

By the use of thermodynamic potentials, problems relating to fusion,
porization, solution, chemical equilibrium, etc., are attacked and solved.

### EXERCISES

**1.** From (V) derive an expression for the change of the heat content $i$
en a gas following the law $pv = BT$ changes state.

**2.** If the gas obeys van der Waal's law, find an expression for the
ange of the heat content $i$.

**3.** Apply equations (II), (IV), and (V) to the characteristic equation
 superheated steam,

**4.** Callendar has proposed for superheated steam the equation

$$p(v - b) = BT - Cp\left(\frac{273}{T}\right)^n.$$

Apply (VII) to this equation and show that $c$ is a function of $p$ and $T$.

**5.** Give geometrical interpretations of the thermodynamic relations (C) and (D).

**6.** From (I) and (II) derive expressions for $dq$ and also for $\frac{dq}{T}$ for a gas following the law $pv = BT$. Show that the expressions for $\frac{dq}{T}$ are integrable, while those for $dq$ are not.

**7.** Derive (VI) and (VII) by the following method: Divide both members of (I) and (II) by $T$, and knowing that $\frac{dq}{T} = ds$ is exact, apply the criterion of exactness to the resulting differentials.

**8.** Deduce the following relation between the specific heats and the functions $F$ and $\Phi$:

$$(a) \ \ c_v = -\,T\frac{\partial^2 F}{\partial T^2}; \quad (b) \ \ c_p = T\frac{\partial^2 \Phi}{\partial T^2}.$$

**9.** Using temperature-entropy coördinates, deduce a system of graphical representation for the three magnitudes $Q$, $U_2 - U_1$, and $W$ that appear in the energy equation.

Suggestion. Through the point representing one state draw an isodynamic, through the other point a constant volume curve.

### REFERENCES

#### General Equations of Thermodynamics

Bryan: Thermodynamics, 107.
Preston: Theory of Heat, 637.
Chwolson: Lehrbuch der Physik **3**, 466, 505.
Buckingham: Theory of Thermodynamics, 117.
Parker: Elementary Thermodynamics, 239.

#### Equilibrium.   Thermodynamic Potentials

Planck: Treatise on Thermodynamics (Ogg), 115.
Gibbs: Equilibrium of Heterogeneous Substances.

# CHAPTER VII

## PROPERTIES OF GASES

**59. The Permanent Gases.** — The term "permanent gas" survives from an earlier period, when it was applied to a series of gaseous substances which supposedly could not by any means be changed into the liquid or solid state. The recent experimental researches of Pictet and Cailletet, of Wroblewski, Olszowski, and others have shown that, in this sense of the term, there are no permanent gases. At sufficiently low temperatures all known gases can be reduced to the liquid state. The following are the temperatures of liquefaction of the more common gases at atmospheric pressure :

| | |
|---|---|
| Atmospheric air | $-192.2°$ C. |
| Nitrogen | $-193.1°$ C. |
| Oxygen | $-182.5°$ C. |
| Hydrogen | $-252.5°$ C. |
| Helium | $-263.9°$ C. |

It appears, therefore, that the so-called permanent gases are in reality superheated vapors far removed from temperature of condensation. We shall understand the term "permanent gas" to mean, therefore, a gas that is liquefied with difficulty and that obeys very closely the Boyle-Gay Lussac law. Gases that show considerable deviations from this law because they lie relatively near the condensation limit will be known as superheated vapors.

**60. Experimental Laws.** — The permanent gases, at the pressures usually employed, obey quite exactly the laws of Boyle and Charles, namely :

1. **Boyle's Law.** *At constant temperature, the volume of a given weight of gas varies inversely as the pressure.*

By the combination of these laws the characteristic equation $pv = BT$ is deduced. (See Art. 14.) In this equation $T$ denotes absolute temperature on the scale of the gas thermometer, and not necessarily temperature on the Kelvin absolute scale.

The classic experiment of Joule showed that permanent gases obey very nearly a third law, namely:

3. **Joule's Law.** *The intrinsic energy of a permanent gas is independent of the volume of the gas and depends upon the temperature only.* In other words, the intrinsic energy of a gas is all the kinetic form.

Joule established this law by the following experiment. Two vessels, $a$ and $b$, Fig. 32, connected by a tube were immersed in a bath of water. In one vessel air was compressed to a pressure of 22 atmospheres, the other vessel was exhausted. The temperature of the water was taken by a very sensitive thermometer. A stopcock $c$ in the connecting tube was then opened, permitting the air to rush from $a$ to $b$, and after equilibrium was established the temperature of the water was again read. No change of temperature could be detected.
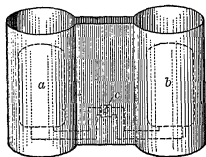


Fig. 32.

From the conditions of the experiment no work external to the vessels $a$ and $b$ was done by the gas; and since the water remained at the same temperature, no heat passed into the gas from the water. Consequently, the internal energy of the air was the same after the expansion into the vessel $b$ as before. Now if the increase of volume had required the expenditure of internal work, *i.e.* work to force the molecules apart against their mutual attractions, that work must necessarily have come from the internal kinetic energy of the gas, and as a result the temperature would have been lowered. As the temperature remained constant, it is to be inferred that no such internal

work was required. A gas has, therefore, no appreciable internal potential energy ; its energy is entirely kinetic and depends upon the temperature only.

Joule's law may be expressed symbolically by the relations :

$$u = f(t), \quad \frac{\partial u}{\partial v} = 0.$$

The more accurate porous-plug experiments of Joule and Lord Kelvin showed that all gases deviate more or less from Joule's law. In the case of the so-called permanent gases, air, hydrogen, etc., the deviation was slight though measurable ; but with the gases more easily liquefied, the deviations were more marked. The explanation of these deviations is not difficult when the true nature of a gas is considered. Presumably the molecules of a gas act on each other with certain forces, the magnitudes of which depend upon the distances between the molecules. When the gas is highly rarefied, that is, when it is far removed from the liquid state, the molecular forces are vanishingly small ; but when the gas is brought nearer the liquid state by increasing the pressure and lowering the temperature, the molecules are brought closer together and the molecular forces are no longer negligible. The gas in this state possesses appreciable potential energy and the deviation from Joule's law is considerable.

**61. Comparison of Temperature Scales.** — Joule's law furnishes a means of comparing the two temperature scales that have been introduced : the scale of the gas thermometer and the Kelvin absolute scale.

Since the intrinsic energy $u$ is, in general, a function of $T$ and $v$, we may write the symbolic equation

$$du = \frac{\partial u}{\partial T} dT + \frac{\partial u}{\partial v} dv. \tag{1}$$

But from the general equation (IV), Art. 56,

$$du = Jc_v dt + \left[ T\left(\frac{\partial p}{\partial T}\right)_v - p \right] dv \tag{2}$$

paring (1) and (2), we obtain

$$\frac{\partial u}{\partial T} = Jc_v, \quad \frac{\partial u}{\partial v} = T\left(\frac{\partial p}{\partial T}\right)_v - p. \qquad (3)$$

For a gas that obeys Joule's law $\dfrac{\partial u}{\partial v} = 0$, whence from (3)

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{p}{T}. \qquad (4)$$

Equation (4) is, however, precisely the equation that expresses Charles' law when $T$ is taken as the absolute temperature on the scale of the constant volume gas thermometer. Thus, if the change of pressure is proportional to the change of temperature when the volume remains constant, we have, taking $p_0$ as the pressure at 0° C.,

$$\frac{p - p_0}{t - t_0} = \frac{p}{t + a} = \frac{p}{T} \quad \text{(see Fig. 2)};$$

that is,

$$\frac{dp}{dt} = \frac{p}{T}.$$

It follows that the value of $T$ is the same whether taken on the Kelvin absolute scale or on the scale of a constant-volume gas thermometer, provided the gas strictly obeys the laws of Boyle and Joule. The fact that any actual gas, as air or nitrogen, does not obey these laws exactly makes the scale of the actual gas thermometer deviate slightly from the scale of the ideal Kelvin thermometer. From the porous-plug experiments of Joule and Kelvin, Rowland has made a comparison between the Kelvin scale and the scale of the air thermometer.

**62. Numerical Value of B.** — The value of the constant $B$ for a given gas can be determined from the values of $p$, $v$, and $T$ belonging to some definite state. The specific weights of various gases at atmospheric pressure and at a temperature of 0° C. are given as follows:

| | | |
|---|---|---|
| Atmospheric air | . . . . . . | 0.08071 lb. per cubic foot. |
| Nitrogen | . . . . . . . | 0.07829 lb. per cubic foot. |
| Oxygen | . . . . . . . | 0.08922 lb. per cubic foot. |
| Hydrogen | . . . . . . . | 0.00561 lb. per cubic foot. |
| Carbonic acid | . . . . . . | 0.12268 lb. per cubic foot. |

A pressure of one atmosphere, 760 mm. of mercury, is 10,333 kg. per square meter = 14.6967 lb. per square inch = 2116.32 lb. per square foot. Taking as 491.6 the value of $T$ on the F. scale corresponding to 0° C., we have for air

$$B = \frac{pv}{T} = \frac{p}{\gamma T} = \frac{2116.32}{0.08071 \times 491.6} = 53.34.$$

In metric units the corresponding calculation gives

$$B = \frac{10333}{273.1 \times 1.293} = 29.26.$$

The values of $B$ for other gases may be found in the same way by inserting the proper values of the specific weight $\gamma$.

**63. Forms of the Characteristic Equation.** — In the characteristic equation as usually written,

$$pv = BT, \tag{1}$$

$v$ denotes the volume of unit weight of gas. It is convenient to extend the equation to apply to any weight. Letting $M$ denote the weight of the gas, we have for the volume $V$ of $M$ lb. (or kg.), $V = Mv$, whence instead of (1) we may write:

$$pV = MBT. \tag{2}$$

This equation is useful in the solution of problems in which three of the four quantities, $p$, $v$, $T$, and $M$, are given and the fourth is required.

Example. Find the pressure when 0.6 lb. of air at a temperature of 70° F. occupies a volume of 3.5 cu. ft.
From (2)

$$p = \frac{MBT}{V} = \frac{0.6 \times 53.34 \times (70 + 459.6)}{3.5} = 4843.7 \text{ lb. per square foot}$$

$$= 33.63 \text{ lb. per square inch.}$$

advantageous in the solution of problems that involve tw[o]
states of the gas. If $(p_1, V_1, T_1)$ and $(p_2, V_2, T_2)$ are the tw[o]
states in question, then

$$\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}. \tag{3}$$

With this equation any consistent system of units may be use[d]

EXAMPLE. Air at a pressure of 14.7 lb. per square inch and having [a]
temperature of 60° F. is compressed from a volume of 4 cu. ft. to a volum[e]
of 1.35 cu. ft. and the final pressure 55 lb. per square inch. The fin[al]
temperature is to be found.

From (3) we have

$$\frac{14.7 \times 4}{60 + 459.6} = \frac{55 \times 1.35}{t_2 + 459.6},$$

whence

$$t_2 = 196.5° \text{ F.}$$

### EXERCISES

**1.** Find values of $B$ for nitrogen, oxygen, and hydrogen.

**2.** Establish a relation between the density of a gas and the value of th[e]
constant $B$ for that gas.

**3.** Find the volume of 13 lb. of air at a pressure of 85 lb. per square inc[h]
and a temperature of 72° C.

**4.** If the air in Ex. 3 expands to a volume of 30 cu. ft. and the fin[al]
pressure is 20 lb. per square inch, what is the final temperature?

**5.** What weight of hydrogen at atmospheric pressure and a temperatu[re]
of 70° F. will be required to fill a balloon having a capacity of 12,000 cu. f[t.]

**6.** A gas tank contains 2.1 lb. of oxygen at a pressure of 120 lb. p[er]
square inch and at a temperature of 60° F. The pressure in the tank shou[ld]
not exceed 300 lb. per square inch and the temperature may rise to 100°[.]
Find the weight of oxygen that may safely be added to the contents of th[e]
tank.

**64. General Equations for Gases.** — The general equation[s]
deduced in Chapter VI take simple forms when applied t[o]
perfect gases. From the characteristic equation

$$pv = BT$$

we obtain by differentiation

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{B}{v}, \qquad \left(\frac{\partial v}{\partial T}\right)_p = \frac{B}{p}. \tag{1}$$

Introducing these values of the derivatives in the general equations (I)–(V) and (VIII), the following equations are obtained:

$$dq = c_v dT + AB\,\frac{T}{v}\,dv, \qquad (\text{I } a)$$

$$dq = c_p dT - AB\,\frac{T}{p}\,dp, \qquad (\text{II } a)$$

$$dq = \frac{AB}{c_p - c_v}\Big(c_p\,\frac{T}{v}\,dv + c_v\,\frac{T}{p}\,dp\Big), \qquad (\text{III } a)$$

$$du = Jc_v dT, \qquad (\text{IV } a)$$

$$di = c_p dT, \qquad (\text{V } a)$$

$$c_p - c_v = AB. \qquad (\text{VIII } a)$$

The first two equations may be still further reduced by means of the characteristic equation to the forms

$$dq = c_v dT + Ap\,dv, \qquad (\text{I } b)$$
$$dq = c_p dT - Av\,dp \qquad (\text{II } b)$$

The ratio $\frac{c_p}{c_v}$ of the two specific heats is usually denoted by $k$. The introduction of this ratio reduces (III $a$) to the simpler form,

$$dq = \frac{A}{k-1}[kp\,dv + v\,dp]. \qquad (\text{III } b)$$

Equation (IV $a$) simply expresses symbolically Joule's law that the change of energy of a gas is proportional to the change in temperature. Equation (I $b$) follows independently from (IV $a$) and the energy equation; thus

$$dq = A\,du + Ap\,dv$$
$$= c_v dT + Ap\,dv, \text{ since } AJ = 1.$$

### EXERCISES

**1.** Deduce (VIII $a$) from (I $b$), (II $b$), and the characteristic equation.

**2.** Derive (V $a$) from (IV $a$) and the equation $pv = BT$.

**3.** From (I $a$), (II $a$), and (III $a$) derive expressions for

$$s = \int \frac{dq}{T}.$$

**4.** From (III $b$) deduce the equation of the adiabatic curve in $pv$-coördinates.

**5.** From (I *a*) derive the equation of an adiabatic in $Tv$-coördinates.

**6.** Using the method of graphical representation explained in Art. 32, show a graphical representation of equation (I *b*).

**65. Specific Heat of Gases.** — If a gas obeys the law $pv = BT$, the specific heat of the gas must be independent of the pressure and also independent of the volume. This principle was shown in Art. 57. The specific heat ($c_p$ or $c_v$) may, however, vary with the temperature, and the results of recent accurate experiments over a wide range of temperature show that such a variation exists. As a general rule, the law of variation is expressed by a linear equation; thus

$$c_v = a + bt,$$
$$c_p = a' + bt.$$

When the range of temperature is large, as in the internal combustion motor, the variation of specific heat with temperature must be taken into account. In the greater number of problems that arise in the technical applications of gaseous media it may be assumed with sufficient accuracy that the specific heat has a mean constant value.

For air the value of $c_p$, as determined by Regnault, is 0.2375 from 0° to 200° C. Recent experiments by Swann give the following values:

            0.24173 at 20° C.
            0.24301 at 100° C.

In ordinary calculations we may take $c_p = 0.24$.

The value of $c_p$ for carbon dioxide ($CO_2$) is usually given as 0.2012. Swann found the values

            0.20202 at 20° C.,
            0.22121 at 100° C.

The value of $c_p$ for other gases for temperatures between 0° and 200° C. may be taken as follows:

            Hydrogen  .  .  .  .  3.4240
            Nitrogen  .  .  .  .  0.2438

Values of the ratio $k = \frac{c_p}{c_v}$ have been determined by various experimental methods. For air the results obtained range from $k = 1.39$ to $k = 1.42$. From the experimental evidence it seems probable that the true value lies between 1.40 and 1.405. In calculations that involve this constant, we shall take the value 1.4 as convenient and sufficiently accurate. For air, therefore, $c_v = 0.24 \div 1.4 = 0.171$.

The values of $k$ and of $c_v$ for other gases may be taken as follows:

|  | $k$ | $c_v$ |
|---|---|---|
| Hydrogen . . . . . | 1.4 | 2.446 |
| Nitrogen . . . . . | 1.4 | 0.174 |
| Oxygen . . . . . | 1.4 | 0.155 |
| Carbon dioxide . . . | 1.3 | 0.162 |
| Carbon monoxide . . | 1.4 | 0.173 |
| Ammonia . . . . . | 1.32 | 0.387 |

If in equation (VIII $a$), $c_v$ is replaced by $\frac{c_p}{k}$, the result is the relation

$$c_p \frac{k-1}{k} = AB.$$

Each of the four magnitudes $c_p$, $k$, $A$, and $B$ have been determined experimentally, and this equation serves as a check.

**66. Intrinsic Energy.** — An expression for the intrinsic energy of a gas is obtained by integrating (IV a). Thus

$$u = J \int c_v dT = J c_v T + u_0, \qquad (1)$$

if $c_v$ is assumed to be constant. The constant of integration $u_0$ is evidently the energy of a unit weight of gas at absolute zero. Since, however, we are not concerned with the absolute value of the energy, but the change of energy for a given change of state, the constant $u_0$ drops out of consideration when differences are taken, and we need make no assumption as to its value. Hence, if $(p_1, v_1, T_1)$ and $(p_2, v_2, T_2)$ are the coördinate of the initial and final states, we have

$$u_2 - u_1 = J c_v (T_2 - T_1). \qquad (2)$$

This formula gives the change of energy per unit weight of gas. For a weight $M$ the formula becomes

$$U_2 - U_1 = JMc_v(T_2 - T_1). \qquad (3)$$

A clear understanding of the physical meaning of formula (2) is of such importance that it is desirable to give a second method of derivation, one based directly upon Joule's law.

According to Joule's law the energy of a unit weight of gas is dependent on the temperature only. Hence, if $T_1$, Fig. 33, is an isothermal, the energy of the gas in the state $A$ is the same as in the state $D$; likewise, the energy of the gas at all points on the isothermal $T_2$ is the same. It follows that the change of energy in passing from temperature $T_1$ to temperature $T_2$ is the same, whether the path is $AB$, $AC$, or $DE$.
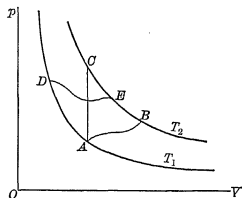
Since the energy is directly proportional to the temperature, the *change* of energy is directly proportional to the *change* of temperature. Hence

$$u_2 - u_1 = a(T_2 - T_1), \qquad (4)$$

in which $a$ denotes a proportionality-factor. To determine the factor $a$, we choose some particular path between the isothermals $T_1$ and $T_2$ (Fig. 33). As we have seen, if this constant is established for one path it holds good for every other path. The most convenient path for this purpose is a constant volume line, as $AC$. The heat required for a rise in temperature from $T_1$ to $T_2$ is

$$q_{12} = c_v(T_2 - T_1).$$

Since in the constant volume change, the external work is zero, we have from the general energy equation

$$Jq_{12} = u_2 - u_1.$$

Comparing these equations, we have

A formula for the change of energy in terms of $p$ and $V$ may be derived from (3). Multiplying and dividing the second member by $B$,

$$U_2 - U_1 = \frac{c_v}{AB}\,(MBT_2 - MBT_1)$$

$$= \frac{c_v}{c_p - c_v}\,(p_2 V_2 - p_1 V_1)$$

$$= \frac{p_2 V_2 - p_1 V_1}{k - 1}. \qquad (5)$$

In (5) $V_2$ and $V_1$ denote the final and initial volumes, respectively, of the weight of gas under consideration; consequently it is not necessary to find the weight $M$ in order to calculate the change of energy. It is to be noted, however, that in using (5) pressures must be taken in pounds per square *foot*.

EXAMPLE. Find the change of energy when 8.2 cu. ft. of air having a pressure of 20 lb. per square inch is compressed to a pressure of 55 lb. per square inch and a volume of 3.72 cu. ft.

Using the value $k = 1.40$,

$$U_2 - U_1 = 144 \times \frac{55 \times 3.72 - 20 \times 8.2}{0.40} = 14{,}616 \text{ ft., lb.}$$

**67. Heat Content.** — The change in heat content corresponding to change of state of a gas is readily derived from the general equation (V $a$).

Thus, $\qquad i = \int c_p dT = c_p T + i_o, \qquad (1)$

and $\qquad i_2 - i_1 = c_p\,(T_2 - T_1). \qquad (2)$

Introducing the factor $AB$ in the second member of (2),

$$i_2 - i_1 = \frac{Ac_p}{AB}(BT_2 - BT_1)$$

$$= A\,\frac{c_p}{c_p - c_v}\,(p_2 v_2 - p_1 v_1)$$

$$= A\,\frac{k}{k - 1}(p_2 v_2 - p_1 v_1). \qquad (3)$$

For a weight of gas $M$, (2) and (3) become, respectively,

$$I_2 - I_1 = Mc_p(T_2 - T_1), \qquad (4)$$

and
$$I_2 - I_1 = A\frac{n}{k-1}(p_2 V_2 - p_1 V_1).$$ (5)

**68. Entropy.** — Expressions for the change of entropy are easily derived from the general equations (I $a$), (II $a$), and (III $a$). Dividing both members of these equations by $T$, we have

$$ds = \frac{dq}{T} = c_v\frac{dT}{T} + AB\frac{dv}{v},$$ (1)

$$ds = \frac{dq}{T} = c_p\frac{dT}{T} - AB\frac{dp}{p},$$ (2)

$$ds = c_p\frac{dv}{v} + c_v\frac{dp}{p}.$$ (3)

Hence for a change of state from $(p_1, v_1, T_1)$ to $(p_2, v_2, T_2)$,

$$s_2 - s_1 = c_v \log_e\frac{T_2}{T_1} + AB \log_e\frac{v_2}{v_1}$$ (4)

$$= c_p \log_e\frac{T_2}{T_1} - AB \log_e\frac{p_2}{p_1}$$ (5)

$$= c_p \log_e\frac{v_2}{v_1} + c_v \log_e\frac{p_2}{p_1}.$$ (6)

These formulæ give the change of entropy per unit weight of gas. For any other weight $M$, the change of entropy is $M(s_2 - s_1)$. Equations (4), (5), and (6) are in reality identical. Each can be derived from either of the other two by means of the relations $pv = BT$, $c_p - c_v = AB$. In the solution of a problem, the equation should be chosen that leads most directly to the desired result.

#### EXERCISES

**1.** From (4), (5), and (6) deduce expressions for the change of entropy corresponding to the following changes of state: (a) isothermal, (b) at constant volume, (c) at constant pressure.

**2.** By making $s_2 - s_1 = 0$ in (4), (5), and (6), deduce relations between $T$ and $v$, $T$ and $p$, and $p$ and $v$ for an adiabatic change of state.

**69. Constant Volume and Constant Pressure Changes.** — In heating a gas at constant volume the external work is zero. Hence,

$$Q = A(U_2 - U_1) = Mc_v(T_2 - T_1).$$ (1)

$$= Me_v \log_e \frac{p_2}{p_1}. \tag{2}$$

en the gas is heated at constant pressure, the external
is

$$W_{12} \quad p(V_2 - V_1). \tag{3}$$

increase of energy is, as in all cases, given by the
on

$$V_2 - V_1 = \frac{pV_2}{k} - \frac{pV_1}{1} = \frac{W_{12}}{k-1}. \tag{4}$$

eat added is, therefore, given by the relation

$$JQ_{12} = V_2 - V_1 + W_{12}$$
$$= \frac{k}{k-1} p(V_2 - V_1); \tag{5}$$

ng the relation $pV = MBT$,

$$Q_{12} = \frac{c_p}{J(c_p - c_v)} MB(T_2 - T_1) = Me_p(T_2 - T_1), \tag{6}$$

might have been written directly.
ncrease of entropy is

$$S_2 - S_1 = Me_p \log_e \frac{T_2}{T_1} = Me_p \log_e \frac{V_2}{V_1}. \tag{7}$$

tions (2) and (7) may
be derived directly from
eneral equations for en-
, Art. 68.
e changes of state just
ered are represented on
'S-plane by curves of the
al form shown in Fig. 34.
curve $AB$, which rep-
ts the constant volume
e, is steeper than the
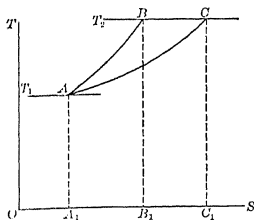


FIG. 34.

$$c_v(T_2 - T_1) < c_p(T_2 - T_1),$$

that is, area $A_1ABB_1 <$ area $A_1ACC_1$.

**70. Isothermal Change of State.** — If $T$ is made constant in the equation $pV = MBT$, the resulting equation

$$pV = p_1V_1 = \text{constant} \tag{1}$$

is the equation of the isothermal curve in $pV$-coördinates. This curve is an equilateral hyperbola. The external work for a change from state 1 to state 2 is given by the general formula

$$W_{12} = \int_{V_1}^{V_2} p\,dV. \tag{2}$$

Using (1) to eliminate $p$, we have

$$W_{12} = p_1V_1 \int_{V_1}^{V_2} \frac{dV}{V} = p_1V_1 \log_e \frac{V_2}{V_1}$$

$$= MBT \log_e \frac{V_2}{V_1}. \tag{3}$$

For the change of energy,

$$U_2 - U_1 = JMc_v(T_2 - T_1) = 0; \tag{4}$$

hence

$$Q_{12} = A W_{12} = Ap_1V_1 \log_e \frac{V_2}{V_1}, \tag{5}$$

and

$$S_2 - S_1 = \frac{Q_{12}}{T} = \frac{Ap_1V_1}{T} \log_e \frac{V_2}{V_1} = ABM \log_e \frac{V_2}{V_1}. \tag{6}$$

Since in isothermal expansion the work done is wholly supplied by the heat absorbed from external sources, it follows that if the expansion is continued indefinitely, the work that may be obtained is infinite. This is also shown by (3), thus:

$$p_1V_1 \int_V^\infty \frac{dV}{V} = p_1V_1 \log_e \frac{\infty}{V} = \infty.$$

**71. Adiabatic Change of State.** — To derive the $pv$-equation of an adiabatic change of state, we may use the general differen-

tial equation containing $p$ and $v$ as variables. The most convenient form of this equation is (III $a$),

$$dq = \frac{A}{k-1}(vdp + kpdv). \qquad (1)$$

During an adiabatic process no heat is supplied to or abstracted from the system; hence in (1) $dq = 0$, and therefore

$$vdp + kpdv = 0. \qquad (2)$$

Separating the variables,

$$\frac{dp}{p} + \frac{kdv}{v} = 0,$$

whence $\qquad \log_e p + k \log_e v = \log C,$

or $\qquad pv^k = C. \qquad (3)$

The relation between temperature and volume or between temperature and pressure is readily derived by combining (3) and the general equation $pv = BT$. Thus from

$$pv^k = C,$$
$$pv = BT,$$

we get by the elimination of $p$,

$$v^{k-1} = \frac{C}{BT};$$

that is, $\qquad Tv^{k-1} = \text{const.} \qquad (4)$

Similarly, by the elimination of $v$, we obtain

$$p^{k-1} = \frac{B^k}{C} T^k;$$

that is, $\qquad \dfrac{p^{\frac{k-1}{k}}}{T} = \text{const.} \qquad (5)$

If we choose some initial state, $p_1$, $v_1$, $T_1$, the constants in (4) and (5) are determined, and the equations may be written in the homogeneous forms

$$\frac{T}{T_1} = \left(\frac{v_1}{v}\right)^{k-1}, \qquad (6)$$

$$\frac{T}{T_1} = \left(\frac{p}{p_1}\right)^{\frac{k-1}{k}} \qquad (7)$$

Since in an adiabatic change the heat $Q$ is zero, the energy equation gives

$$W_{12} = -(U_2 - U_1) = U_1 - U_2;$$

whence using the general expression for the change of energy,

$$W_{12} = \frac{p_1 V_1 - p_2 V_2}{k - 1}. \qquad (8)$$

By means of the equation

$$p_1 V_1^k = p_2 V_2^k,$$

the final volume $V_2$ may be eliminated from (8). The resulting equation is

$$W_{12} = \frac{p_1 V_1}{k - 1}\left[1 - \left(\frac{p_2}{p_1}\right)^{\frac{k-1}{k}}\right]. \qquad (9)$$

EXAMPLE. An air compressor compresses adiabatically 1.2 cu. ft. of free air at atmospheric pressure, 14.7 lb. per square inch) to a pressure of 70 lb. per square inch. Find the work of compression; also the final temperature if the initial temperature is 60° F.

For the final volume, we have

$$V_2 = 1.2\left(\frac{14.7}{70}\right)^{\frac{1}{1.4}} = 0.3936 \text{ cu. ft.}$$

The work of compression is

$$\frac{p_1 V_1 - p_2 V_2}{k - 1} = \frac{144(14.7 \times 1.2 - 70 \times 0.3936)}{0.4} = -3568 \text{ ft.-lb.}$$

The initial temperature being $60° + 459.6° = 519.6°$ absolute, we have for the final temperature

$$T_2 = 519.6\left(\frac{70}{14.7}\right)^{\frac{0.4}{1.4}} = 811.6 \text{ abs.,}$$

whence    $t_2 = 352°$ F.

## 72. Polytropic Change of State. — The changes of state considered in the preceding sections are special cases of the more general change of state defined by the equation

By giving $n$ special values we get the constant volume, constant pressure, and other familiar changes of state. Thus:

$$\text{for } n = 0, \quad pv^0 = \text{const.}, \quad i.e. \quad p = \text{const.}$$

$$\text{for } n = \infty, \quad p^{\frac{1}{\infty}}v = \text{const.}, \quad v = \text{const.}$$

$$\text{for } n = 1, \quad pv = \text{const.}, \quad \text{isothermal.}$$

$$\text{for } n = k, \quad pv^k = \text{const.}, \quad \text{adiabatic.}$$

The curve on the $pV$-plane that represents Eq. (1) is called by Zeuner the **polytropic** curve.

By combining (1) with the characteristic equation $pV = MBT$, as in Art. 71, the following relations are readily derived

$$\frac{T}{T_1} = \left(\frac{V_1}{V}\right)^{n-1} = \left(\frac{p}{p_1}\right)^{\frac{n-1}{n}}. \tag{2}$$

For the external work done by a gas expanding according to the law $\qquad pV^n = p_1 V_1^n = \text{const.},$

from the volume $V_1$ to the volume $V_2$, we have

$$W_{12} = \int_{V_1}^{V_2} p\,dV = p_1 V_1^n \int_{V_1}^{V_2} \frac{dV}{V^n}$$

$$= p_1 V_1^n \left[\frac{V_2^{1-n} - V_1^{1-n}}{1-n}\right]$$

$$= \frac{p_2 V_2 - p_1 V_1}{1-n}. \tag{3}$$

The change of energy, as in every change of state, is

$$U_2 - U_1 = \frac{p_2 V_2 - p_1 V_1}{k-1}. \tag{4}$$

Hence, from the energy equation, we have for the heat absorbed by the gas during expansion

$$JQ_{12} = U_2 - U_1 + W_{12} = \frac{p_2 V_2 - p_1 V_1}{k-1} + \frac{p_2 V_2 - p_1 V_1}{1-n},$$

$$\text{or} \quad JQ_{12} = \frac{k-n}{(k-1)(1-n)}(p_2 V_2 - p_1 V_1). \tag{5}$$

Comparing (3), (4), and (5) we note that the common factor $(p_2 V_2 - p_1 V_1)$ occurs in the second member of each expression.

useful relations :

$$\frac{W}{U_2 - U_1} = \frac{k-1}{1-n},$$ (6)

$$\frac{W}{JQ} = \frac{k-1}{k-n},$$ (7)

$$\frac{JQ}{U_2 - U_1} = \frac{k-n}{1-n}.$$ (8)

These may be combined in the one expression

$$W : U_2 - U_1 : JQ = k-1 : 1-n : k-n.$$ (9)

EXAMPLE. Let a gas expand according to the law

$$p V^{1.2} = \text{const.}$$

Taking $k = 1.4$, we have

$$W : U_2 - U_1 : JQ = 0.4 : -0.2 : 0.2 = 2 : -1 : 1;$$

that is, the external work is double the equivalent of the heat absorbed by the gas and also double the *decrease* of energy.

**73. Specific Heat in Polytropic Changes.** — From Eq. (5), Art. 72, an expression for $Q_{12}$ in terms of the initial and final temperatures of the gas may be readily derived.    Since

$$p_1 V_1 = MBT_1, \text{ and } p_2 V_2 = MBT_2,$$

(5) becomes

$$Q_{12} = \frac{MAB}{k-1} \frac{k-n}{1-n} (T_2 - T_1).$$

But

$$\frac{AB}{k-1} = c_v ;$$

hence,

$$Q_{12} = Mc_v \frac{k-n}{1-n} (T_2 - T_1).$$ (1)

We have, in general,

$$Q_{12} = Mc(T_2 - T_1).$$ (2)

where $c$ denotes the specific heat for the change of state under consideration.    Comparing (1) and (2), it appears that

$$c = c_v \frac{k-n}{1-n}.$$ (3)

Hence, for the polytropic change of state, *the specific heat is con-*

*stant* (assuming $c_v$ to be constant) and its value depends on the value of $n$ in the equation $pV^n = $ const.

It is instructive to observe from (3) the variation of $c$ as $n$ is given different values.  For $n = 0$, $c = kc_v = c_p$, and the change of state is repre-
sented by the constant-
pressure line $aa$, Fig. 35,
36.  For $n = 1$, $c = \infty$, and
the change of state is iso-
thermal (line $b$).  If $n = k$,
then $c = 0$, and the ex-
pansion is adiabatic (line
$d$).  For values of $n$ lying
between 1 and $k$, the value
of $c$ as given by (3) is
evidently negative; that
is, for any curve lying
between the isothermal $b$
and adiabatic $d$, rise of temperature accompanies abstraction of
heat, and *vice versa*.  This is shown by the curve $c$.



FIG. 35.

It will be observed that
in passing through the
region between curves $a$
and $b$, $n$ increases from 0
to 1 and $c$ increases from $c_p$
to $\infty$; then as $n$ keeps on
increasing from 1 to $k$, $c$
changes sign at curve $b$ by
passing through $\infty$, and
increases from $-\infty$ to 0.
As $n$ increases from $n = k$
to $n = +\infty$, $c$ increases
from $c = 0$ to $c = c_v$; and
for $n = \infty$, the constant
volume case, $c$ becomes $c_v$.



FIG. 36.

**74. Determination of $n$.** — It is frequently desirable in experimental investigation to fit a curve determined experimentally — as, for example, the compression curve of the indicator diagram of the air compressor — by a theoretical curve having the general equation $pV^n = c$. To find the value of the exponent $n$ we assume two points on the curve and measure to any convenient scale $p_1$, $p_2$, $V_1$, and $V_2$. Then since

$$p_1 V_1^n = p_2 V_2^n,$$

we have
$$n = \frac{\log p_2 - \log p_1}{\log V_1 - \log V_2}. \qquad (1)$$

EXAMPLE. In a test of an air compressor the following data were determined from the indicator diagram:

At the beginning of compression,     $p_1 = 14.5$ lb. per square inch.
                                                    $V_1 = 2.56$ cu. ft.
At the end of compression,     $p_2 = 68.7$ lb. per square inch.
                                                    $V_2 = 0.77$ cu. ft.

Assuming that the compression follows the law $pV^n = $ const., we have for the value of the exponent

$$n = \frac{\log 68.7 - \log 14.5}{\log 2.56 - \log 0.77} = 1.32.$$

The work of compression is

$$W_{12} = \frac{p_2 V_2 - p_1 V_1}{1 - n} = \frac{144(68.7 \times 0.77 - 15.5 \times 2.56)}{-0.32} = -7100 \text{ ft.-lb.}$$

The increase of intrinsic energy is

$$U_2 - U_1 = \frac{p_2 V_2 - p_1 V_1}{k - 1} = \frac{144(68.7 \times 0.77 - 14.5 \times 2.56)}{0.4} = 5680 \text{ ft.-lb.};$$

and the heat absorbed is

$$Q_{12} = \frac{5680 - 7100}{778} = -1.83 \text{ B. t. u.}$$

The negative sign indicates that heat is given up by the air during compression; this is always the case with a water-jacketed cylinder.

If the initial temperature of the air is 60° F., or 519.6° absolute, the final temperature is

$$T_2 = 519.6 \left(\frac{2.56}{0.77}\right)^{0.32} = 763.2,$$

**1.** A curve whose equation is $pV^n = C$ is passed through the points $p_1 = 40$, $V_1 = 6$ and $p_2 = 16$, $V_2 = 12.5$. Find the value of $n$.

**2.** Air changes state according to the law $pV^n = C$. Find the value of $n$ for which the decrease of energy is one half of the external work; also the value of $n$ for which the heat abstracted is one third of the increase of energy.

**3.** If 32,000 ft.-lb. are expended in compressing air according to the law $pV^{1.28} = $ const., find the heat abstracted, and the change of energy.

**4.** In heating air at constant pressure 35 B. t. u. are absorbed. Find the increase of energy and the external work.

**5.** A mass of air at a pressure of 60 lb. per square inch absolute has a volume of 12 cu. ft. The air expands to a volume of 20 cu. ft. Find the external work and change of energy: (a) when the expansion is isothermal; (b) when the expansion is adiabatic; (c) when the air expands at constant pressure.

**6.** If the initial temperature of the air in Ex. 5 is 62° F., what is the weight? Find the heat added and the change of entropy for each of the three cases.

**7.** Find the specific heat of air when expanding according to the law $pv^{1.25} = $ const. If during the expansion the temperature falls from 90° F. to − 10° F., what is the change of entropy?

**8.** Find the latent heat of expansion of air at atmospheric pressure and at a temperature of 32° F.

**9.** The volume of a fire balloon is 120 cu. ft. The air inside has a temperature of 280° F., and the temperature of the surrounding air is 70° F. Find the weight required to prevent the balloon from ascending, including the weight of the balloon itself.

**10.** A tank having a volume of 35 cu. ft. contains air compressed to 90 lb. per square inch absolute. The temperature is 70° F. Some of the air is permitted to escape, and the pressure in the tank is then found to be 63 lb. per square inch and the temperature 67° F. What volume will be occupied by the air removed from the tank at atmospheric pressure and at 70° F.?

**11.** Air in expanding isothermally at a temperature of 130° F. absorbs 35 B. t. u. Find the heat that must be absorbed by the same weight of air at constant pressure to give the same change of entropy.

**12.** Air in the initial state has a volume of 8 cu. ft. at a pressure of 75 lb. per square inch. In the final state the volume is 18 cu. ft. and the pressure is 38 lb. per square inch. Find: (a) the change of energy; (b) the change in the heat content; (c) the change of entropy.

**13.** Find the work required to compress 30 cu. ft. of free air to a pressure of 65 lb. per square inch, gauge according to the law $pv^{1.3} = $ const. Find the heat abstracted during compression.

recourse to general equations.

SUGGESTION. Let one pound of gas be heated through the temperature range $T_2 - T_1$ (a) at constant volume, (b) at constant pressure. Find an expression for the excess of heat required for the second case and then make use of the energy equation.

**15.** Suppose the specific heat of a gas to be given by the linear relation $c_v = a + bt$. Deduce relations between $p$, $v$, and $T$ for an adiabatic change.

SUGGESTION. Use the general equation $dq = c_v dT + Ap\,dv$ and the characteristic equation $pv = BT$.

## REFERENCES

CHARACTERISTIC EQUATION OF GASES. DEVIATION FROM THE BOYLE-GAY LUSSAC LAW

Zeuner: Technical Thermodynamics (Klein) **1**, 93.
Preston: Theory of Heat, 403.
Barus: The Laws of Gases. N.Y. 1899. (Contains the researches of Boyle and Amagat.)
Regnault: Relation des Experiences **1**.
Weyrauch: Grundriss der Wärme-Theorie **1**, 124, 127.

THE POROUS-PLUG EXPERIMENT. THE ABSOLUTE SCALE OF TEMPERATURE

Thomson and Joule: Phil. Trans. **143**, 357 (1853); **144**, 321 (1854); **152**, 579 (1862).
Rose-Innes: Phil. Mag. (6) **15**, 301. 1908.
Callendar: Phil. Mag. (6) **5**, 48. 1903.
Olszewski: Phil. Mag. (6) **3**, 535. 1902.
Buckingham: Bul. of the Bureau of Standards **3**, 237. 1908.
Preston: Theory of Heat, 695.
Bryan: Thermodynamics, 128.
Chwolson: Lehrbuch der Physik **3**, 546.

SPECIFIC HEAT OF GASES

Regnault: Relation des Experiences **2**, 303.
Swann: Proc. Royal Soc. **82 A**, 147. 1909.
Zeuner: Technical Thermodynamics (Klein) **1**, 116.
Chwolson: Lehrbuch der Physik **3**, 226.
Preston: Theory of Heat, 339, 243.
Weyrauch: Grundriss der Wärme-Theorie **1**, 146.

GENERAL EQUATIONS

Zeuner: Technical Thermodynamics **1**, 122.
Weyrauch: Grundriss der Wärme-Theorie **1**, 152.
Bryan: Thermodynamics, 116.

# CHAPTER VIII

## GASEOUS MIXTURES AND COMPOUNDS. COMBUSTION

**75. Preliminary Statement.** — In the preceding chapter we discussed the properties of simple gases with the implied assumption that chemical action was excluded. For many technical applications a knowledge of such properties is sufficient for the consideration of all questions that arise. On the other hand, investigations of the greatest importance, those relating to combustion in internal combustion motor, have to deal with gaseous substances that enter into chemical combination and (after combustion) with mixtures of inert gases. In the present chapter, therefore, we shall consider some of the properties of gaseous compounds as dependent on chemical composition, and also the properties of mixtures of gases.

**76. Atomic and Molecular Weights.** — Let $E_1$, $E_2$, etc. denote different chemical elements and $a_1$, $a_2$, etc. their corresponding atomic weights. Then if $n_1$, $n_2$, etc. denote the number of atoms of $E_1$, $E_2$, etc. entering into a molecule of a given combination, the molecular weight of the compound is

$$m = n_1 a_1 + n_2 a_2 + \cdots \text{etc.} = \sum na. \tag{1}$$

For the elements that enter into subsequent discussions the atomic weights (referred to the value 16 for oxygen) are as follows:

|           | EXACT VALUE | APPROXIMATE INTEGRAL VALUE |
|-----------|-------------|----------------------------|
| Hydrogen  | 1.008       | 1                          |
| Oxygen    | 16.000      | 16                         |
| Nitrogen  | 14.040      | 14                         |
| Carbon    | 12.000      | 12                         |
| Sulphur   | 32.060      | 32                         |

The approximate integral values are sufficiently exact for practical purposes, in view of unavoidable errors in experimental results.

Using these values, we have as the molecular weights of certain important substances the following :

| | | |
|---|---|---|
| Water | $H_2O$ | $m = 2 \times 1 + 1 \times 16 = 18$ |
| Carbon monoxide | $CO$ | $1 \times 12 + 1 \times 16 = 28$ |
| Carbon dioxide | $CO_2$ | $1 \times 12 + 2 \times 16 = 44$ |
| Ammonia | $NH_3$ | $1 \times 14 + 3 \times 1 = 17$ |
| Methane | $CH_4$ | $1 \times 12 + 4 \times 1 = 16$ |
| Nitrogen | $N_2$ | $2 \times 14 = 28$ |
| Hydrogen | $H_2$ | $2 \times 1 = 2$ |

The composition by weight of a compound is readily determined from the value of $n$, $a$, and $m$. Thus in a unit weight (pound) of compound there is

$$\frac{n_1 a_1}{m} \text{ lb. of element } E_1,$$

$$\frac{n_2 a_2}{m} \text{ lb. of element } E_2, \text{ etc.}$$

For example, $CO_2$ is composed by weight of $\frac{12}{44}$ carbon and $\frac{32}{44}$ oxygen, $NH_3$ is composed by weight of $\frac{14}{17}$ nitrogen and $\frac{3}{17}$ hydrogen.

**77. Relations between Gas Constants.** — If in the characteristic equation $pv = BT$, which holds approximately for any gaseous substance (mixture or compound), we replace $v$ by $\frac{1}{\gamma}$ we have

$$B\gamma = \frac{p}{T}. \qquad (1)$$

Here $\gamma$ denotes the weight of unit volume of the gas. From this relation it is seen that for a chosen standard pressure and temperature, for example, atmospheric pressure and $0°$ C., the product $B\gamma$ is the same for all gases. But since the specific weight $\gamma$ of a gas is directly proportional to the molecular weight $m$, it follows that the product $Bm$ is likewise the same

for all gases.  Denoting this product $Bm$ by $R$, we have for the characteristic equation of any gas

$$pv = \frac{R}{m}T. \qquad (2)$$

From (1) we obtain the relation

$$R = Bm = \frac{pm}{\gamma T}; \qquad (3)$$

hence the numerical value of $R$ can be found when the values of $m$ and $\gamma$ are accurately known for any one gas.  From Morley's accurate experiments, we have for oxygen $\gamma = 0.089222$ lb. per cubic foot at atmospheric pressure and $32°$ F.; and for oxygen $m = 32$.  Inserting these numerical values in (3), we obtain

$$R = \frac{2116.3 \times 32}{0.089222 \times 491.6} = 1544.$$

The constant $R$ is called the **universal gas constant.**  From it the characteristic constant $B$ of any gas can be determined at once from the molecular weight.  Thus for carbonic acid we have

$$B = \frac{1544}{44} = 35.09.$$

From the general formula

$$c_p - c_v = AB \qquad (4)$$

for the difference between the specific heats of a gas, we have

$$c_p - c_v = \frac{AR}{m} = \frac{1544}{777.64}\frac{1}{m} = \frac{1.9855}{m}. \qquad (5)$$

This relation gives a ready method of calculating one specific heat from the other when the molecular weight $m$ is known.  Thus for $CO_2$, $c_p - c_v = \frac{1.9855}{44} = 0.0451$, and if $c_p = 0.2020$, we have $c_v = 0.2020 - 0.0451 = 0.1569$.

It is convenient to express the specific weight $\gamma$ and the specific volume $v$ of a gas in terms of the molecular weight $m$.  These constants are referred to standard conditions, namely, atmospheric pressure and a temperature of $32°$ F.  From (3) we have

$$\gamma = \frac{p}{RT}m, \qquad (6)$$

whence inserting the numerical values, $p = 2116.8$, $R = 1941$,

$T = 491.6$,

$$\gamma = 0.002788 \; m. \tag{7}$$

For the normal specific volume, we have

$$v = \frac{1}{\gamma} = \frac{RT}{p} \frac{1}{m}, \tag{8}$$

or

$$v = \frac{358.65}{m}. \tag{9}$$

From the preceding relations, the following values are readily found for the constants of certain gases.

| Gas | Chemical Symbol | Molecular Weight $m$ | Characteristic Constant $B$ | Difference of Specific Heats $c_p - c_v$ | Weight per cubic foot at 32° F. and Atmospheric Pressure | Volume per pound at 32° F. and Atmospheric Pressure |
|---|---|---|---|---|---|---|
| Oxygen . . . . | $O_2$ | 32 | 48.249 | 0.0621 | 0.089222 | 11.208 |
| Hydrogen . . . | $H_2$ | 2.016 | 765.86 | 0.9849 | 0.005621 | 177.9 |
| Nitrogen . . . | $N_2$ | 28.08 | 54.985 | 0.0707 | 0.07829 | 12.773 |
| Carbon dioxide . | $CO_2$ | 44 | 35.09 | 0.0451 | 0.12268 | 8.151 |
| Carbon monoxide | $CO$ | 28 | 55.142 | 0.0700 | 0.078028 | 12.81 |
| Methane . . . . | $CH_4$ | 16.032 | 96.314 | 0.1238 | 0.04470 | 22.37 |
| Ethylene . . . . | $C_2H_4$ | 28.032 | 55.079 | 0.0708 | 0.078036 | 12.794 |
| Air . . . . . | —— | —— | 53.34 | 0.0686 | 0.08071 | 12.39 |

**78. Mixtures of Gases. Dalton's Law.** — A mixture of several gases that have no chemical action on each other obeys very closely the following law first stated by Dalton:

*The pressure of the gaseous mixture upon the walls of the containing vessel is the sum of the pressures that the constituent gases would exert if each occupied the vessel separately.*

Like Boyle's law, Dalton's law is obeyed strictly by mixtures of ideal perfect gases only. Mixtures of actual gases show deviations from the law, these being greater with gases most easily liquefied. For the purpose of technical thermodynamics, however, it is permissible to assume the validity of Dalton's law even in the case of a mixture of vapors.

Let $V$ denote the volume of a given mixture, $M_1$, $M_2$, $M_3$, . . . the weights of the constituent gases, and $B_1$, $B_2$, $B_3$, . . . the

constants for those constituents; then the **partial pressures** of
the constituents, that is, the pressures they would exert sepa-
rately if occupying the volume $V$, are:

$$p_1 = \frac{M_1 B_1 T}{V}, \; p_2 = \frac{M_2 B_2 T}{V}, \; p_3 = \frac{M_3 B_3 T}{V}, \; \cdots \qquad (1)$$

According to Dalton's law the pressure $p$ of the mixture is

$$p = p_1 + p_2 + p_3 + \cdots = \frac{T}{V}(M_1 B_1 + M_2 B_2 + M_3 B_3 + \cdots). \qquad (2)$$

Furthermore, if $M$ is the weight of the mixture,

$$M = M_1 + M_2 + M_3 + \cdots = \Sigma M_i. \qquad (3)$$

Let us now introduce a magnitude $B_m$ defined by the equation

$$M B_m = M_1 B_1 + M_2 B_2 + M_3 B_3 + \cdots ; \qquad (4)$$

then (2) takes the form

$$p V = M B_m T. \qquad (5)$$

The constant $B_m$ may be regarded as the characteristic con-
stant of the mixture. It is obtained from (4), which may be
written in the more convenient form

$$B_m = \frac{\Sigma M_i B_i}{M}. \qquad (6)$$

The partial pressures may readily be expressed in terms of
the pressure of the mixture. Thus combining (1) and (5),
we obtain

$$\frac{p_1}{p} = \frac{M_1 B_1}{M B_m}, \; \frac{p_2}{p} = \frac{M_2 B_2}{M B_m}, \; \text{etc.} \qquad (7)$$

EXAMPLE. A fuel gas has the composition by weight given below. The
value of the constant $B_m$ for this gas is found as indicated by the following
arrangement:

| CONSTITUENTS | WEIGHT | $B$ | $MB$ |
|---|---|---|---|
| CO$_2$ . . . . . . | 0.04 | 35.09 | 1.4036 |

Since $M = 1$ and $\Sigma MB = 103.24$, we have

$$B_m = 103.24.$$

The apparent molecular weight of the mixture is

$$m = \frac{1544}{103.24} = 14.96,$$

and the weight per cubic foot under standard conditions is, therefore,

$$\gamma = 0.002788 \times 14.96 = 0.0417 \text{ lb.}$$

**79. Volume Relations.** — Let $V_1$, $V_2$, $V_3$, $\cdots$, denote the volume that would be occupied at pressure $p$ and temperature $T$ by several gaseous constituents; then if $B_1$, $B_2$, $B_3$, $\cdots$, denote the characteristic constants of these gases, we have

$$p V_1 = M_1 B_1 T, \quad p V_2 = M_2 B_2 T, \quad p V_3 = M_3 B_3 T, \cdots. \quad (1)$$

If now the gases are mixed, keeping the same pressure and temperature, the mixture will occupy the volume

$$V = V_1 + V_2 + V_3 + \cdots, \quad (2)$$

and its weight will be necessarily

$$M = M_1 + M_2 + M_3 + \cdots \quad (3)$$

Taking $B_m$ as the characteristic constant of the mixture, we have

$$p V = M B_m T. \quad (4)$$

Comparing (1) and (4), we obtain the relations

$$\frac{V_1}{V} = \frac{M_1 B_1}{M B_m}, \quad \frac{V_2}{V} = \frac{M_2 B_2}{M B_m}, \quad \cdots \quad (5)$$

It will be seen that the volume ratios given by (5) are equal to the pressure ratios given by (7) of Art. 78.

If $\gamma$ denotes the weight of a unit volume (1 cu. ft.) of gas, then

$$\gamma = \frac{1}{v} = \frac{M}{V}. \quad (6)$$

For the several constituents of a mixture, we have, therefore,

$$M_1 = \gamma_1 V_1, \quad M_2 = \gamma_2 V_2, \quad M_3 = \gamma_3 V_3, \cdots, \quad (7)$$

and for the mixture

Similarly, we have for the specific volume of the mixture

$$v = \frac{V}{M} = \frac{1}{M}(v_1 M_1 + v_2 M_2 + v_3 M_3 + \cdots). \quad (9)$$

Since $\gamma = 0.002788\, m = km$ (see Art. 77), we have from (7)

$$M_1 = km_1 V_1, \quad M_2 = km_2 V_2, \cdots,$$

and

$$M = M_1 + M_2 + \cdots = k\Sigma m_i V_i.$$

Therefore,

$$\frac{M_1}{M} = \frac{m_1 V_1}{\Sigma m_i V_i}, \quad \frac{M_2}{M} = \frac{m_2 V_2}{\Sigma m_i V_i}, \cdots \quad (10)$$

If further we denote by $m_m$ the quotient $\dfrac{\gamma_m}{k}$, we have from (8)

$$m_m = \frac{1}{V}\Sigma m_i V_i. \quad (11)$$

The constant $m_m$ we may regard as the apparent molecular weight of the mixture, and from it we may determine the constants $B_m$, $c_p - c_v$, $\gamma$, and $v$ of the mixture.

Equations (10) and (11) are useful in the investigation of a mixture when the composition *by volume* is given. The following example shows the method of procedure.

EXAMPLE. A producer gas has the composition by volume given below. Required the composition by weight and the constants of the mixture.

| CONSTITUENTS | VOLUME $V$ | $m$ | $mV$ | $\dfrac{mV}{\Sigma m_i V_i}$ |
|---|---|---|---|---|
| $H_2$ | 0.08 | 2 | 0.16 | 0.006 |
| CO | 0.22 | 28 | 6.16 | 0.2308 |
| $CH_4$ | 0.024 | 16 | 0.384 | 0.0144 |
| $CO_2$ | 0.066 | 44 | 2.904 | 0.1088 |
| $N_2$ | 0.61 | 28 | 17.08 | 0.64 |
| | 1.000 | | 26.688 | 1.000 |

According to (10) the last column gives the composition by weight. The constant $m_m$ is 26.688; hence we have

$$B_m = \frac{1544}{26.688} = 57.85. \qquad \gamma = 0.002788 \times 26.688 = 0.07441.$$

$$c_p - c_v = \frac{1.9855}{26.688} = 0.0744. \qquad v = \frac{358.65}{26.688} = 13.44.$$

80. Combustion : Fuels. — The elements that chiefly combine with oxygen to produce reactions characterized by the evolution of heat are hydrogen and carbon. Compounds that are made

up largely of these elements are fuels; for example, methane $CH_4$, benzol $C_6H_6$, alcohol $C_2H_6O$. The product of complete combustion of hydrogen is $H_2O$, water; that of complete combustion of carbon is $CO_2$, carbon dioxide. Sulphur is a possible constituent of fuels, and the product of combustion is $SO_2$, sulphur dioxide.

Chemical reactions are, in general, characterized by the evolution or absorption of heat. The union of a combustible with oxygen is accompanied by the evolution of a considerable quantity of heat, and the heat evolved by the combustion of a unit weight of the combustible is called the **heating value** of the combustible. The heating value of hydrogen alone or carbon alone must be determined by experiment, but the heating value of a compound of C and H may be calculated, at least approximately.

Hydrogen and compounds containing hydrogen have two heating values, called respectively the higher and the lower. This arises from the fact that the product $H_2O$ may be either water or steam. If the temperature after combustion is above 212°, the product exists as vapor, and the heat necessary to keep it in the vapor form is not set free; hence, we have the lower heating value. If, however, the vapor condenses, the heat of vaporization is recovered, and we have the higher heating value.

The heating values of various fuels are given in the following table.

| FUEL | | B. T. U. PER POUND | | B. T. U. PER CUBIC FOOT AT 32° F. |
| | | High | Low | Low |
| --- | --- | --- | --- | --- |
| Hydrogen . . . . | $H_2$ | 62100 | 52230 | 294 |
| Carbon . . . . | $C_2$ | 14600 | 14600 | — |
| Carbon monoxide . | CO | 4380 | 4380 | 342 |
| Methane . . . . | $CH_4$ | 23842 | 21385 | 956 |
| Ethylene . . . . | $C_2H_4$ | 21429 | 20025 | 1563 |
| Acetylene . . . . | $C_2H_2$ | 21429 | 20673 | 1499 |

The heating value of a fuel mixture is determined from the heating values of the separate constituents. Denoting by $M$,

$M_2$, $\cdots$, the weights of the constituents, by $H_1$, $H_2$, $H_3$, $\cdots$, the corresponding heating values per pound, and by $H_m$ the heating value of the mixture, we have

$$(M_1 + M_2 + M_3 + \cdots) H_m = M_1H_1 + M_2H_2 + M_3H_3 + \cdots,$$

whence

$$H_m = \frac{\Sigma M_i H_i}{M}. \qquad (1)$$

By a similar procedure the heating value per cubic foot may be obtained when the composition by volume is given.

EXAMPLE. Required the lower heating value of the producer gas described in the example of Art. 79.

For the heating value per pound we have

|        | $M$ | $H$ | $MH$ |
|--------|--------|--------|--------|
| $H_2$ . . . . . . . . | 0.006 | 52230 | 313.38 |
| CO . . . . . . . | 0.2308 | 4380 | 1010.9 |
| $CH_4$ . . . . . . . | 0.0144 | 21385 | 307.94 |
|        |        |        | $\Sigma MH = \overline{1632.2}$ |

Since $M = 1$, we have $H_m = \Sigma\, MH = 1632.2$ B. t. u. per lb.

The heating value per cubic foot (at 32° F. and atmospheric pressure) is evidently the product

$$H_m \gamma = 1632.2 \times 0.07441 = 121.5 \text{ B. t. u.}$$

Or from the composition, we have

|        | $V$ | $H$ | $VH$ |
|--------|--------|--------|--------|
| $H_2$ . . . . . . . . | 0.08 | 294 | 23.52 |
| CO . . . . . . . | 0.22 | 342 | 75.24 |
| $CH_4$ . . . . . . . | 0.024 | 956 | 22.94 |
|        |        |        | $\overline{121.7}$ B. t. u. per cu. ft. |

The difference in the two results is due to approximations in the calculation, and is of no importance.

**81. Air required for Combustion and Products of Combustion.** —The oxygen required for the complete combustion of a given fuel is determined from the equation of the reaction. For example, the combustion of methane, $CH_4$, is given by the equation

$$CH_4 + 2\,O_2 = CO_2 + 2\,H_2O\,;$$
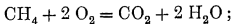
and two molecules of $H_2O$. Since by Avogadro's law the volumes are proportional to the numbers of molecules entering into the equation, we may also read the preceding chemical equation as follows: two volumes of oxygen combine with one volume of $CH_4$, producing one volume of $CO_2$ and two volumes of $H_2O$.

Taking the molecular weights of the four gases into consideration, we may write the equation

$$16 + 2 \times 32 = 44 + 2 \times 18.$$

From this it appears that one pound of $CH_4$ requires for complete combustion $\frac{64}{16} = 4$ lb. of oxygen and the products are $\frac{44}{16} = 2.75$ lb. of $CO_2$ and $\frac{36}{16} = 2.25$ lb. of $H_2O$. Since oxygen is 23 per cent of air by weight, the weight of air required for the complete combustion of one pound of $CH_4$ is $\frac{4}{0.23} = 17.4$ lb. The *volume* of air required for the burning of one cubic foot of $CH_4$ is $\frac{2}{0.21} = 9.52$ cu. ft.

We may generalize the process illustrated by the preceding example as follows:

Let the gaseous fuel have the composition $C_{n_1}H_{n_2}O_{n_3}$, and let $a_1, a_2, a_3$ denote the atomic weights of C, H, and O, respectively. Then the molecular weight of the fuel in question is

$$m = a_1 n_1 + a_2 n_2 + a_3 n_3.$$

The equation of the reaction may be written

$$C_{n_1}H_{n_2}O_{n_3} + xO_2 = yCO_2 + zH_2O,$$
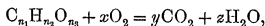
where $x$, $y$, and $z$ indicate the number of molecules of the respective substances. Comparing the two members of the equation, we find

$$y = n_1,$$
$$z = \tfrac{1}{2} n_2,$$
$$n_3 + 2x = 2y + z,$$

whence     $x = \tfrac{1}{2}(2y + z - n_3) = n_1 + \tfrac{1}{4}n_2 - \tfrac{1}{2}n_3.$

for alcohol $C_2H_6O$, $x = 2 + \frac{6}{4} - \frac{1}{2} = 3$, $y = 2$, and $z = 3$, showing that for the combustion of one cubic foot of alcohol vapor, 3 cu. ft. of oxygen are required, and the resulting products are 2 cu. ft. of $CO_2$ and 3 cu. ft. of $H_2O$.

To get the relations between the weights of the substances under consideration we must introduce the molecular weights in the reaction equation. Thus we obtain

$$m + 2\,a_3 x = y(a_1 + 2\,a_3) + z\,(2\,a_2 + a_3),$$

from which follow the ratios:

$$x' = \frac{\text{weight of oxygen}}{\text{weight of fuel}} = \frac{2\,a_3 x}{m} = \frac{a_3}{m}(2\,n_1 + \tfrac{1}{2}n_2 - n_3);$$

$$y' = \frac{\text{weight of } CO_2}{\text{weight of fuel}} = \frac{y(a_1 + 2\,a_3)}{m} = \frac{n_1}{m}(a_1 + 2\,a_3);$$

$$z' = \frac{\text{weight of } H_2O}{\text{weight of fuel}} = \frac{z(2\,a_2 + a_3)}{m} = \frac{n_2}{2\,m}(2\,a_2 + a_3).$$

If we make use of the integral values of the atomic weights, namely, $a_1 = 12$, $a_2 = 1$, $a_3 = 16$, we have for the complete combustion of one pound of the combustible:

$$x' = \text{oxygen required} = \frac{16}{m}(2\,n_1 + \tfrac{1}{2}n_2 - n_3) \text{ lb.};$$

$$y' = CO_2 \text{ produced} = 44\,\frac{n_1}{m} \text{ lb.};$$

$$z' = H_2O \text{ produced} = 9\,\frac{n_2}{m} \text{ lb.}$$

Taking alcohol, $C_2H_6O$, for example, we have

$$n_1 = 2,\ n_2 = 6,\ n_3 = 1,\ m = 2 \times 12 + 6 \times 1 + 16 = 46,\ \text{whence}$$

$$x' = \tfrac{16}{46}(2 \times 2 + \tfrac{1}{2} \times 6 - 1) = 2.087;$$

$$y' = \frac{44 \times 2}{46} = 1.913;$$

$$z' = \frac{9 \times 6}{46} = 1.174.$$

The weight of air required per pound of alcohol is

and the weight of nitrogen appearing among the products of combustion is, therefore, $9.075 - 2.087 = 6.988$ lb.

If a gaseous fuel is a mixture of several combustible constituents, the values of $x'$, $y'$, and $z'$ may be found for the individual constituents separately. Then if $M_1$, $M_2$, $M_3$, $\cdots$, are the weights of the constituents respectively, we have

$$x' = \frac{\Sigma Mx'}{M}, \quad y' = \frac{\Sigma My'}{M}, \quad z' = \frac{\Sigma Mz'}{M}.$$

EXAMPLE. For the producer gas heretofore investigated, we have the following values:

|        | $M$    | $x'$  | $y'$  | $z'$  | $Mx'$  | $My'$  | $Mz'$  |
|--------|--------|-------|-------|-------|--------|--------|--------|
| $H_2$  | 0.006  | 8     | 0     | 9     | 0.048  | 0      | 0.054  |
| CO     | 0.2308 | 0.571 | 1.571 | 0     | 0.1318 | 0.3626 | 0      |
| $CH_4$ | 0.0144 | 4     | 2.75  | 2.25  | 0.0576 | 0.0396 | 0.0324 |
| $CO_2$ | 0.1088 | 0     | 1     | 0     | 0      | 0.1088 | 0      |
| $N_2$  | 0.64   | 0     | 0     | 0     | 0      | 0      | 0      |
|        | 1.00   |       |       |       | 0.2374 | 0.511  | 0.0864 |

One pound of the gas requires 0.2374 lb. of oxygen for complete combustion. The weight of air required is, therefore, $0.2374 \div 0.23 = 1.032$ lb., and this air brings with it $1.032 - 0.2374 = 0.7946$ lb. of nitrogen. We have then the following balance:

| CONSTITUENTS | | PRODUCTS | |
|---|---|---|---|
| Fuel gas | 1.00 lb. | $CO_2$ | 0.511 lb. |
| Air | 1.032 | $H_2O$ | 0.0864 |
|  | 2.032 lb. | $N_2$ | $0.64 + 0.7946 = 1.4346$ |
|  |  |  | 2.032 lb. |

Taking the composition by volume, the following results are found:

|        | $V$   | $x$ | $y$ | $z$ | $Vx$  | $Vy$  | $Vz$  |
|--------|-------|-----|-----|-----|-------|-------|-------|
| $H_2$  | 0.08  | 0.5 | 0   | 1   | 0.04  | 0     | 0.08  |
| CO     | 0.22  | 0.5 | 1   | 0   | 0.11  | 0.22  | 0     |
| $CH_4$ | 0.024 | 2   | 1   | 2   | 0.048 | 0.024 | 0.048 |
| $CO_2$ | 0.066 | 0   | 1   | 0   | 0     | 0.066 | 0     |
| $N_2$  | 0.61  | 0   | 0   | 0   | 0     | 0     | 0     |
|        | 1.00  |     |     |     | 0.198 | 0.31  | 0.128 |

Since 0.198 cu. ft. of oxygen is required per cubic foot of gas, the volume of air required is $0.198 \div 0.21 = 0.943$ cu. ft., and the volume of nitrogen corresponding to this is $0.943 - 0.198 = 0.745$ cu. ft., which is added to the 0.61 cu. ft. in the fuel gas. The volume of gas and air before combustion is $1 + 0.943 = 1.943$ cu. ft., and the volume of the products is $0.31 + 0.128 + 0.61 + 0.745$

**82. Specific Heat of Gaseous Products.** — In deducing the special equations for gases we assumed that the specific heat of any gas remains constant at all pressures and temperatures. In many technical applications this assumption is sufficiently near the truth and is justified by the simplicity of the analysis based upon it; but when a very wide range of temperature is encountered, as in the case of the internal combustion motor, the assumption of constant specific heat is no longer permissible.

The gaseous products that come under consideration may be separated into two classes. (1) The simple or diatomic gases, as nitrogen, oxygen, air, etc.; (2) the compounds, like carbon dioxide ($CO_2$) and steam ($H_2O$), which may be regarded as superheated vapors rather than as gases. For the products in the first group, the law $pv = BT$ holds quite exactly, and, therefore (see Art. 57), the specific heat must be independent of the pressure, but may vary with the temperature. The substances in the second group, which are comparatively near the liquid state, do not follow the gas law closely, and for these the specific heat may vary with the pressure as well as with the temperature. The character of the variation of the specific heat of steam is shown in Fig. 71, Art. 133. At the lower temperatures the specific heat increases with the pressure, but as the temperature rises the influence of the pressure becomes negligible and the specific heat rises with the temperature. It is probable that the specific heat of $CO_2$ varies in somewhat the same manner.

Experiments on the specific heats of various gases show that in general the specific heat rises with the temperature, and that the law governing the variation is expressed sufficiently well by the simple linear equation

$$c = a + bt.$$

The formulas, as usually stated, give *molecular* specific heats, the molecular specific heat being numerically equal to the thermal capacity of a weight of the substance expressed by the molecular weight. Thus, since the molecular weight of carbon monoxide (CO) is 28, the molecular specific heat of CO is numerically equal to the thermal capacity of 28 pounds of CO. We may denote molecular specific heat by the product $mc$. It

is an interesting fact that while the spe... ... ...p... .... .....
gases are quite different, the molecular specific heats are substantially identical.

The results of Langen's experiments are given by the following formulas, in which $t$ denotes temperature in degrees C.

For all simple gases

$$mc_v = 4.8 + 0.0012\,t. \tag{1}$$

For carbon dioxide

$$mc_v = 6.7 + 0.0052\,t. \tag{2}$$

For water vapor

$$mc_v = 5.9 + 0.0043\,t. \tag{3}$$

Dividing by the appropriate value of the molecular weight $m$, the heat capacity of a gas per unit weight is readily found. Thus for oxygen $m = 32$, and from (1) we have

$$c_v = 0.15 + 0.0000375\,t;$$

for $CO_2$, $m = 44$, and from (2) we obtain

$$c_v = 0.1523 + 0.0001182\,t.$$

Formulas (1), (2), and (3) give molecular specific heats at constant volume. From the relation $m(c_p - c_v) = 1.9855$ (see Art. 77), we have approximately $mc_p = mc_v + 2$. Therefore, from the preceding equations we obtain corresponding equations for $c_p$, namely:

$$mc_p = 6.8 + 0.0012\,t; \tag{4}$$

$$mc_p = 8.7 + 0.0052\,t; \tag{5}$$

$$mc_p = 7.9 + 0.0043\,t. \tag{6}$$

For temperatures F. the preceding formulas become respectively:

1. For simple gases

$$\left.\begin{aligned} c_v &= \frac{1}{m}(4.77 + 0.000667\,t) \\ &= \frac{1}{m}(4.48 + 0.000667\,T) \end{aligned}\right\}. \tag{7}$$

$$\left.\begin{aligned} c_p &= \frac{1}{m}(6.75 + 0.000667\,t) \\ &= \frac{1}{m}(6.46 + 0.000667\,T) \end{aligned}\right\}. \tag{8}$$

2. For carbon dioxide

$$c_v = 0.15 + 0.000066\,t \\ = 0.12 + 0.000066\,T \Big\} \qquad (9)$$

$$c_p = 0.195 + 0.000066\,t \\ = 0.165 + 0.000066\,T \Big\}. \qquad (10)$$

3. For superheated water vapor

$$c_v = 0.324 + 0.000133\,t \\ = 0.263 + 0.000133\,T \Big\} \qquad (11)$$

$$c_p = 0.435 + 0.000133\,t \\ = 0.374 + 0.000133\,T \Big\}. \qquad (12)$$

**83. Specific Heat of a Gaseous Mixture.** — Let $M_1$, $M_2$, $\cdots$ respectively, denote the weights of the constituents of a mixture and $c_{v_1}$, $c_{v_2}$, $\cdots$, the corresponding specific heats. It is assumed that for a given temperature rise each constituent requires the same quantity of heat when mixed with other constituents as it would if separated from them. Hence, the heat $Q$ required for a temperature change $T_2 - T_1$ is

$$Q = M_1 c_{v_1}(T_2 - T_1) + M_2 c_{v_2}(T_2 - T_1) + \cdots.$$

But we have also

$$Q = M c_v (T_2 - T_1),$$

where $M = M_1 + M_2 + \cdots$, and $c_v$ denotes the specific heat of the mixture. Combining these expressions, we obtain

$$M c_v = M_1 c_{v_1} + M_2 c_{v_2} + \cdots,$$

or

$$c_v = \frac{\Sigma M c_v}{M}. \qquad (1)$$

Likewise,

$$c_p = \frac{\Sigma M c_p}{M}. \qquad (2)$$

EXAMPLE. Find the specific heat $c_v$ of a mixture of 1 lb. of the producer gas described in the example of Art. 79 and 1.25 lb. of air, which is about 20 per cent in excess of the air required for complete combustion. Find also the specific heat $c_v$ of the products of combustion.

Of the 1.25 lb. of air furnished 0.2875 lb. is oxygen and 0.9625 lb. is

nitrogen. Adding this nitrogen to the *back lb. in the* gas, the total nitrogen is 1.6025 lb. We have

| | $M$ | $c_v$ | $Mc_v$ |
|---|---|---|---|
| $H_2$ | 0.008 | 2 | $\frac{0.008}{2}(1.48 + 0.000667\,T)$ |
| $CO$ | 0.2308 | 28 | $\frac{0.2308}{28}(1.48 + 0.000667\,T)$ |
| $CH_4$ | 0.0144 | 16 | $\frac{0.0144}{16}(1.48 + 0.000667\,T)$ |
| $CO_2$ | 0.1088 | | $0.1088(0.12 + 0.000086\,T)$ |
| $N_2$ | 1.6025 | 28 | $\frac{1.6025}{28}(1.48 + 0.000667\,T)$ |
| $O_2$ | 0.2875 | 32 | $\frac{0.2875}{32}(1.48 + 0.000667\,T)$ |

$$\Sigma M = 2.25 \qquad \Sigma Mc_v = 0.3641 + 0.00005917\,T$$

Hence,
$$c_v = \frac{0.3641 + 0.00005917\,T}{2.25} = 0.1618 + 0.00002643\,T.$$

For the products of combustion, we have (see Art. 81)

| | $M$ | $Mc_v$ |
|---|---|---|
| $CO_2$ | 0.511 | $0.511(0.12 + 0.000086\,T)$ |
| $H_2O$ | 0.0861 | $0.0861(0.263 + 0.000133\,T)$ |
| $N_2$ | 1.6025 | $\frac{1.6025}{28}(1.48 + 0.000667\,T)$ |
| $O_2$ | 0.0501 | $\frac{0.0501}{32}(1.48 + 0.000667\,T)$ |

$$\Sigma M = 2.25 \qquad \Sigma Mc_v = 0.31715 + 0.00008444\,T$$

Therefore,
$$c_v = \frac{0.31715 + 0.00008444\,T}{2.25} = 0.144 + 0.0000375.63\,T.$$

## 84. Adiabatic Changes with Varying Specific Heats. —

When the specific heat of a gas is taken as a function of temperature, thus

$$c_v = a + bT,$$
$$c_p = a' + bT,$$

the simple relations derived in Art. 71 no longer apply. We have as before, however,

$$dq = c_v\,dT + Ap\,dv, \tag{1}$$
$$c_p - c_v = AB, \tag{2}$$
$$c_p = c_v \tag{3}$$

For an adiabatic change $dq = 0$; hence from (1), we have
$$c_v dT = -Apdv,$$
or
$$(a + bT)dT = -ABT\frac{dv}{v}. \tag{4}$$

From (4) we obtain upon integration
$$a \log_e \frac{T_2}{T_1} + b(T_2 - T_1) = AB \log_e \frac{v_1}{v_2}. \tag{5}$$

From the characteristic equation $pv = BT$, we have $\frac{T_2}{T_1} = \frac{p_2 v_2}{p_1 v_1}$, therefore (5) becomes
$$a \log_e \frac{p_2 v_2}{p_1 v_1} + b(T_2 - T_1) = AB \log_e \frac{v_1}{v_2},$$
or
$$a \log_e \frac{p_2}{p_1} + b(T_2 - T_1) = (AB + a)\log_e \frac{v_1}{v_2}. \tag{6}$$

Finally, if in (5) we substitute for $\frac{v_1}{v_2}$ its equivalent $\frac{T_1 p_2}{T_2 p_1}$, we obtain
$$a \log_e \frac{T_2}{T_1} + b(T_2 - T_1) = AB \log_e \frac{p_2}{p_1} - AB \log_e \frac{T_2}{T_1};$$
whence
$$AB \log_e \frac{p_2}{p_1} = (a + AB) \log_e \frac{T_2}{T_1} + b(T_2 - T_1). \tag{7}$$

For the external work of adiabatic expansion, we have
$$W = U_1 - U_2 = JM \int_{T_2}^{T_1} c_v dT$$
$$= JM \int_{T_2}^{T_1} (a + bT) dT$$
$$= JM \left[ a(T_1 - T_2) + \frac{b}{2}(T_1^2 - T_2^2) \right]. \tag{8}$$

Equations (5), (6), and (7) are readily applied when the initial and final temperatures are given. When, however, the final temperature is required, the equation in $T$ is transcendental and its solution requires a process of successive approximations. The illustrative example of the following article shows the method of procedure.

85. Temperature of Combustion. — A close analysis of the process of burning a fuel gas under given conditions involves complicated equations, especially when the specific heat is taken as variable. The temperature and pressure at the end of the pro-

cess are the results usually desired, and these may be found, at least approximately, by a simple method.

Let $T_1$ denote the temperature of the gaseous mixture at the beginning of combustion and $T_2$ the desired final temperature; $H$ the lower heating value of the fuel per pound, and $M$ the combined weight of one pound of fuel and the air furnished for combustion ($M$ is evidently also the weight of the products of combustion). It is assumed that the combustion is complete, and that the heat $H$ is all expended in raising the temperature of the products from $T_1$ to $T_2$. As a matter of fact, the composition of the mixture during the combustion process is continually changing, but as the specific heat changes but little, it is considered permissible to base the calculation on the final products alone. We have then

$$H = M \int_{T_1}^{T_2} (a + bT)dT, \qquad (1)$$

where $a + bT$ is the expression for the variable specific heat of the products. From (1) we obtain upon integration

$$a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) = \frac{H}{M}, \qquad (2)$$

from which $T_2$ may be calculated.

EXAMPLE. The mixture of producer gas and air in the example of Art. 83 is compressed adiabatically from an initial pressure of 14.7 lb. per square inch to a pressure of 150 lb. per square inch absolute. The initial temperature is 530° absolute. The mixture is then burned at constant volume and the products of combustion expand adiabatically to the initial volume. Required the temperature and pressure after combustion, and after expansion. Also the work of compression and the work of expansion.

The characteristic constants of the fuel mixture and of the mixture of the products, respectively, are first required. For the fuel mixture we have

|        |   |   |   |   |   |   | $M$    | $B$     | $MB$     |
|--------|---|---|---|---|---|---|--------|---------|----------|
| $H_2$  | . | . | . | . | . | . | 0.006  | 765.86  | 4.59516  |
| $CO$   | . | . | . | . | . | . | 0.2308 | 55.142  | 12.72677 |
| $CH_4$ | . | . | . | . | . | . | 0.0144 | 96.314  | 1.38692  |
| $CO_2$ | . | . | . | . | . | . | 0.1088 | 35.09   | 3.81779  |
| $N_2$  | . | . | . | . | . | . | 1.6025 | 54.985  | 88.11346 |
| $O_2$  | . | . | . | . | . | . | 0.2875 | 48.249  | 13.87159 |
|        |   |   |   |   |   |   | 2.25   |         | 124.512  |

$$B = 124.512 \div 2.25 = 55.34; \ AB = 0.07116.$$

For the mixture of products, we obtain $B = 51.50$; $AB = 0.06621$.

For the fuel mixture, the expression for the specific heat is

$$c_v = 0.1618 + 0.00002643\ T.$$

We have, therefore, from (7), Art. 84

$$0.23296 \log_e \frac{T_2}{T_1} = 0.07116 \log_e \frac{150}{14.7} - 0.00002643\ (T_2 - T_1).$$

To solve this equation for $T_2$ let us assume as a first approximation $T_2 - T_1 = 500$. Then

$$\log_e \frac{T_2}{T_1} = \frac{0.16529 - 0.013215}{0.23296} = 0.6528,$$

and

$$\frac{T_2}{T_1} = 1.921.$$

Therefore,

$$T_2 = 1.921 \times 530 = 1018.1,$$

and

$$T_2 - T_1 = 488.1.$$

As a second approximation, we assume $T_2 - T_1 = 490$. We obtain

$$\log_e \frac{T_2}{T_1} = \frac{0.16529 - 0.012951}{0.23296} = 0.6539.$$

$$\frac{T_2}{T_1} = 1.9231, \quad T_2 = 1.9231 \times 530 = 1019.2,$$

$$T_2 - T_1 = 489.2.$$

As the assumed value of $T_2 - T_1$ is so nearly attained, we may take the value $T_2 = 1020$ as sufficiently exact.

The ratio of initial and final volumes is now readily found from the

relation

$$\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}.$$

Thus,

$$\frac{V_2}{V_1} = \frac{p_1}{p_2} \cdot \frac{T_2}{T_1} = \frac{14.7}{150} \times \frac{1020}{530} = 0.1887.$$

For the external work required to compress *one pound* of the mixture, we have

$$W = J \int_{530}^{1020} (0.1618 + 0.00002643\ T) dT = 69460 \text{ ft.-lb.}$$

If $T_3$ denotes the temperature after combustion, we have from (2), taking $c_v = 0.1544 + 0.00003753\ T$ for the products of combustion,

$$0.1544 (T_3 - 1020) + \frac{0.00003753}{2} (T_3{}^2 - 1020^2) = \frac{1632.2}{2.25};$$

whence

$$T_3 = 3949°.$$

To find the pressure $p_3$, we must take account of the change of composition during combustion. For the initial state, $p_2 V = 55.34\ T_2$, at the end of combustion $p_3 V = 51.50\ T_3$. Hence, we have

$$p_3 = p_2 \frac{T_3}{T_2} \cdot \frac{51.50}{55.34} = 150 \times \frac{3949}{1020} \times \frac{51.50}{55.34} = 540.4 \text{ lb. per sq. in.}$$

For the adiabatic expansion, the ratio of volumes is the same as for the adiabatic compression. That is, $\frac{V_2}{V_4} = 0.1887$.

From (5) Art. 84, we have

$$a \log_e \frac{T_4}{T_3} = b(T_3 - T_4) + AB \log_e \frac{V_3}{V_4},$$

which may be written in the form

$$\log T_4 = \log T_3 + \frac{AB}{a} \log \frac{V_3}{V_4} + \frac{b}{2.3026\,a}(T_3 - T_4).$$

Inserting the known values $AB = 0.06621$, $a = 0.1544$, $b = 0.00003753$,



$$T_3 = 3949, \frac{V_3}{V_4} = 0.1887, \text{ we get}$$

$$\log T_4 = 3.7028 - 0.0001056\,T_4.$$

This equation may be solved graphically, as shown in Fig. 37. As the value of $T_4$ evidently lies between 2500° and 3000° we plot the curves

$$y = \log T_4$$

and    $$y = 3.7028 - 0.0001056\,T_4$$

between these limits. The intersection gives the desired value,

$$T_4 = 2649°.$$

The external work of expansion is

$$W = J \int_{2649}^{3949} (0.1544 + 0.00003753\,T)\,dT$$
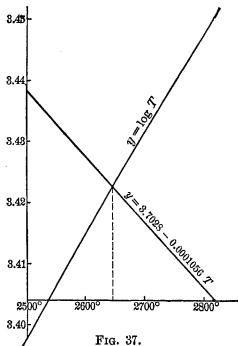$$= 287,940 \text{ ft.-lb.}$$

FIG. 37.

## EXERCISES

The following are the compositions by volume of two gases, one a rich natural gas, the other a blast furnace gas:

| NATURAL GAS (Indiana) | | BLAST FURNACE GAS | |
|---|---|---|---|
| $H_2$ | 0.02 | $H_2$ | 0.05 |
| CO | 0.007 | CO | 0.27 |
| $CH_4$ | 0.931 | $CH_4$ | 0.015 |

Work the following examples for each of these gases:

**1.** Find the composition by weight.

**2.** Find the heating value:

  (*a*) per cubic foot under standard conditions;
  (*b*) per pound.

**3.** Calculate the constants $B_m$, $\gamma$, $v$, and $c_p - c_v$.

**4.** Find the volume of air required for the combustion of one cubic foot.

**5.** Find the weight of air required for the combustion of one pound.

**6.** Find the products of combustion, by weight.

**7.** Find the specific heat $c_v$ of a mixture of the gas with air, the weight of air being 15 per cent in excess of that required for complete combustion.

**8.** Find $c_v$ for the products of combustion, assuming that 15 per cent excess of air is used.

**9.** Find the constants $B_m$, $\gamma$, and $v$ of the mixture of Ex. 7; also of the products of combustion.

**10.** The mixture of Ex. 7 is compressed adiabatically from a pressure of 14.7 lb. per square inch to a pressure of 120 lb. per square inch in the case of the natural gas and to a pressure of 175 lb. per square inch in the case of the blast furnace gas. The initial temperature in each case is 80° F. Find the temperature at the end of compression in each case.

**11.** Find the work of adiabatic compression.

**12.** Find the ratio of initial to final volume.

**13.** If at the end of adiabatic compression the mixture is ignited and burns at constant volume, find the temperature at the end of the process, assuming that no heat is lost by radiation.

**14.** After combustion the products expand adiabatically to the initial volume. Calculate the final temperatures.

**15.** Find the work of adiabatic expansion.

**16.** Assume that the adiabatic compression follows the law $pV^n = \text{const.}$ Find the values of $n$. Find also the values of $n$ for the adiabatic expansion.

## REFERENCES

### Gas Mixtures

Preston : Theory of Heat, 350.

Bryan : Thermodynamics, 121.

Zeuner : Technical Thermodynamics (Klein) 1, 107.

Weyrauch : Grundriss der Wärme-Theorie 1, 137, 140.

Levin: Modern Gas Engine and Gas Producer, 80.

Carpenter and Diederichs: Internal Combustion Engines, 129.

Zeuner: Technical Thermodynamics **1**, 405, 416.

Weyrauch: Grundriss der Wärme-Theorie, 216, 255.

Jones: The Gas Engine, 293.

Poole: The Calorific Power of Fuels.

In the field of thermochemistry reference may be made to the exten
sive researches of Favre and Silbermann, Berthelot, and J. Thomsen.  Fo
tables of heating values see Landolt and Börnstein: Physik.-chemisch
Tabellen.

### VARIABLE SPECIFIC HEAT OF GASES

Mallard and Le Chatelier: Annales des Mines **4**.  1883.

Vieille: Comptes rendus **96**, 1358.  1883.

Langen: Zeit. des Verein. deutsch. Ing. **47**, 622.  1903.

Haber: Thermodynamics of Technical Gas Reactions, 208.

Clerk: Gas, Petrol, and Oil Engines, 341, 361.

Zeuner: Technical Thermodynamics **1**, 146.

Carpenter and Diederichs: Internal Combustion Engines, 220.

### THERMODYNAMICS OF COMBUSTION

Zeuner: Technical Thermodynamics **1**, 423, 428.

Lorenz: Technische Wärmelehre, 392.

Stodola: Zeit. des Verein. deutsch. Ing. **42**, 1045, 1086.  1898.

# CHAPTER IX

## TECHNICAL APPLICATIONS.  GASEOUS MEDIA

**86. Cycle Processes.** — In any heat motor, heat is conveyed from the source of supply to the motor by some medium, which thus simply acts as a vehicle or carrier.  In practically all cases the medium is in the liquid or gaseous state, though a motor with a solid medium is easily conceivable.  The performance of work is brought about by a change in the specific volume of the medium due to the heat received from the source.  By a proper arrangement of working cylinder and movable piston this change of volume is utilized in overcoming external resistances.  (In the steam turbine another principle is employed.)  The medium must pass through a series of changes of state and return eventually to its initial state, the series of changes thus forming a closed cycle.  To use a crude illustration, the medium taking its load of heat from the source at high temperature, delivering that heat to the working cylinder and to the cold body (condenser) and returning to the source for another supply may be compared with an elevator taking freight from an upper story to a lower level and returning empty for another load.

Where the medium is expensive it is used over and over, and thus passes through a true closed cycle.  Examples are seen in the ammonia refrigerating machine and in the engines and boilers of ocean steamers, in which fresh water must be used.  In such cases we may speak of the motor as a **closed** motor.  If the medium, on the other hand, is inexpensive or available in large quantities, as air or water, **open** motors are quite generally used.  In these the working fluid is discharged into the atmosphere and a fresh supply is taken from the source of supply.  Even in this case the medium may pass through a closed cycle,

but all the changes of state are not completed in the organs of the motor.

In this chapter we shall take up the analysis of several cycles that are of importance in the technical applications of gaseous media. In general, we shall assume ideal conditions, which cannot be attained in actual heat motors. However, the conclusions deduced from the analysis of such ideal cycles are usually valid for the modified actual cycles; furthermore, the ideal cycle furnishes a standard by which to measure the efficiency of the actual cycle.

**87. The Carnot Cycle.** — Although the Carnot cycle is of no practical importance, it possesses the greatest interest from a theoretical point of view. Hence an analysis of it is included.

Referring to Fig. 18, the heat absorbed from the source during the isothermal expansion $AB$ is given by the equation

$$Q_{ab} = A p_a V_a \log_e \frac{V_b}{V_a}, \tag{1}$$

and the heat rejected to the refrigerator is

$$Q_{cd} = A p_c V_c \log_e \frac{V_d}{V_c}. \tag{2}$$

The heat transformed into work is, therefore,

$$A W = Q_{ab} + Q_{cd} = A\left(p_a V_a \log_e \frac{V_b}{V_a} - p_c V_c \log_e \frac{V_c}{V_d}\right). \tag{3}$$

Since in the state $A$ the temperature is $T_1$, we have

$$p_a V_a = MBT_1, \tag{4}$$

and likewise

$$p_c V_c = MBT_2. \tag{5}$$

Furthermore, for the adiabatic $BC$ we have the relation

$$\left(\frac{V_c}{V_b}\right)^{k-1} = \frac{T_1}{T_2}, \tag{6}$$

and for the adiabatic $DA$ the relation

$$\left(\frac{V_d}{V_a}\right)^{k-1} = \frac{T_1}{T_2}. \tag{7}$$

From (6) and (7) we have

$$\frac{V_c}{V_d} = \frac{V_b}{V_a}. \tag{8}$$

Introducing in (3) the results given by (4), (5), and (8), we obtain

$$W = MB(T_1 - T_2) \log_e \frac{V_b}{V_a};    (9)$$

whence

$$\eta = \frac{AW}{Q_{ab}} = \frac{MB(T_1 - T_2) \log_e \frac{V_b}{V_a}}{MBT_1 \log_e \frac{V_b}{V_a}} = \frac{T_1 - T_2}{T_1}.    (10)$$

This expression for the efficiency is identical with that deduced from the Kelvin absolute scale of temperature. We have in Eq. (10) a proof, therefore, that the Kelvin absolute scale coincides with the perfect gas scale.

**88. Conditions of Maximum Efficiency.** — On the $TS$-plane the Carnot cycle is the simple rectangle $ABCD$ (Fig. 38), having the isothermals $AB$ and $CD$ at the temperatures $T_1$ and $T_2$ of the source and refrigerator, respectively. This geometrical representation affords an intuitive insight into the property of maximum efficiency. Between the same isothermals let us assume some other form of cycle, as the trapezoidal cycle $EBCD$. For the rectangular cycle the efficiency is
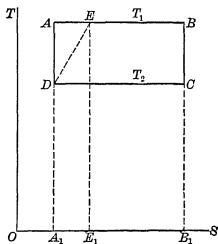


FIG. 38.

$$\frac{\text{heat transformed into work}}{\text{heat supplied}} = \frac{\text{area } ABCD}{\text{area } A_1ABB_1}.$$

For the trapezoidal cycle, likewise, the efficiency is

$$\frac{\text{area } DEBC}{\text{area } A_1DEBB_1}.$$

But    $$\frac{DEBC}{A_1DEBB_1} = \frac{ABCD - AED}{A_1ABB_1 - AED} < \frac{ABCD}{A_1AB_1B};$$

that any cycle lying wholly within the rectangular cycle $ABCD$ has a smaller efficiency than the rectangular cycle.

With a source and refrigerator, the conditions of maximum efficiency, which may be approached but never actually attained, are the following:

1. The medium must receive heat from the source at the temperature of the source. No heat must be received at lower temperature.

2. The medium must reject heat to the refrigerator at the temperature of the refrigerator.

3. Provided the medium, source, and refrigerator are the only bodies involved in the transfer of heat, it follows from 1 and 2 that the intermediate processes must be adiabatic, as any departure from the adiabatic would mean passage of heat to or from some body at a temperature different from either the source or refrigerator.
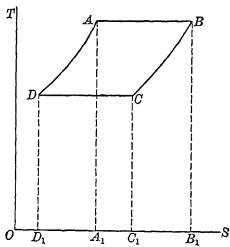


FIG. 39.

**89. Isoadiabatic Cycles.** — Let a cycle be formed with the isothermals $AB$ and $CD$ as in the Carnot cycle, but with the adiabatics replaced by similar curves $BC$ and $AD$ (Fig. 39); that is, curve $BC$ is simply curve $DA$ shifted horizontally a distance $AB$. Then $AB = DC$, as in the Carnot cycle. If the cycle is traversed in the clockwise sense, the heat entering the medium is

$$Q_{da} + Q_{ab} = \text{area } D_1DAA_1 + \text{area } A_1ABB_1,$$

while the heat rejected by the medium is

$$Q_{bc} + Q_{cd} = \text{area } B_1BCC_1 + \text{area } C_1CDD_1.$$

The heat transformed into work is the same as in the Carnot cycle, for the area of the figure $ABCD$ is equal to that of the

$D_1DAA_1$ is taken from the source of heat, the efficiency of the cycle is

$$\eta = \frac{\text{heat transformed}}{\text{heat taken from source}} = \frac{\text{area } ABCD}{\text{area } D_1DABB_1},$$

and this is manifestly smaller than the efficiency of the Carnot cycle. Let it be observed, however, that

$$Q_{bc} = Q_{da},$$

that is,        area $B_1BCC_1 = $ area $D_1DAA_1$.

If the heat rejected by the medium during the process $BC$ could be used instead of thrown away, then this heat might be used again during the process $DA$, thus saving the source the heat $Q_{da}$. In this case we should have the following series of steps:

1.  Medium absorbs heat $Q_{ab}$ from source.
2.  Medium rejects heat $Q_{bc}$, which is stored.
3.  Medium rejects heat $Q_{cd}$ to refrigerator.
4.  Medium absorbs the heat $Q_{da}$ ($= Q_{bc}$) stored during step 2.

Since in this case the source furnishes only the heat $Q_{ab}$, the efficiency is

$$\eta = \frac{\text{area } ABCD}{\text{area } A_1ABB_1},$$

which is the same as that of the Carnot cycle. A cycle in which the adiabatics of the Carnot cycle are replaced by similar curves, along which the interchanges of heat are balanced, is called an **isoadiabatic** cycle. Any such cycle has the same ideal efficiency as the Carnot cycle.

**90. Classification of Air Engines.** — Heat motors that employ air or some other practically perfect gas as a working fluid may be divided into two chief classes: (1) Motors in which the furnace is exterior to the working cylinder, so that the medium is heated by conduction through metal walls. (2) Motors in which the medium is heated in the working cylinder by the combustion of some gaseous or liquid fuel. These are called **internal combustion motors**.

We may make a second division based on the manner in

which the working fluid is used. In the *closed-cycle* type of motor, the same mass of air is used over and over again, fresh air being supplied merely to replace leakage losses. In the *open-cycle* type a fresh charge of air is drawn in at each stroke, and after passing through its cycle is discharged again into the atmosphere.

Air motors of the first class, namely, those with the furnace exterior to the working cylinder, are usually designated as **hot-air engines**. Motors of this class are no longer constructed except in small sizes for pumping and domestic purposes ; they are, however, of historical interest, and besides they furnish instructive illustrations of the application of the regenerative principle. We shall, therefore, describe briefly the two leading types of hot-air engines and give an analysis of the cycles.

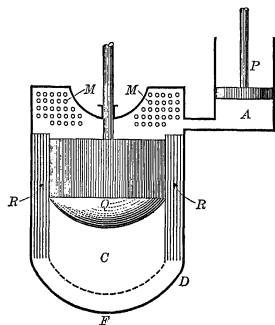**91. Stirling's Engine.** — The engine designed by Robert Stirling in 1816, and bearing his name, is of the external furnace closed-cycle type. The general features of the engine are shown in Fig. 40. A displacer piston $Q$ works in a cylinder $C$. Between $C$ and an outer cylinder $D$ is placed a regenerator $RR$, made of thin metal plates or wire gauze. At the upper end of the cylinder is a refrigerator $M$, composed of a pipe coil through which cold water is made to circulate. At the lower end is the fire $F$. The piston $Q$ is filled with some non-conducting material. The working cylinder $A$ has free communication with the displacer cylinder. In the actual engine there are two displacers



FIG. 40.

piston $P$ to be at the beginning of its upward stroke and the displacer piston at the bottom of its cylinder. The air is, therefore, all in the upper part of the cylinder in contact with the refrigerator, and its state may be represented by the point $D$ (Fig. 39). Now let the displacer piston be moved suddenly to the upper end of its cylinder. The air is forced through $R$ and the perforations in $C$ into the lower end of the cylinder. The air remains at constant volume, since the piston $P$ has not yet moved, and has received heat in passing through $R$. Hence the change of state is a heating at constant volume represented by $DA$ in the diagram. The air now receives heat from the furnace and expands at constant temperature during the upward working stroke of piston $P$. This process is represented by $AB$. When the piston $P$ reaches the upper end of its stroke, the displacer piston $Q$ is suddenly moved to the bottom of the cylinder, thus forcing the air back through $R$ into the refrigerator $M$. This again is a constant volume change and is represented by $BC$. Lastly, during the return stroke the air is compressed isothermally, as represented by $CD$, and heat is rejected to the refrigerator.

The ideal cycle is seen to be an isoadiabatic cycle with the adiabatics of the Carnot cycle replaced by constant-volume curves. The cycle given by the actual engine deviates considerably from the ideal cycle on account of the large clearance necessary between the two cylinders.

A double acting Stirling engine of 50 i. h. p. was used for some years at the Dundee foundry, but was eventually abandoned because of the failure of the regenerators. This engine had an efficiency of 0.3 and consumed 1.7 lb. of coal per i. h. p.

**92. Ericsson's Air Engine.** — The Swedish engineer Ericsson made several attempts to design hot-air engines of considerable power. His large engines proved failures, however, because of their enormous bulk and the rapid deterioration of the regenerators. The engines for the 2200-ton vessel *Ericsson* had four single-acting working cylinders 14 ft. in diameter and 6 ft.

stroke and ran at 9 r.p.m. They developed 300 h.p. with a fuel consumption of 1.87 lb. of coal per h.p.-hour.

The working of the Ericsson engine was substantially as follows: A pump compressed air at atmospheric temperature into a receiver, whence it passed through the regenerator into a working cylinder. The pump was water-jacketed so as to act as a refrigerator. During the passage through the regenerator the air was heated at constant pressure. After the air was cut off in the working cylinder, it expanded isothermally, the nec-



FIG. 41.

essary heat being furnished by a furnace external to the working cylinder. On the return stroke the air was discharged through the regenerator at constant pressure.

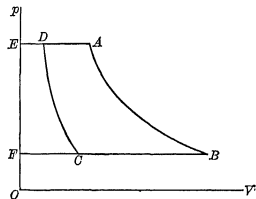The $pV$-diagram is shown in Fig. 41. The pump cycle is $DCFE$, the motor cycle $EABF$. The operations are as follows:

(1) Compression in pump from $C$ to $D$, heat abstracted by pump water-jacket. (2) Discharge from pump to regenerator, represented by $DE$. (3) Suction of air into working cylinder represented by $EA$. (4) Isothermal expansion from $A$ to $B$, during which air receives heat from furnace. (5) Discharge of air, represented by $BF$. (6) Suction of air into pump, represented by $FC$.

Deducting the work of the pump from that of the motor, the effective work is given by the diagram $ABCD$ composed of the two isothermals and two constant-pressure lines.

**93. Analysis of Cycles.**—The ideal cycles of the Stirling and Ericsson engines are isoadiabatic cycles. In the Stirling cycle the constant-volume lines $DA$ and $BC$ (Fig. 39) replace the adiabatics of the Carnot cycle. Using the $TS$-plane we have

$$Q_{ab} = A p_a V_a \log_e \frac{V_b}{V_a} = ABT_1 M \log_e \frac{V_b}{V_a}$$

$$Q_{ab} = M_a (T_a - T_b)$$

$$Q_{cd} = Ap_c V_c \log_e \frac{V_d}{V_c} = - AMBT_2 \log_e \frac{V_c}{V_d}.$$

$$Q_{da} = Mc_v (T_1 - T_2).$$

$$AW = Q_{ab} + Q_{bc} + Q_{cd} + Q_{da}$$

$$= AMB \left[ T_1 \log_e \frac{V_b}{V_a} - T_2 \log_e \frac{V_c}{V_d} \right].$$

But since $V_a = V_d$ and $V_c = V_b$,

$$AW = AMB (T_1 - T_2) \log_e \frac{V_b}{V_a}.$$

The heat $Q_{da}$ is taken from a regenerator, and therefore the heat $Q_{ab}$ alone is supplied from the source; hence the efficiency is

$$\eta = \frac{AW}{Q_{ab}} = \frac{T_1 - T_2}{T_1}.$$

For the Ericsson cycle $DA$ and $BC$ are constant-pressure lines and the analysis is essentially the same except that $c_v$ is replaced by $c_p$.

**94. Heating by Internal Combustion.\*** — While the hot-air engine with exterior furnace should apparently be an efficient heat motor, experience has proved the contrary. The difficulty lies in the slow rate of absorption of heat by any gas. Even with high furnace temperatures and comparatively large heating surfaces it has been found impossible to get a high temperature in the working medium. Furthermore, if the air could be effectively heated, the metal surfaces separating the furnace from the hot medium would be destroyed; hence, while high temperature of air is necessary for high efficiency, low temperature is necessary to secure the durability of the metal.

These contradictory conditions are completely obviated by the method of heating by internal combustion. The rapid chemical action supported by the medium itself makes possible the rapid heating of large quantities of air to a very high temperature. The medium and the furnace being within the cylinder, the outer surface of the metal walls can be kept at

low temperature by a water jacket, and consequently the inner surface can be exposed to the high temperature desired without danger of destruction. Furthermore, the low conductivity of gases becomes here an advantage as it prevents a rapid flow of heat from the medium to the cylinder walls. The low gas temperature of the hot-air engine results in a small effective pressure and makes the engine very bulky for the power obtained. The high temperature possible in the internal combustion motor, on the other hand, permits high effective pressures, and therefore gives a relatively small bulk per horsepower.

**95. The Otto Cycle.** — The cycle of the well-known Otto gas engine has five operations as follows:
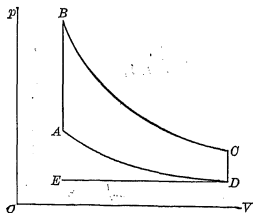


Fig. 42.

1. The explosive mixture is drawn into the cylinder. Represented by $ED$, Fig. 42.

2. The mixture is compressed, as represented by $DA$.

3. The charge is ignited, causing a rise of temperature and pressure, as shown by $AB$.

4. The gases in the cylinder expand adiabatically as shown by $BC$.

5. The burned gases are expelled in part. Represented by $DE$.

In the case of the four-cycle Otto engine, each of the operations 1, 2, 4, and 5 occupies one stroke of the piston, while operation 3 occurs at the beginning of a stroke. The cycle is completed in four strokes, whence the term **four-cycle.**

It is customary in the analysis of gas-engine cycles to assume in the first instance that the medium is pure air throughout the cycle and that the air receives during the process $AB$ an amount of heat equal to that developed by the combustion of the fuel in the actual cycle. This assumed ideal cycle is referred to as the *air standard.*

On the $TS$-plane, the ideal cycle has the form shown in Fig. 43, $AB$ and $CD$ being constant volume curves. The medium in the state represented by point $A$ is heated at constant volume, as shown by the curve $AB$. For this process we have (assuming that $c_v$ is constant)

$$Q_{ab} = Mc_v(T_b - T_a),$$
$$W_{ab} = 0.$$

For the adiabatic expansion represented by $BC$,

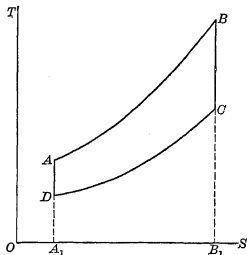$$Q_{bc} = 0,$$
$$W_{bc} = \frac{p_b V_b - p_a V_a}{k-1}.$$



FIG. 43.

For the cooling at constant volume, represented by $CD$, we have $\quad Q_{cd} = Mc_v(T_d - T_c) = -Mc_v(T_c - T_d),$

$$W_{cd} = 0.$$

Finally the medium is compressed adiabatically from $D$ to $A$, and for this change of state

$$Q_{da} = 0,$$
$$W_{da} = \frac{p_d V_d - p_a V_a}{k-1}.$$

The heat changed into work is

$$(Q_{ab} + Q_{bc} + Q_{cd} + Q_{da}) = Mc_v[(T_b - T_a) - (T_c - T_d)]. \quad (1)$$

The work of the cycle is

$$W = W_{ab} + W_{bc} + W_{cd} + W_{da} = \frac{(p_b V_b - p_c V_c) - (p_a V_a - p_d V_d)}{k-1}. \quad (2)$$

It is easily shown that these results are identical.

The efficiency is

$$\eta = \frac{W}{JQ} = \frac{Jc_v[(T_b - T_a) - (T_c - T_d)]}{}$$

This expression for $\eta$ may be simplified as follows: From Fig. 43 we have

$$S_b - S_a = S_c - S_d = Mc_v \log_e \frac{T_b}{T_a} = Mc_v \log_e \frac{T_c}{T_d};$$

hence,    $\dfrac{T_b}{T_a} = \dfrac{T_c}{T_d}$,   or   $\dfrac{T_c}{T_b} = \dfrac{T_d}{T_a} = \dfrac{T_c - T_d}{T_b - T_a}$.

Therefore,    $\eta = 1 - \dfrac{T_c}{T_b}$

or    $\eta = 1 - \dfrac{T_d}{T_a}$    $\Bigg\}$.    (4)

It appears, therefore, that the Otto cycle has the same efficiency as a Carnot cycle having the extreme temperatures $T_a$ and $T_d$ or the extreme temperatures $T_b$ and $T_c$ of the adiabatics, but a smaller efficiency than a Carnot cycle having $T_b$ and $T_d$ as extreme temperature limits.

The expression for the ideal efficiency may be written in another convenient form. Since the curve $DA$ represents an adiabatic process, we have

$$\frac{T_d}{T_a} = \left(\frac{V_a}{V_d}\right)^{k-1} = \left(\frac{p_d}{p_a}\right)^{\frac{k-1}{k}};$$

whence    $\eta = 1 - \left(\dfrac{V_a}{V_d}\right)^{k-1}$

or    $\eta = 1 - \left(\dfrac{p_d}{p_a}\right)^{\frac{k-1}{k}}$    $\Bigg\}$.    (5)

It appears from the last expression that the higher the compression pressure $p_a$, the greater the ideal efficiency.

If the ratio of volumes $\dfrac{V_d}{V_a}$ be denoted by $r$, we have for the ideal efficiency the expression

$$\eta = 1 - \frac{1}{r^{k-1}}.    (6)$$

EXAMPLE. If the air is compressed from 14.7 lb. to 45 lb., the ideal

The temperature and pressure represented by the point $B$ are readily calculated for this ideal case. Let $q_1$ denote the heat absorbed *per pound of air* during the process $AB$; then

$$q_1 = c_v(T_b - T_a);$$

whence

$$\frac{T_b}{T_a} = \frac{q_1}{c_v T_a} + 1. \qquad (7)$$

Since

$$V_a = V_b,$$

we have

$$\frac{p_b}{p_a} = \frac{T_b}{T_a} = \frac{T_b}{T_d r^{k-1}}. \qquad (8)$$

The value of $q_1$ for a given fuel depends upon the heating value of the fuel and the weight of air required for the combustion of a unit weight of the fuel.

**96. The Joule or Brayton Cycle.** — In the Otto type of motor, the fuel gas is mixed with air previous to compression, and when the mixture is ignited the combustion is so rapid as to produce an explosion; the heat is supplied, therefore, at practically constant volume. Another type of motor was first suggested by Joule and was developed in working form by Brayton (1872). In the Brayton engine the mixture of air and gas was compressed into a reservoir to a pressure of perhaps 60 lb. per square inch and from the reservoir flowed into the working cylinder, where it was ignited by a flame. A wire gauze diaphragm was used to prevent the flame from striking back into the reservoir. The mixture was thus burned quietly in the working cylinder during about one half the stroke of the piston, and by proper regulation of the admission valve the rate of combustion was so regulated as to give practically constant pressure during the period of admission. The ideal cycle of operations is as follows:

1. Charge drawn into compressor cylinder, $ED$ (Fig. 44).
2. Adiabatic compression, $DA$.

L

3. Expulsion at constant pressure from compressor, $AF$; simultaneous admission to motor cylinder, $FB$. The charge during the passage from compressor to motor is heated at constant pressure and the volume is thereby increased as indicated by $AB$.

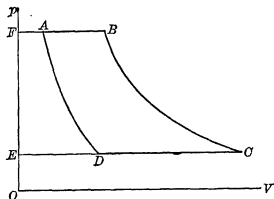4. Adiabatic expansion, $BC$, after cut off.

5. Expulsion of burned gases, $CE$.

The area $EDAF$ represents the negative work of the compressor, the area $FBCE$ the work obtained from the motor; hence, area $ABCD$ represents the net available work.

On the $TS$-plane, the ideal Joule cycle has the same form as the Otto cycle (Fig. 43). The curves $AB$ and $CD$, however, represent, respectively, heating and cooling at constant pressure. We have, therefore,

$$Q_{ab} = Mc_p\,(T_b - T_a), \tag{1}$$

$$Q_{cd} = Mc_p\,(T_d - T_c), \tag{2}$$

$$W = Q_{ab} + Q_{cd} = Mc_p\,(T_b - T_a + T_d - T_c), \tag{3}$$

$$\eta = 1 - \frac{T_c - T_d}{T_b - T_a} = 1 - \frac{T_c}{T_b} = 1 - \frac{T_d}{T_a}. \tag{4}$$

Also,    $\dfrac{T_b}{T_a} = \dfrac{q_1}{c_p T_a} + 1.$ \hfill (5)

**97. The Diesel Cycle.** — The principle of gradual and quiet combustion as opposed to explosion was seized upon by Diesel in the design of the Diesel motor. In this motor air without fuel is compressed in the working cylinder to a pressure approximating 500 lb. per square inch. The temperature at the end of compression is consequently higher than the ignition tempera-

expand at practically constant pressure, or if desired, with falling pressure and nearly constant temperature. As in the Brayton engine, governing is effected by cutting off the fuel injection earlier or later.



FIG. 45.

The ideal cycle of the Diesel engine is shown in Fig. 45. It resembles the Otto cycle except that the process $AB$ in this case represents a constant pressure rather 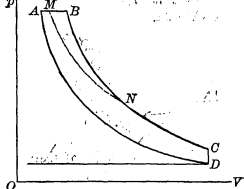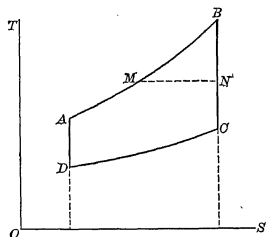than a constant volume combustion. It was the original aim of Diesel so to regulate the injection of fuel that a short period of combustion $AM$ would be followed by isothermal expansion $MN$, the fuel being cut off at the point $N$.

On the $TS$-plane the ideal Diesel cycle is shown in Fig. 46, in which $AB$ is a constant-pressure curve and $CD$ a constant-volume curve. We have then



FIG. 46.

$$Q_{ab} = Mc_p\,(T_b - T_a), \qquad (1)$$

$$Q_{cd} = Mc_v\,(T_d - T_c), \qquad (2)$$

$$W = JM\,[c_p(T_b - T_a) - c_v\,(T_c - T_d)], \qquad (3)$$

$$\eta = \frac{c_p\,(T_b - T_a) - c_v\,(T_c - T_d)}{c_p\,(T_b - T_a)} = 1 - \frac{1}{k}\left(\frac{T_c - T_d}{T_b - T_a}\right). \qquad (4)$$

If the cycle includes an isothermal process, as $MN$, we have

$$Q_{am} = Mc_p\,(T_m - T_a), \qquad (5)$$

$$Q_{mn} = AMB\,T_m \log_e \frac{V_n}{V_m}, \qquad (6)$$

$$\text{and } \eta = \frac{Q_{am} + Q_{mn} + Q_{cd}}{Q_{am} + Q_{mn}} = 1 - \frac{T_c - T_d}{k(T_m - T_a) + (k-1)T_m \log_e \frac{V_n}{V_m}}. \qquad (7)$$

**98. Comparison of Cycles.** — The three principal cycles are shown superimposed in Fig. 47. The minimum temperature at $D$ and maximum temperatur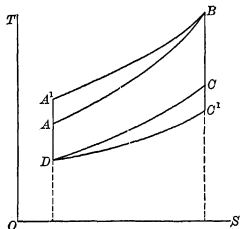e at $B$ are the same for all three. With this assumption it is seen that the Brayton cycle $A'BC'D$ has the largest area, the Otto cycle $ABCD$, the smallest. Hence, between the same temperature limits and with the same maximum pressure $p_b$, the Brayton cycle is the most efficient, the Otto cycle the least efficient. Comparing the maximum volumes, it is seen that the Otto and Diesel cycles have the same maximum volumes $V_c$, while the Brayton cycle requires a greater volume, as indicated by the point $C'$. The Diesel cycle, therefore, combines the advantages of the high efficiency of the Brayton cycle due to the high compression pressure and the smaller cylinder volume of the Otto cycle.

FIG. 47.

**99. Closer Analysis of the Otto Cycle.** — In the preceding analysis of gas-engine cycles two assumptions have been made : (1) That the medium employed has throughout the cycle the properties of air. (2) That the specific heat of the medium is constant. While the approximate analyses based on these assumptions are of value in giving the essential characteristics of the various cycles, and an idea of their relative efficiencies, they give misleading notions regarding the absolute magnitudes of those efficiencies. To obtain the true value of the maximum possible efficiency of a gas-engine cycle, it is necessary to take account of the properties of the fuel mixture entering the cylinder and of the mixture of the products of combustion after the fuel is burned. Making use of the principles and methods laid down in Chapter VIII, we may thus make an accurate

nished by the example of Art. 85, shows such an analysis for the Otto cycle.

EXAMPLE. Determine the ideal efficiency of an Otto cycle in which the compression, combustion, and expansion follow the course described in the example of Art. 85. Compare this efficiency with the "air standard" efficiency under the same conditions.

In the example quoted, the work of adiabatic compression was found to be 69,460 ft.-lb., the work of expansion 287,940 ft.-lb. These results refer to 1 lb. of the fuel mixture. The heating value of the fuel per pound was found to be 1632.2 B. t. u.; hence the heating value per pound of fuel mixture is 1632.2 ÷ 2.25 = 725.4 B. t. u. The net work derived from the cycle per pound of mixture is 287,940 − 69,460 = 218,480 ft.-lb. Therefore, the efficiency is

$$\eta = \frac{218480}{J \times 725.4} = 0.387.$$

The "air standard" efficiency depends upon the ratio of initial and final volumes, which ratio was found to be $\frac{V_2}{V_1} = 0.1887$. Hence, for this efficiency we have

$$\eta = 1 - 0.1887^{0.4} = 0.487.$$

The discrepancy between the two efficiencies is in a large measure due to the assumption of constant specific heat in the analysis of Art. 95.

**100. Air Refrigeration.** — The term **refrigeration** is applied to the process of keeping a body permanently at a temperature lower than that of surrounding bodies. Since heat naturally flows from the surroundings to the body at lower temperature, this heat must be continually removed if the body is to remain permanently at its lower temperature. Hence a refrigerating machine has the office of removing heat from a body of low temperature and depositing it in some other convenient body of higher temperature.

The operation of a refrigerating machine is thus precisely the reverse of the operation of the direct-heat motor; and if the cycle of a heat motor be traversed in the reverse direction, it will give a possible cycle for a refrigerating machine. When air is used as a medium for refrigeration, the reversed Joule cycle is employed. Fig. 48 shows diagrammatically the arrangement of the refrigerating machine, Fig. 49 the ideal $pV$-diagram, and Fig. 50 the $TS$-diagram. Air in the state $A$ in the cold room is drawn into the compressor $c$ and is com-

pressed adiabatically as indicated by $AB$.  It then passes into
the cooling coils, about which cold water circulates, and is
cooled at constant pressure, as indicated by $BC$.  In the state



FIG. 48.

$C$ the air passes
into the expansion
cylinder $e$ and is
permitted to ex-
pand adiabatically
down to the pres-
sure in the cold
room, *i.e.* atmos-
pheric pressure.
The final state is
represented by

point $D$.  Finally the air absorbs heat from the cold room, and
its temperature rises to the original value $T_a$.  Referring to
Fig. 49, the actual compression diagram is $ABFE$, while the
diagram $FCDE$ taken clockwise is the diagram of the expan-
sion cylinder.  The net work done on the air is, therefore,
given by the diagram $ABCD$.

The Allen dense-air machine has a closed cycle and the air
is always under a pressure much higher than that of the atmos-
phere.  Thus the pressure $DA$ (Fig. 49) is perhaps 40 to 60,
and the upper pressure, say
200 lb. per square inch.  The
air, after expanding to the
lower pressure, is led through
coils immersed in brine and
absorbs heat from the brine.

In the following analysis of
the air-refrigerating machine
we shall assume ideal condi-
tions.  In the actual machine
these conditions are to some
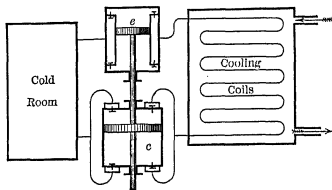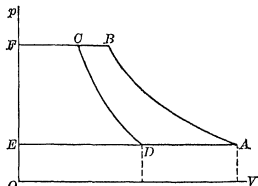


FIG. 49.

minute, and $M$ the weight of air circulated per minute. Then since in passing through the cold body the temperature of the air is raised from $T_d$ to $T_a$ (Fig. 50), we have



FIG. 50.

$$Q = Mc_p(T_a - T_d). \qquad (1)$$

Let $p_1$ denote the suction pressure of the compressor cycle (atmospheric pressure, in the case of the open cycle) and $p_2$ the pressure at the end of compression; then, assuming adiabatic compression, we have

$$\frac{T_b}{T_a} = \left(\frac{p_2}{p_1}\right)^{\frac{k-1}{k}}, \qquad (2)$$

and if the pressure at cut-off in the expansion cylinder is also $p_2$ (as in the ideal case), we have also

$$\frac{T_c}{T_d} = \left(\frac{p_2}{p_1}\right)^{\frac{k-1}{k}}, \qquad (3)$$

whence

$$\frac{T_c}{T_d} = \frac{T_b}{T_a}. \qquad (4)$$

The work required per minute is

$$W = JQ \times \frac{\text{area } ABCD}{\text{area } C_1DAB_1} = JQ\frac{T_b - T_a}{T_a}, \qquad (5)$$

and the heat rejected to the cooling water, represented by the area $B_1BCC_1$ (Fig. 50), is

$$Q' = Q + \frac{W}{J} = Q\frac{T_b}{T_a}. \qquad (6)$$

The compressor cylinder draws in per minute $M$ pounds of air having the pressure $p_1$ and temperature $T_a$. Denoting by $N$ the number of working strokes per minute and by $V_s$ the volume displaced by the compressor piston, we have for the ideal case
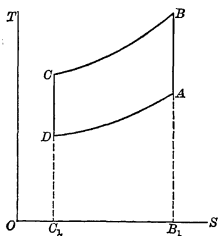
or

$$V_c = \frac{MBT_a}{Np_1}. \tag{7}$$

Likewise, the volume $V_e$ of the expansion cylinder is given by the relation

$$V_e = \frac{MBT_d}{Np_1}. \tag{8}$$

EXAMPLE. An air-refrigerating machine is to abstract 600 B.t.u. per minute from a cold chamber. The pressure in the cold room is 14.7 lb. per square inch, and the air is compressed adiabatically to 65 lb. per square inch absolute. The temperature in the cold room is 36° F. and the air leaves the cooling coils at 80° F. The machine makes 120 working strokes per minute. Required the ideal horsepower required to drive the machine, and the volumes of the compression and expansion cylinders.

The first step is the determination of the temperature $T_d$ at the end of expansion. From the relation

$$\frac{T_c}{T_d} = \left(\frac{p_2}{p_1}\right)^{\frac{k-1}{k}},$$

we have

$$T_d = 539.6 \left(\frac{14.7}{65}\right)^{\frac{0.4}{1.4}} = 352.9.$$

From (1) we obtain for the weight of air that must be circulated per minute

$$M = \frac{Q}{c_p(T_a - T_d)} = \frac{600}{0.24(495.6 - 352.9)} = 17.52 \text{ lb.}$$

The work required per minute is

$$W = JQ\frac{T_c - T_d}{T_d} = 778 \times 600 \times \frac{539.6 - 352.9}{352.9} = 246,950 \text{ ft. lb.,}$$

and the horsepower under these ideal conditions is therefore

$$\frac{246950}{33000} = 7.5.$$

For the volume of the compressor cylinder, we have

$$V_c = \frac{17.52 \times 53.34 \times 495.6}{120 \times 14.7 \times 144} = 1.82 \text{ cu. ft.,}$$

and for the volume of the expansion cylinder

$$V_e = V_c \frac{T_d}{T_a} = 1.8 \times \frac{352.9}{495.6} = 1.30 \text{ cu. ft.}$$

lly in mining, tunneling, and metallurgical processes. ompression of air may be effected by rotary fans and s or by piston compressors. In the piston compressor, atmospheric pressure is drawn into a cylinder through in-ves and is then compressed upon the return stroke of the

When the desired pressure is attained, the outlet valves ened and the air is discharged into a receiver. The ideal or diagram of an air essor has, therefore, the hown in Fig. 51. The $A$ represents the drawing he air; the curve $AB$ rep-the compression from wer pressure $p_1$ to the er pressure $p_2$; and $BC$ ents the expulsion of the higher pressure. It be noted that the curve
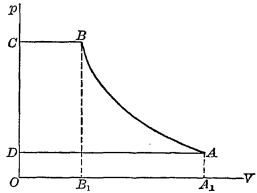


FIG. 51.

presents a change of state, while lines $DA$ and $BC$ nt merely change of locality; thus $BC$ represents the e of the air (in the same state) from the compressor er to the receiver.

$V_1$ denote the volume denoted by point $A$, and $V_2$ the e after compression; then the work of compression (area $B_1$) is

$$W_{ab} = \frac{p_1 V_1 - p_2 V_2}{n-1},$$

ng that the compression curve follows the law $pV^n = \text{const.}$ ork of expulsion (represented by area $B_1 BCO$) is evidently

$$W_{bc} = -p_2 V_2,$$

work done by the air during the intake (area $ODAA_1$) is

$$W_{da} = p_1 V_1.$$

, the total work represented by the area of the diagram is

$$W = \frac{p_1 V_1 - p_2 V_2}{n-1} + p_1 V_1 - p_2 V_2$$

$$= \frac{n}{n-1} (p_1 V_1 - p_2 V_2). \tag{1}$$

$$V_2 = V_1 \left(\frac{p_1}{p_2}\right)^{\frac{1}{n}}, \qquad (2)$$

whence combining (1) and (2) we get

$$W = \frac{n}{n-1} p_1 V_1 \left[1 - \left(\frac{p_2}{p_1}\right)^{\frac{n-1}{n}}\right], \qquad (3)$$

a formula that does not contain the final volume $V_2$.



FIG. 52.

For the temperature at the end of compression we have the usual formula

$$\frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)^{\frac{n-1}{n}} \qquad (4)$$

The action of the air compressor may be studied advantageously by means of the $TS$-diagram. Let the point $A$ (Fig. 52) represent the state of the air at the beginning of compression, and suppose that $AB$ represents the compression process. Thro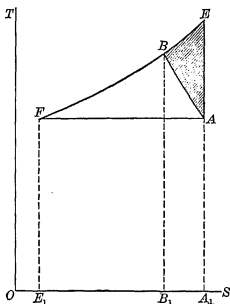ugh $B$ a line representing the constant pressure $p_2$ is drawn, intersecting at $F$ an isothermal through $A$. It can be shown that the area $A_1ABFF_1$ represents the work $W$ given by (1). Denoting by $T_2$ the final temperature corresponding to point $B$, we have

$$\text{area } A_1ABB_1 = Mc_v \frac{n-k}{n-1}(T_2 - T_1),$$

$$\text{area } B_1BFF_1 = Mc_p (T_1 - T_2),$$

$$\text{area } A_1ABFF_1 = M\left(c_p - c_v \frac{n-k}{n-1}\right)(T_1 - T_2)$$

$$= M\frac{n}{n-1}(c_p - c_v)(T_1 - T_2)$$

$$= \frac{n}{n-1}\frac{c_p - c_v}{B}(MBT_1 - MBT_2)$$

$$= \frac{1}{L}\frac{n}{-1}(p_1V_1 - p_2V_2). \qquad (5)$$

**102. Water-jacketing.** — Unless some provision is made for withdrawing heat during the compression, the temperature will rise according to the adiabatic law. Ordinarily the energy stored in the air due to its increase of temperature, that is, the energy

$$U_2 - U_1 = Mc_v(T_2 - T_1),$$

is never utilized because during the transmission of the air through the mains heat is lost by radiation and the temperature falls to the initial value. Hence a rise in the temperature during compression indicates a useless expenditure of work. The water jacket prevents in some degree this rise in temperature and decreases the work required for compression. The curve $AE$ (Fig. 53) represents adiabatic compression. If the compression could be made isothermal, the curve would be $AF$, less steep than $AE$, and the work of the engine would be reduced per stroke by the area $AEF$. The water jacket gives the curve $AB$ lying between $AE$ and $AF$, and the shaded area represents the saving in work. Because of the water jacket the value of the exponent $n$ in the equation $pV^n = \text{const.}$ lies somewhere between 1 and 1.40. Under usual working conditions, $n$ is about 1.3.
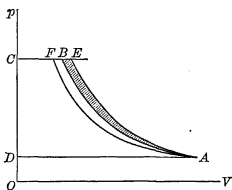


FIG. 53.

For any value of $n$ the relation between the heat abstracted, work done, and change of energy is given by the proportion

$$JQ : (U_2 - U_1) : W = (k - n) : (1 - n) : (k - 1).$$

This applies only to the compression $AB$ not to the expulsion of the air represented by $BC$.

The influence of the water jacket is shown more clearly by the $TS$-diagram, Fig. 52. The vertical line $AE$ indicates adiabatic compression from $p_1$ to $p_2$, the horizontal line $AF$, isother-

mal compression, and the intermediate curve $AB$, compression according to the law $pV^n = $ const., with $n$ between 1 and 1.4. The area $A_1ABB_1$ represents the heat abstracted from the air during compression, and the area $AEB$ represents the work saved by the use of the jacket. A more efficient jacket would give a compression curve with its extremity lying nearer its point $F$. In the case of the isothermal compression represented by $AF$, the area $A_1AFF_1$ represents the heat absorbed from the air and also the work done on the air. These must necessarily be equivalent, since there is no change in the internal energy.

**103. Compound Compression.** — The excess of work required by the increase of temperature during compression may be obviated in some m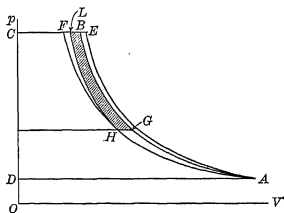easure by dividing the compression into two or more stages. Air is compressed from the initial pressure $p_1$ to an intermediate pressure $p'$, it is then passed through a cooler where the temperature (and consequently the volume) is reduced, and finally it is compressed from $p'$ to the desired pressure $p_2$. In Fig. 54, $DA$ represents the entrance of air into the cylinder, and $AG$, which lies between the adiabatic $AE$ and the isothermal $AF$, the compression in the first cylinder. From $G$ to $H$ the air is cooled at constant pressure in the intercooler. The curve $HL$ shows the compression in the second cylinder, and the line $LC$ the expulsion into the receiver. In a single cylinder the diagram would be $ABCD$; hence compounding saves the work indicated by the area $BGHL$.



FIG. 54.

The saving is shown even more clearly if we use the $TS$-plane (Fig. 55). During the first compression $AG$ the heat represented by the area $A_1AGG_1$ is absorbed by the water jacket. Then the heat $G_1GHH_1$ is abstracted by the intercooler. During the second compression the heat $H_1HLL_1$ is

abstracted by the water jacket, and finally the heat $L_1LFF_1$ is radiated from the receiver and main. As shown in the preceding article, the area $A_1AG\text{-}HLFF_1$ gives the work of the compressor. Evidently area $BG\text{-}HL$ represents the work saved by compounding.



Fig. 55.

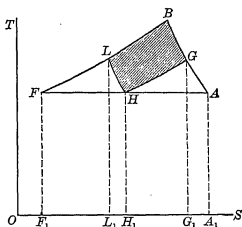If we take (3) of Art. 101, we find for the work done in the first cylinder

$$W_1 = \frac{n}{n-1} p_1 V_1 \left[ 1 - \left( \frac{p'}{p_1} \right)^{\frac{n-1}{n}} \right],$$

and for the work done in the second cylinder

$$W_2 = \frac{n}{n-1} p' V' \left[ 1 - \left( \frac{p_2}{p'} \right)^{\frac{n-1}{n}} \right],$$

where $V'$ is the volume indicated by point $H$ (Fig. 54). But since point $H$ is on the isothermal $AF$, we have

$$p' V' = p_1 V_1,$$

and, therefore,

$$W_2 = \frac{n}{n-1} p_1 V_1 \left[ 1 - \left( \frac{p_2}{p'} \right)^{\frac{n-1}{n}} \right].$$

The total work is, consequently,

$$W_2 + W_1 = \frac{n}{n-1} p_1 V_1 \left[ 2 - \left( \frac{p_2}{p'} \right)^{\frac{n-1}{n}} - \left( \frac{p'}{p_1} \right)^{\frac{n-1}{n}} \right]. \qquad (1)$$

The work required is numerically a minimum when the expression

is variable. Using the ordinary method of the calculus, we find that this expression is a maximum when

$$p' = \sqrt{p_1 p_2}. \tag{2}$$

Equation (2) is useful in proportioning the cylinders of a compound compressor.

Referring to Fig. 55, we have

$$\frac{T_g}{T_a} = \left(\frac{p'}{p_1}\right)^{\frac{n-1}{n}}; \quad \frac{T_l}{T_h} = \frac{T_l}{T_a} = \left(\frac{p_2}{p'}\right)^{\frac{n-1}{n}}$$

With the condition expressed by (2) we have

$$\left(\frac{T_g}{T_a}\right)^2 = \left(\frac{p'^2}{p_1^2}\right)^{\frac{n-1}{n}} = \left(\frac{p_1 p_2}{p_1^2}\right)^{\frac{n-1}{n}} = \left(\frac{p_2}{p_1}\right)^{\frac{n-1}{n}}$$

and likewise,

$$\left(\frac{T_l}{T_a}\right)^2 = \left(\frac{p_2^2}{p_1 p_2}\right)^{\frac{n-1}{n}} = \left(\frac{p_2}{p_1}\right)^{\frac{n-1}{n}}$$

Hence, $$T_l = T_g;$$

that is, for a minimum work of compression the points $G$ and $L$ should lie on the same temperature level. The same statement applies to three-stage compression.

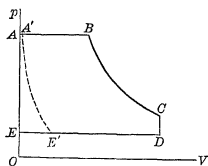**104. Compressed-air Engines.** — Compressed air may be used as a working fluid in a motor in substantially the same way as steam. In fact, compressed air has in some instances been used in ordinary steam engines. The indicator diagram for the motor should approach the form shown in Fig. 56. With clearance and compression, $A'E'$ will replace $AE$. The work per stroke is readily calculated in either case. The expansion curve $BC$ may be taken as an adiabatic.



FIG. 56.

**105. TS-diagram of Combined Compressor and Engine.** — The TS-diagram shows clearly the losses in a compressed-air system and the effects of various expedients employed to obviate such

losses. In the following discussion we shall take up first an ideal case and afterwards several modifications that may be made.

In Fig. 57, $m$ represents the compressor diagram, $n$ the motor diagram, both without clearance. Air in the state represented by point $A$ is taken into the compressor at atmospheric pressure and temperature. The compression, assumed here to be adiabatic, is represented on the $TS$-
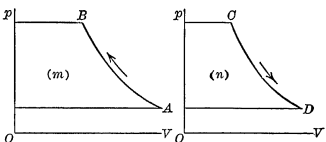


FIG. 57.

plane by the vertical line $AB$ (Fig. 58). The expulsion of the air into the receiver and thence into the main is merely a change of locality and does not itself involve any change of state; hence, it is not represented on the $TS$-plane. However, the passage of the air along the main is usually accompanied by a cooling, and this is represented by $BC$ (Fig. 58), the final point $C$ representing the state of the air at the beginning of expansion in the motor. The adiabatic expansion to atmospheric pressure in the motor is represented by $CD$. This is accompanied by a drop in temperature which is given by the equation



FIG. 58.

$$\frac{T_c}{T_d} = \left(\frac{p_c}{p_d}\right)^{\frac{k-1}{k}}.$$

The air discharged from the motor in the state $D$ is now heated at the constant pressure of the atmosphere until it regains its original temperature $T_a$. This heating is represented by $DA$.
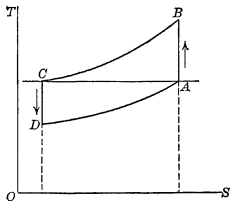
The complete process is a cycle of four distinct operations,

what does the area $ABCD$ of the cycle represent — something useful or something wasteful? To answer this question let us recur to the original energy equation

$$JQ = U_2 - U_1 + W,$$

and apply it to the air which passes through the cycle process just described. We have

Work done on air = area of diagram $m = -W_m$.

Work done by air = area of diagram $n = +W_n$.

Total work $= W_n - W_m$.

Heat absorbed by air = area under $DA$.

Heat rejected by air = area under $BC$.

Total heat put into system $= -$ area $ABCD$.

Change of energy $= U_a - U_a = 0$.

Hence,     $J \times$ area $ABCD = W_m - W_n$;

that is, the area $ABCD$ represents the difference between the work done by the compressor and the work delivered by the motor. Consequently it represents a waste, which is to be avoided as far as possible.



FIG. 59.

Various modifications of the simple cycle of Fig. 58 are shown in Fig. 59. The effect of using a water jacket is shown at $(a)$. The shaded area represents the saving.
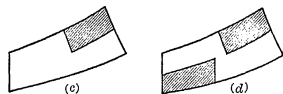
Figure 59 $(b)$ shows the effect of reheating the air before it enters the motor. In the main the air cools, as indicated by $BC$, but in passing through the reheater it is heated again at constant pressure, and the state point retraces its path, say to $D$. Then follows adiabatic expansion $DE$, and constant-pressure heating $EA$. This reheating saves work

represented by the area $CDEF$. It would be possible to carry $D$ to the right of $B$, in which case the waste would become zero or even negative. The area $CDEF$ does not, however, represent clear gain, as account must be taken of the heat expended in the process $CD$.

In Fig. 59 (c) is shown the effect of compound compression, and in Fig. 59 (d) the effect of compound compression with a compound motor. In each case the shaded area represents the saving.

It would not be difficult to represent also the loss of pressure in the main due to friction.

## EXERCISES

**1.** Find the efficiency of a Stirling hot-air engine working under ideal conditions between the temperatures 1340° F. and 140° F. Find the weight of air that must be circulated per minute per horsepower.

**2.** An air compressor with 18 in. by 24 in. cylinder makes 140 working strokes per minute and compresses the air to a pressure of 52 lb. per square inch, gauge. Assuming that there is no clearance, find the net horsepower required to drive the compressor. Take the equation of the compression curve as $pV^{1.3} = \text{const.}$

**3.** If 200 cu. ft. of air at 14.7 lb. is compressed to a pressure of 90 lb. per square inch, gauge, find the saving in the work of compression and expulsion by the use of a water jacket that reduces the exponent $n$ from 1.4 to 1.27.

**4.** Find the efficiency of the ideal Otto cycle (air standard) when the compression is carried to 120 lb. per square inch absolute.

**5.** Draw a curve showing the relation between the efficiency of the Otto cycle and the compression pressure. Take values of $p$ from 40 to 200 lb. per square inch.

**6.** An air-refrigerating machine takes air from the cold chamber at a pressure of 40 lb. per square inch and a temperature of 20° F., and compresses it adiabatically to a pressure of 200 lb. per square inch. The air is then cooled at this pressure to 80° F. and expanded adiabatically to 40 lb. per square inch, whence it passes into the coils in the cold chamber. The machine is required to abstract 45,000 B. t. u. per hour from the cold room. (a) Find the net horsepower required to drive the machine. (b) If the machine makes 80 working strokes per minute, find the necessary cylinder volumes.

**7.** Air is to be compressed from 14.7 lb. per square inch to 300 lb. per square inch absolute. If a compound compressor is used, find the intermediate pressure that should be chosen.

**8.** In Ex. 7, the compression in each cylinder follows the law $pV^{1.3} =$ const. Find the saving in work effected by compounding, expressed in per cent of the work required of a single cylinder.

**9.** Using the results of Ex. 10–15 of Chapter VIII, find the efficiencies of the Otto cycle with the natural gas and the blast furnace gas, respectively, under the conditions stated. Compare these efficiencies with corresponding air standard efficiencies.

**10.** On the $TS$-plane draw accurately an ideal Diesel cycle from the following data: Adiabatic compression of air from 14.7 to 500 lb. per square inch absolute; heating at constant pressure to a temperature of 2200° F.; adiabatic expansion to initial volume; cooling at constant volume to initial state. Calculate the ideal efficiency of the cycle.

**11.** Modify the Diesel cycle of the preceding example by stopping the constant-pressure heating at 1600° F. and continuing with an isothermal expansion (as shown by $MN$, Fig. 46). Calculate the efficiency of this modified cycle.

**12.** The ideal Lenoir cycle has three operations, as follows: heating of air at constant volume, adiabatic expansion to initial pressure (atmospheric), and cooling at constant pressure. Show the cycle on $pV$- and $TS$-planes, and derive an expression for its efficiency.

**13.** Let the expansion in the Otto cycle be continued to atmospheric pressure. Show the resulting cycle on $pV$- and $TS$-planes and derive an expression for the efficiency.

### REFERENCES

#### HOT–AIR ENGINES

Ennis: Applied Thermodynamics for Engineers, 129.
Zeuner: Technical Thermodynamics (Klein) **1**, 340.
Rankine: The Steam Engine (1897), 370.
Ewing: The Steam Engine, 402.

#### GAS–ENGINE CYCLES

Clerk: Gas, Petrol, and Oil Engines, 67.
Carpenter and Diederichs: Internal Combustion Engines, 65.
Levin: The Modern Gas Engine, 43.
Berry: The Temperature Entropy Diagram, 167.
Ennis: Applied Thermodynamics, 154.
Peabody: Thermodynamics of the Steam Engine, 5th ed., 304.
Lorenz: Technische Wärmelehre, 421.
Weyrauch: Grundriss der Wärme-Theorie, 277.

Ennis: Applied Thermodynamics, 396.
Ewing: The Mechanical Production of Cold, 38.
Peabody: Thermodynamics of the Steam Engine, 5th ed., 397.
Zeuner: Technical Thermodynamics, 384.


AIR COMPRESSION

Peabody: Thermodynamics, 5th ed., 358.
Ennis: Applied Thermodynamics, 96.

## SATURATED VAPORS

**106. The Process of Vaporization.** — The term vaporization may refer either (1) to the slow and quiet formation of vapor at the free surface of a liquid or (2) to the formation of vapor by ebullition. In the latter case, heat being applied to the liquid, the temperature rises until at a definite point vapor bubbles begin to form on the walls of the containing vessel and within the liquid itself. These rise to the liquid surface, and breaking, discharge the vapor contained in them. The liquid, meanwhile, is in a state of violent agitation. If this process takes place in an inclosed space — as a cylinder fitted with a movable piston — so arranged that the pressure may be kept constant while the inclosed volume may change, the following phenomena are observed:

1. With a given constant pressure, the temperature remains constant during the process; and the greater the assumed pressure, the higher the temperature of vaporization. The temperature here referred to is that of the vapor above the liquid. As a matter of fact, the temperature of the liquid itself is slightly greater than that of the vapor, but the difference is small and negligible.

2. At a given pressure a unit weight of vapor assumes a definite volume, that is, the vapor has a definite density; and if the pressure is changed, the density of the vapor changes correspondingly. The density (or the specific volume) of a vapor is, therefore, a function of the pressure.

3. If the process of vaporization is continued at constant pressure until all the liquid has been changed to vapor, then if heat be still added to the vapor alone, the temperature will rise and the specific volume will increase; that is, the density will decrease.

case is said to be **saturated** and the constant temperature corresponding to the pressure at which the process is carried on is the **saturation temperature**. If no liquid is present, and through absorption of heat the temperature of the vapor rises above the saturation temperature, the vapor is said to be **superheated**. The difference between the temperature of the vapor and the saturation temperature is called the **degree of superheat**.

The process just described may be represented graphically on the $pV$-plane. See Fig. 60. Consider a unit weight of liquid subjected to a pressure $p$ represented by the ordinate of the line $A'A''$; and let the volume of the liquid (denoted by $v'$) be represented by $A'$. As vaporization proceeds at this constant pressure, the volume of the mixture of liquid and vapor increases, and the point representing the state of the mixture moves along the line $A'A''$. 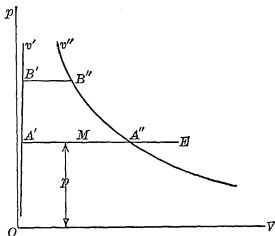The point $A''$ represents the volume $v''$ of the saturated vapor at the completion of vaporization; therefore, the segment $A'A''$ represents the increase of volume $v'' - v'$. Any point between $A'$ and $A''$, as $M$, represents the state of a mixture of liquid and vapor, and the position of the point depends on the ratio of the weight of the vapor to the weight of the mixture. Denoting this ratio by $x$, we have

$$x = \frac{A'M}{A'A''},$$ whence it appears that at $A'$, $x = 0$, while at $A''$,

$x = 1$. This ratio $x$ is often called the **quality** of mixture.

If the mixture is subjected to higher pressure during vaporization, the state-point will move along some other line, as $B'B''$. The specific volume indicated by $B''$ is smaller than that indicated by $A''$. The curve $v''$, giving the specific volumes of the satu-



FIG. 60.

rated vapor for different pressures, is called the **saturation curve**; while the curve $v'$, giving the corresponding liquid volume, is the **liquid curve**. These curves $v'$, $v''$ are in a sense boundary curves. Between them lies the region of liquid and vapor mixtures, and to the right of $v''$ is the region of superheated vapor. Any point in this latter region, as $E$, represents a state of the superheated vapor.

**107. Functional Relations. Characteristic Surfaces.** — For a mixture of liquid and saturated vapor, the functional relations connecting the coördinates $p$, $v$, and $t$ are essentially different from the relation for a permanent gas. As explained in the preceding article, the temperature of the mixture depends upon the pressure only, and we cannot, as in the case of a gas, give $p$ and $t$ any values we choose. The volume of a unit weight of the mixture depends (1) upon the specific volume of the vapor for the given pressure and (2) upon the quality $x$. Hence we have for a mixture the following functional relations:

$$t = f(p), \text{ or } p = F(t), \tag{1}$$

$$v = \phi(p, x). \tag{2}$$

With superheated steam, as with gases, $p$ and $t$ may be varied independently, and consequently the functional relation between $p$, $v$, and $t$ has the general form

$$\psi(p, v, t) = 0. \tag{3}$$
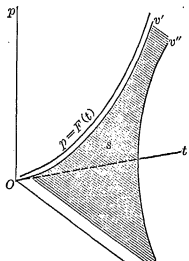


The characteristic surface of a saturated vapor is shown in Fig. 61. It is a cylindrical surface $S$ whose generating elements cut the $pt$-plane in the curve $p = F(t)$. These elements are limited by the two space curves $v'$ and $v''$, which when projected on the $pv$-plane give the curves $v'$, $v''$ of Fig. 60. The space curve $v''$ is the intersection of the

**Relation between Pressure and Temperature.** — The relation $p = F(t)$ between the pressure $p$ and temperature $t$ of a saturated vapor must be determined by experiment. To Regnault are due the experimental data for a large number of vapors. Further experiments on water vapor have been made by Ramsey and Young, by Battelli, and very recently by Holborn and Henning. These last-mentioned experiments were made with the greatest accuracy and with all the refinements of modern apparatus; they may, therefore, be regarded as furnishing the most reliable data at present available on the pressure and temperature of saturated water vapor. Experiments on other saturated vapors of technical importance, carbon dioxide, sulphur dioxide, ammonia, etc., have been made by Amagat, Pictet, Cailletet, Dieterici, and others. It is likely, however, that further experiments must be made before the data for these vapors are as reliable as those for water vapor.

If the experimentally determined values of $p$ and $t$ be plotted, they will give the curve whose equation is $p = f(t)$ (Fig. 61). To express this relation many formulas have been proposed, some purely empirical, some having a more or less rational basis. A few of these formulas are the following:

1. *Biot's Formula.* — As used by Regnault, Biot's equation has the form

$$\log p = a - b\alpha^n + c\beta^n, \qquad (1)$$

where

$$n = t - C.$$

This formula is purely empirical. Having five constants, the curve may be made to pass through five experimentally determined points; hence, the formula may be made to fit the experimental values very closely throughout a considerable range. The following are the values of the constants as given by Prof. Peabody:

| FOR STEAM FROM 32° TO 212° F., $p$ IN POUNDS PER SQUARE INCH. | FOR STEAM FROM 212° TO 428° F., $p$ IN POUNDS PER SQUARE INCH. |
|---|---|
| $a = 3.125906$ | $a = 3.743976$ |
| $\log b = 0.611740$ | $\log b = 0.412002$ |
| $\log c = 8.13204 - 10$ | $\log c = 7.74168 - 10$ |
| $\log \alpha = 9.998181 - 10$ | $\log \alpha = 9.998562 - 10$ |
| $\log \beta = 0.0038134$ | $\log \beta = 0.0042454$ |
| $n = t - 32$ | $n = t - 212$ |

2. *Rankine's Formula.* — Rankine proposed an equation of the form

$$\log p = A + \frac{B}{T} + \frac{C}{T^2},\qquad(2)$$

in which $T$ denotes the absolute temperature. This formula has been much used in calculating steam tables, especially in England. Having but three constants, it is not as accurate as the Biot formula. The following are the values for the constants, when $p$ is taken in pounds per square inch, and $T = t + 460$:

$A = 6.1007$; $B = -2719.8$; $C = 400125$.

3. The *Dupré-Hertz* formula has the form

$$\log p = a - b \log T - \frac{c}{T}.\qquad(3)$$

This equation has been derived rationally by Gibbs, Bertrand, and others, and gives, with a proper choice of constants, results that agree well with experiment. Using the results of Regnault's experiments, Bertrand found the following values of the constant for various vapors (metric units).

|  | $a$ | $b$ | $c$ |
|---|---|---|---|
| Water . . . . . . . . | 17.44324 | 3.8682 | 2795.0 |
| Ether . . . . . . . . | 13.42311 | 1.9787 | 1729.97 |
| Alcohol . . . . . . . | 21.44687 | 4.2248 | 2734.8 |
| Chloroform . . . . . . | 19.29793 | 3.9158 | 2179.1 |
| Sulphur dioxide . . . . | 16.99036 | 3.2198 | 1604.8 |
| Ammonia . . . . . | 13.37156 | 1.8726 | 1449.8 |
| Carbon dioxide . . . . | 6.41443 | − 0.4186 | 819.77 |
| Sulphur . . . . . . . | 19.1074 | 3.4048 | 4684.5 |

4. *Bertrand's Formulas.* — Bertrand has suggested two equations, namely :

$$p = k \frac{T^a}{(T + a)^\beta},\qquad(4)$$

and

$$p = k \left(\frac{T - b}{T}\right)^n.\qquad(5)$$

The latter may be written in the more convenient form

$$\log p = \log k - n \log \frac{T}{\quad}.\qquad(6)$$

Bertrand's second formula (6) has the advantage over the others suggested by lending itself to quick and easy computation. Furthermore, although it has but three constants, it gives results that agree remarkably well with the experiments of Holborn and Henning on water vapor. The constants are as follows (English units):

$$T = t + 459.6$$
$$n = 50.$$

| From 32° – 90° F. | From 90° – 237° F. | From 238° – 420° F. |
|---|---|---|
| $b = 140.1$ | $b = 141.43$ | $b = 140.8$ |
| $\log k = \quad 6.23167$ | $\log k = \quad 6.30217$ | $\log k = \quad 6.27756$ |

The agreement between observed and calculated values is shown in the following table. The maximum difference is one tenth of one per cent.

| TEMPERATURE, C. | PRESSURE IN MM. OF MERCURY | |
|---|---|---|
| | Bertrand's Formula *H.C.Cheeseman* | Experiments of Holborn and Henning |
| 0 | 4.577 | 4.579 |
| 10 | 9.208 | 9.205 |
| 20 | 17.511 | 17.51 |
| 30 | 31.682 | 31.71 |
| 40 | 55.121 | 55.13 |
| 50 | 92.325 | 92.30 |
| 60 | 149.21 | 149.19 |
| 70 | 233.55 | 233.53 |
| 80 | 354.97 | 355.1 |
| 90 | 525.64 | 525.8 |
| 100 | 760 | 760 |
| 110 | 1075.2 | 1074.5 |
| 120 | 1489.7 | 1488.9 |
| 130 | 2025.2 | 2025.6 |
| 140 | 2708.3 | 2709.5 |
| 150 | 3566.7 | 3568.7 |
| 160 | 4631.1 | 4633 |
| 170 | 5935.2 | 5937 |
| 180 | 7515 | 7514 |
| 190 | 9409.1 | 9404 |
| 200 | 11658 | 11647 |

**5. Marks' Equation.** — Professor Marks has deduced an equation that gives with remarkable accuracy the relation between $p$ and $T$ throughout the range 32° F. to 706.1° F., the latter temperature being the critical temperature, as established by the recent experiments of Holborn and Baumann. The form of the equation is

$$\log p = a - \frac{b}{T} - cT + eT^2. \tag{7}$$

The constants have the following values: $a = 10.515354$, $b = 4873.71$, $c = 0.00405096$, $e = 0.000001392964$.

**109. Expression for $\dfrac{dp}{dt}$.** — In the Clapeyron-Clausius formula for the specific volume of a saturated vapor, the derivative $\dfrac{dp}{dt}$ is required. An expression for this derivative is obtained by differentiating any one of the equations (1) to (7) of Art. 108. Thus from (6),

$$\frac{dp}{dt} = np\left(\frac{1}{T-b} - \frac{1}{T}\right) = \frac{nbp}{T(T-b)}; \tag{1}$$

whence

$$\log \frac{dp}{dt} = \log nb + \log p - \log T - \log (T-b).$$

Values of $\dfrac{dp}{dt}$ are readily calculated since the terms $\log T$, $\log (T-b)$, and $\log p$ appear in the calculation of $p$ from (6).

**110. Energy Equation applied to the Vaporization Process.** — It is customary in estimating the energy, entropy, heat content, etc., of a saturated vapor to assume liquid at 32° F. (0°C.) as a datum from which to start. Thus the energy of a pound of steam is assumed to be the energy above that of a pound of water at 32° F.

Suppose that a pound of liquid at 32° is heated until its temperature reaches the boiling point corresponding to the pressure to which the liquid is subjected. The heat required is given by the equation

$$q' = \int_{32}^{t} c' dt, \tag{1}$$

where $c'$ denotes the specific heat of the liquid. This process

s represented on the $TS$-plane by a curve $AA'$ (Fig. 62).
The ordinate $OA$ represents the initial absolute temperature
$32 + 459.6 = 491.6$, the ordinate $A_1A'$ the temperature of va-
porization given by the relation $t = f(p)$, and the area $OAA'A_1$
the heat $q'$ absorbed by the liquid. This heat $q'$ is called the
heat of the liquid.*

When the temperature of vaporization is reached, the liquid
begins to change to vapor, the temperature remaining constant
during the process. A definite quantity of heat, dependent
upon the pressure, is required to change the liquid completely
into vapor. This is called the
heat of vaporization and is de-
noted by the symbol $r$. In Fig.
62, the passage of the state-
point from $A'$ to $A''$ represents
the vaporization, and the heat
$r$ is represented by the area
$A_1A'A''A_2$. For a higher pres-
sure the curve $AB'$ represents
the heating of the liquid and
the line $B'B''$ the vaporization.

During the heating of the
liquid the change in volume is
very small and may be neg-


FIG. 62.

lected; hence, the external work done is negligible also, and
substantially all of the heat $q'$ goes to increase the energy of
the liquid. During the vaporization, however, the volume
changes from $v'$ (volume of 1 lb. of liquid) to $v''$ (volume of
1 lb. of saturated vapor). Since the pressure remains constant,
the external work that must be done to provide for the increase
of volume is
$$L = p(v'' - v'). \tag{2}$$

According to the energy equation, the heat $r$ added during
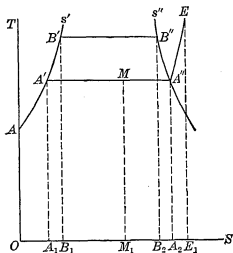vaporization is used in increasing the energy of the system and

is the heat required to increase the energy of the unit weight of substance when it changes from liquid to vapor. This heat is denoted by $\rho$ and is called the **internal latent heat**. Since during the vaporization the temperature is constant, there is no change of kinetic energy; it follows that $\rho$ is expended in increasing the potential energy of the system. The heat equivalent of the external work, namely, $Ap\,(v'' - v')$, is called the **external latent heat**, and for convenience may be denoted by $\psi$. We have then

$$r = \rho + \psi. \tag{4}$$

The **total heat** of the saturated vapor is evidently the sum of the heat of the liquid and the heat of vaporization. Thus,

$$q'' = q' + r,$$

or
$$q'' = q' + \rho + \psi. \tag{5}$$

Comparing (5) with the general energy equation, it is evident that the sum $q' + \rho$ gives the increase of energy of the saturated vapor over the energy of the liquid at 32° F. Denoting this by $u''$, we have

$$Au'' = q' + \rho. \tag{6}$$

If the vaporization is not completed, the result is a mixture of saturated vapor and liquid of quality $x \left( x = \dfrac{A'M}{A'A''} \right)$, as indicated by the point $M$ (Fig. 60 and 62). In this case the heat required to vaporize the part $x$ is $xr$ heat units and the total heat of the mixture, which may be denoted by $q_x$, is given by

$$q_x = q' + xr$$
$$= q' + x\rho + x\psi. \tag{7}$$

The energy of the mixture (per unit weight) above the energy of water at 32° F. is, therefore, given by the relation

$$Au_x = q' + x\rho, \tag{8}$$

and the external work done is

$$L_x = Jx\psi. \tag{9}$$

If heat is added at constant pressure, after the vaporization is completed, the vapor will be superheated. The state-point will move along the curve $A''E$ (Fig. 48) and the heat $c\,(t - t'')$

represented by the area $A_2A''EE_1$ will be added. Here $c_p$ denotes the mean specific heat of the superheated vapor, $t_e$ the final temperature, and $t''$ the saturation temperature corresponding to the pressure $p$. The total heat corresponding to the point $E$ and represented by the area $OAA'A''EE_1O$ is, therefore,

$$q_e = q' + r + c_p \left( t_e - t'' \right). \tag{10}$$

If $v_e$ denotes the final volume, and $u_e$ the energy above liquid at 32° F., then the external work for the entire process is

$$L = p \left( v_e - v' \right), \tag{11}$$

and, therefore,

$$Au_e = q_e - Ap \left( v_e - v' \right). \tag{12}$$

**111. Heat Content of a Saturated Vapor.** — By definition we have for the heat content of a unit weight of saturated vapor

$$i'' = A(u'' + pv'') = q' + \rho + Apv''. \tag{1}$$

Since the total heat is

$$q'' = q' + \rho + Ap \left( v'' - v' \right), \tag{2}$$

it appears that $i''$ is larger than $q''$ by the value of the term $Apv'$. As $v'$, the specific volume of water, is small compared with $v''$, the term $Apv'$ may be neglected except for very high pressures, and $q''$ and $i''$ may be considered equal.

In most of the older steam tables values of $q''$ were given; in the more recent tables, the values of $i''$ instead of $q''$ are usually tabulated.

**112. Thermal Properties of Water Vapor.** — From the relation

$$q'' = q' + r,$$

it appears that if any two of the three magnitudes $q''$, $q'$, $r$ are determined by experiment, the third may be found by a combination of those two. Various experiments have been made to determine each of these magnitudes for the range of temperature ordinarily employed, and as a result several empirical formulas have been deduced. Naturally the greatest amount of attention has been given to water vapor, and we may consider the properties of this medium as quite accurately known at the present time. Ammonia, sulphur dioxide, and other vapors have not

been studied with the same completeness, and their properties
are as yet only imperfectly known.

In the sections immediately following we shall give briefly the
results of the latest and most accurate experiments on water
vapor.

**113. Heat of the Liquid.** — Denoting $c'$ the specific heat of
water, the heat of the liquid above 32° F. is given by the re-
lation

$$q' = \int_{32}^{t} c' dt. \tag{1}$$

If the specific heat $c'$ were constant at all temperatures, this
equation would reduce to the simple form $q' = c'(t - 32)$. As
a matter of fact, however, $c'$ is not constant, and its variation
with the temperature must be known before (1) can be used to
calculate $q'$. Between 0° C. and 100° C. (32°–212° F.) the
experiments of Dr. Barnes may be regarded as the most trust-
worthy. Taking $c' = 1$ at a temperature of 17.5° C., the fol-
lowing values are given by Griffiths as representing the results
obtained by Barnes.

| TEMPERATURE | | SPECIFIC HEAT | TEMPERATURE | | SPECIFIC HEAT |
|---|---|---|---|---|---|
| C. | F. | | C. | F. | |
| 0 | 32 | 1.0083 | 55 | 131 | 0.9981 |
| 5 | 41 | 1.0054 | 60 | 140 | 0.9987 |
| 10 | 50 | 1.0027 | 65 | 149 | 0.9993 |
| 15 | 59 | 1.0007 | 70 | 158 | 1.0000 |
| 20 | 68 | 0.9992 | 75 | 167 | 1.0007 |
| 25 | 77 | 0.9978 | 80 | 176 | 1.0015 |
| 30 | 86 | 0.9975 | 85 | 185 | 1.0023 |
| 35 | 95 | 0.9974 | 90 | 194 | 1.0031 |
| 40 | 104 | 0.9973 | 95 | 203 | 1.0040 |
| 45 | 113 | 0.9974 | 100 | 212 | 1.0051 |
| 50 | 122 | 0.9977 | | | |

These values are shown graphically in Fig. 63. From them
values of $q'$ may be obtained by means of relation (1).

In the actual calculation of the tabular values of $q'$, the fol-
lowing method may be used advantageously. Since the specific
heat $c'$ does not differ greatly from 1, let

$$c' = 1 + k,$$

where $k$ is a small correction term. Then for $q'$ we have

$$q' = \int_{32}^{t} c' dt = t - 32 + \int_{32}^{t} k dt.$$

If now values of $k$ are plotted as ordinates with corresponding temperatures as abscissas, the values of the integral $\int k dt$ may easily be determined by graphical integration.

For temperatures above 212° F. the only available experiments giving the heat of the liquid are those of Regnault and Dieterici. The results of these experiments are somewhat discordant and unsatisfactory. Fortunately, we have for the range 212° to 400° F. reliable formulas for the total heat $q''$ and the latent heat $r$, and we may therefore determine $q'$ from the relation
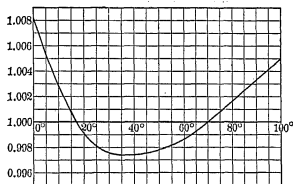


Fig. 63.

$$q' = q'' - r.$$

**114. Latent Heat of Vaporization.** — The latent heat of water vapor for the range 0° to 180° C. (32°–356° F.) has been accurately determined by direct experiment. The results of the experiments of Dieterici at 0° C., Griffiths at 30° and 40° C., Smith over the range 14°–40° C., and Henning over the range 30°–180° C. show a remarkable agreement, all of the values lying on, or very near, a smooth curve. The observed values are given in the third column of the following table. As the thermal units employed by the different investigators were not precisely the same, all values have been reduced to a common unit, the joule.

It is readily found that a second-degree equation satisfactorily represents the relation between $r$ and $t$. Taking $r$ in joules, the following equation gives the values in the fourth

LATENT HEAT OF WATER, IN JOULES

|  | TEMPERA-TURE, C. | LATENT HEAT | | DIFFERENCE PER CENT |
|---|---|---|---|---|
|  |  | Observed | Calculated |  |
| Dieterici . . . . . . | 0 | 2493.8 | 2495.8 | − 0.08 |
| Griffiths . . . . . . | 30.00 | 2429.3 | 2430.8 | − 0.06 |
|  | 40.15 | 2403.6 | 2407.5 | − 0.16 |
| Smith   . . . . . . | 13.95 | 2467.6 | 2466.3 | + 0.05 |
|  | 21.17 | 2451.2 | 2450.5 | + 0.03 |
|  | 28.06 | 2435.0 | 2435.2 | − 0.01 |
|  | 39.80 | 2405.8 | 2408.3 | − 0.10 |
| Henning, First Series . . . . | 30.12 | 2424.8 | 2430.6 | − 0.24 |
|  | 49.14 | 2385.3 | 2386.2 | − 0.04 |
|  | 64.85 | 2343.0 | 2347.7 | − 0.20 |
|  | 77.34 | 2313.7 | 2316.0 | − 0.10 |
|  | 89.29 | 2285.6 | 2284.6 | + 0.05 |
|  | 100.59 | 2254.2 | 2254.0 | + 0.01 |
| Henning, Second Series . . . | 102.34 | 2248.7 | 2249.2 | − 0.02 |
|  | 120.78 | 2200.2 | 2197.2 | + 0.14 |
|  | 140.97 | 2134.2 | 2137.6 | − 0.16 |
|  | 160.56 | 2077.0 | 2077.2 | − 0.01 |
|  | 180.72 | 2018.6 | 2012.3 | + 0.31 |

The differences between the observed values and those calcu-
lated from this formula are shown in the last column.

The mean calorie is equivalent to 4.184 joules; hence, divid-
ing the constants of Eq. (1) by 4.184, the resulting equation
gives $r$ in calories. This equation is readily changed to give
$r$ in B. t. u. with $t$ in degrees F. We thus obtain finally

$$r = 970.4 - 0.655\,(t - 212) - 0.00045\,(t - 212)^2. \qquad (2)$$

This formula may be accepted as giving quite accurately the
latent heat from 32° F. to perhaps 400° F.*

**115. Total Heat. Heat Content.** — For the temperature range
32° to 212° F. the total heat $q''$ is obtained from the relation
$q'' = q' + r$. As has been shown, values of $q'$ and of $r$ can be
accurately determined for this range. For temperatures be-
tween 212° and 400°, we are indebted to Dr. H. N. Davis for
the derivation of a formula for the heat content of saturated
vapor of water. The earlier experiments of Regnault led to
the formula $\qquad q'' = 1091.7 + 0.305\,(t - 32)$,
which has been extensively used in the calculation of tabu-
lar values. By making use of the throttling experiments of
Grindley, Griessmann, and Peake, Dr. Davis* has shown that
Regnault's linear equation is incorrect, and that a second-degree
equation of the form

$$q'' = a + b\,(t - 212) + c\,(t - 212)^2$$

may be adopted. Dr. Davis obtains for the heat content $i''$
the formula

$$i'' = 1150.4 + 0.3745\,(t - 212) - 0.00055\,(t - 212)^2. \qquad (3)$$

From this formula the total heat $q''$ is readily determined from
the relation $q'' = i'' - Apv'$. It is found, however, that slight
changes in the constants are desirable in view of Henning's sub-
sequent experiments on latent heat. The modified formula

$$i'' = 1150.4 + 0.35\,(t - 212) - 0.000333\,(t - 212)^2 \qquad (4)$$

may be accepted as giving with reasonable accuracy values of
$i''$ for the range 212° to 400° F.

**116. Specific Volume of Steam.** — The specific volume $v''$ of
a saturated vapor at various pressures may be determined
experimentally. For water vapor accurate measurements of
$v''$ for temperatures between 100° and 180° C. have been made
by Knoblauch, Linde, and Klebe. It is possible, however, to
calculate the volume $v''$ from the general equations of thermo-
dynamics; and the agreement between the calculated values
and those determined by experiment serves as a valuable check

critical temperature, 689° F. At the higher temperatures it doubtless gives more
accurate values than the second-degree formula. See *Proceedings of the Amer.
Acad. of Arts and Sciences* **45**, 284.

* *Trans. Am. Soc. of Mech. Engrs.* **30**, 1419, 1908. See Art. 164 for a dis-
cussion of the method employed in the derivation of formula (3).

on the accuracy with which the factors entering into the theoretical formula have been determined.

The general equation (Art. 56)

$$dq = c_v dT + A T \left(\frac{\partial p}{\partial t}\right)_v dv \qquad (1)$$

applies to any reversible process. Let us apply it to the process of changing a liquid to saturated vapor at a given constant temperature. For a saturated vapor, the partial derivative $\left(\frac{\partial p}{\partial t}\right)_v$ is simply the derivative $\frac{dp}{dt}$, and this is a constant for any given temperature (Art. 107). Hence, for the process in question, we have (since $dT = 0$)

$$q = A T \frac{dp}{dt} \int_{v'}^{v''} dv = A T \frac{dp}{dt}(v'' - v'). \qquad (2)$$

But in this case $q$ is the heat of vaporization $r$; hence we have

$$v'' - v' = \frac{r}{A T \dfrac{dp}{dt}} = \frac{Jr}{T} \frac{1}{\dfrac{dp}{dt}}. \qquad (3)$$

This is the Clapeyron-Clausius formula for the increase of volume during vaporization.

Having for any temperature the derivative $\frac{dp}{dt}$ (Art. 109) and the latent heat $r$, the change of volume $v'' - v'$ is readily calculated. The following table shows a comparison between the values of $v''$ determined experimentally by Knoblauch, Linde, and Klebe, and those calculated by Henning from the Clapeyron equation, using the values of $r$ determined from his own experiments. The third line gives values of $v''$ calculated from the characteristic equation of superheated steam. (See Art. 132.)

|  | SPECIFIC VOLUMES, CU. METERS PER KG. | | | | |
|---|---|---|---|---|---|
|  | 100° | 120° | 140° | 160° | 180° C. |
| Experimental . . . . | 1.674 | 0.8922 | 0.5091 | 0.3073 | 0.1943 |
| Henning . . . . . . | 1.673 | 0.8912 | 0.5078 | 0.3071 | 0.1947 |
| From the equation for superheated steam . . | 1.673 | 0.8915 | 0.5084 | 0.3071 | 0.1945 |

The relation between the pressure and specific volume $v''$ of saturated steam may be represented approximately by an equation of the form

$$pv''^n = C. \tag{4}$$

Zeuner, from the values of $v''$ given in the older steam tables, deduced the value $n = 1.0646$.    Taking the more accurate values of $v''$ given in the later steam tables, we find

$$n = 1.0631, \qquad C = 484.2.$$

**117. Entropy of Liquid and of Vapor.** — During the process of heating the liquid from its initial temperature to the temperature of vaporization the entropy of the liquid increases. Thus, referring to Fig. 62, if the initial temperature be 32° F., denoted by point $A$, and if the temperature be raised to that denoted by $A'$, the increase of entropy of the liquid is represented by $OA_1$, the heat of the liquid by area $OAA'A_1$.

Since $dq' = c'dT$, we have as a general expression for the entropy $s'$ of the liquid corresponding to a temperature $T$,

$$s' = \int_{491.6}^{T} \frac{dq'}{T} = \int_{491.6}^{T} \frac{c'dT}{T}. \tag{1}$$

If the specific heat $c'$ is given as a function of $T$, the integration is readily effected. In the case of water, where the specific heat varies somewhat irregularly, as shown by the table of Art. 115, the following expedient may be used. Put $c' = 1 + k$; then $k$ is a small correction term that is negative between 63° and 150° F. and positive elsewhere. From (1) we have, therefore,

$$s' = \int \frac{dT}{T} + \int \frac{kdT}{T}. \tag{2}$$

The first term is readily calculated and the small correction term may be found by graphical integration.    This method was used in calculating the values of $s'$ in table I.

The increase of entropy during vaporization, represented by $A'A''$ (Fig. 62), is evidently the quotient $\dfrac{r}{T}$.    Hence the entropy of the saturated vapor in the state $A''$ is

For a mixture of quality $x$, as represented by the point $M$, the entropy is

$$s = s' + \frac{xr}{T}. \tag{4}$$

**118. Steam Tables.** — The various properties of saturated steam considered in the preceding articles are tabulated for the range of pressure and temperature used in ordinary technical applications. Many such tabulations have appeared. The older tables based largely upon Regnault's data are now known to be inaccurate to a degree that renders them valueless. The recent tables of Marks and Davis [*] and of Peabody, [†] however, embody the latest and most accurate researches on saturated steam.

Table I at the end of the book has been calculated from the formulas derived in Arts. 108–116. The values differ but little from those obtained by Marks and Davis. The first column gives the pressures in inches of mercury up to atmospheric pressure, and in pounds per square inch above atmospheric pressure; the second column contains the corresponding temperatures. Columns 3 and 4 give the heat content of the liquid and saturated vapor, respectively. The values in column 3 may be taken also as the heat of the liquid $q'$; similarly, column 4 may be considered as giving the total heat $q''$ of the saturated vapor. As we have seen, the difference between $i''$ and $q''$ is negligible except at high pressures.

**119. Properties of Saturated Ammonia.** — Several tables of the properties of saturated vapor of ammonia have been published. Among these may be mentioned those of Wood, Peabody, Zeuner, and Dieterici. The values given by the different tables are very discordant, as they are for the most part obtained by theoretical deductions based on meager experimental data. For temperatures above 32° F. the values obtained by Dieterici as the result of direct experiment are most worthy of confidence.

Dieterici determined experimentally the specific volume $v''$ of the saturated vapor for the temperature range 0° to 40° C.

* Marks and Davis, *Steam Tables and Diagrams*, Longmans, 1908.

($32°$ to $104°$ F.) and also for the same range the specific heat $c'$ of the liquid ammonia. The formula deduced by Dieterici for specific heat is, for the Fahrenheit scale,

$$c' = 1.118 + 0.001156 \ (t - 32). \qquad (1)$$

From this formula, the heat of the liquid $q'$ and the entropy of the liquid $s'$ are readily calculated by means of the relations

$$q' = \int_{32}^{t} c'dt, \quad s' = \int_{491.6}^{T} c' \frac{dT}{T}.$$

The relation between pressure and temperature is given by the experiments of Regnault. The results of these experiments are expressed quite accurately by Bertrand's formula

$$\log p = 5.87395 - 50 \log \frac{T}{T - 84.3}. \qquad (2)$$

Above $32°$, having Dieterici's experimental values of $v''$ and from (2) the derivative $\dfrac{dp}{dT}$, we may find the latent heat $r$ from the Clapeyron-Clausius formula

$$r = A \ (v'' - v') \ T\frac{dp}{dT}. \quad \text{(See Art. 116.)} \quad (3)$$

For temperatures below $32°$ we have neither $v''$ nor $r$ given experimentally; hence for this region values of various properties can only be determined by extrapolation, and the accuracy of the results thus obtained is by no means assured. In calculating the values of table III the following method was used. The values of $r$ for temperatures above $32°$ were calculated by means of (3). It was found that these values may be represented quite accurately by the equation

$$\log r = 1.7920 + 0.4 \log (266 - t), \qquad (4)$$

in which $266°$ is the critical temperature of ammonia. (See p. 176, footnote.) Formula (4) was assumed to hold for the range $32°$ to $-30°$; and from the values of $r$ thus obtained values of $v''$ were calculated by means of the Clapeyron relation (3).

**120. Other Saturated Vapors.** — Several saturated vapors in addition to the vapors of water and ammonia have important technical applications. Sulphur dioxide and carbon dioxide in

particular are used as media for refrigerating machines. The properties of the former fluid have been investigated by Cailletet and Mathias, those of the latter by Amagat and Mollier. The results of these investigations are embodied in tables.*

The properties of several vapors of minor importance have also been tabulated, the data being furnished for the most part by Regnault. These include ether, chloroform, carbon bisulphide, carbon tetrachloride, aceton, and vapor of alcohol.†

**121. Liquid and Saturation Curves.** — If for various temperatures the corresponding values of $s'$, the entropy of the liquid, be laid off as abscissæ, the result is a curve $s'$, Fig. 62. This is called the **liquid** curve. If, likewise, values of

$$s'' = s' + \frac{r}{T'}$$

be laid off as abscissæ, a second curve $s''$ is obtained. This is called the **saturation** curve.

As already stated (Art. 106), any point between the curves $s'$ and $s''$ represents a mixture of liquid and vapor, the ratio $x$ depending upon the position of the point. It is possible, therefore, to draw between the curves $s'$ and $s''$ a series of constant-$x$ lines. Each of the horizontal segments $A'A''$, $B'B''$, etc., is divided into a convenient number (say 10) of equal parts, and corresponding points are joined by curves. The successive curves, therefore, are the loci of points for which $x = 0.1$, $x = 0.2$, etc.

The form of the saturation curve has an important relation to the behavior of a saturated vapor. For nearly all vapors, the curve has the general form shown in Fig. 62; that is, the entropy $s''$ decreases with rising temperature. In the case of ether vapor, however, the entropy increases with rising temperature and the curve has, therefore, the same general direction as the liquid curve $s'$.

**122. Specific Heat of a Saturated Vapor.** — Referring to the saturation curve of Fig. 62, suppose the state-point to move

<hr/>

\* For tables of the properties of saturated vapor of $SO_2$ and $CO_2$ in English units, see Zeuner's *Technical Thermodynamics*, Klein's translation, Part II.

† See Peabody's *Steam and Entropy Tables*, or Zeuner's *Technical Thermodynamics*, Part II.

from $A''$ to $B''$. This represents a rise of temperature of the saturated vapor during which the vapor remains in the saturated condition. The process must evidently be accompanied by the withdrawal of heat represented by the area $A_2A''B''B_2$; and the reverse process, fall in temperature from $B''$ to $A''$, is accompanied by the *addition* of heat represented by the same area. It appears, therefore, that along the saturation curve the ratio $\dfrac{\Delta q}{\Delta t}$ is negative (except in the case of ether); that is, the specific heat of a saturated vapor is, in general, negative.

An expression for the specific heat $c''$ of the saturated vapor may be obtained as follows. The entropy of the saturated vapor is given by the equation

$$s'' = s' + \frac{r}{T}; \qquad (1)$$

hence the change of entropy corresponding to a change of temperature is obtained by differentiating (1), thus

$$ds'' = ds' + d\left(\frac{r}{T}\right). \qquad (2)$$

But

$$ds' = \frac{c'\,dT}{T}, \qquad (3)$$

and similarly for the saturation curve,

$$ds'' = \frac{c''\,dT}{T}. \qquad (4)$$

Substituting these values $ds'$ and $ds''$ in (2), the result is

$$c'' = c' + T\frac{d}{dT}\left(\frac{r}{T}\right),$$

or

$$c'' = c' + \frac{dr}{dT} - \frac{r}{T}. \qquad (5)$$

But since $c' = \dfrac{dq}{dT}$, (5) may be written

$$c'' = \frac{d(q'+r)}{dT} - \frac{r}{T}$$

$q''$ is known. Thus for water vapor above 212°, we have

$$q'' = a + b(t - 212) - c(t - 212)^2;$$

whence

$$\frac{dq''}{dT} = b - 2\,c(t - 212),$$

where

$$b = 0.35 \text{ and } c = 0.000333.$$

At 212°, we have, for example,

$$c'' = 0.35 - \frac{r}{T} = 0.35 - \frac{970.4}{212 + 459.6} = -1.095.$$

**123. General Equation for Vapor Mixtures.** — Let heat be added to a unit weight of mixture of liquid and saturated vapor, of which the part $x$ is vapor and the part $1 - x$ is liquid. In general, the temperature $T$ and quality $x$ will change; hence the heat added is the sum of two quantities: (1) the heat required to increase the temperature with $x$ remaining constant; (2) the heat required to increase $x$ with the temperature constant. The first is evidently $c'(1 - x)dT + c''x dT$; and the second is $r dx$; hence we have

$$dq = c'(1 - x)dT + c''x dT + r dx \qquad (1)$$

as the general differential equation for the heat added to a mixture.

From (1) the general expression for the change of entropy of a mixture is given by

$$ds = \frac{dq}{T} = \frac{c'(1 - x) + c''x}{T}dT + \frac{r}{T}dx. \qquad (2)$$

The fact that $ds$ is an exact differential leads at once to the relation

$$\frac{\partial}{\partial x}\left[\frac{c'(1 - x) + c''x}{T}\right]_T = \frac{\partial}{\partial T}\left(\frac{r}{T}\right)_x, \qquad (3)$$

whence

$$\frac{c'' - c'}{T} = \frac{\partial}{\partial T}\left(\frac{r}{T}\right),$$

or

$$c'' = c' + \frac{dr}{dT} - \frac{r}{T}, \qquad (4)$$

the relation that was obtained in Art. 122.

**124. Variation of $x$ during Adiabatic Changes.** — Let the point $A''$ (Fig. 64) represent the state of saturated vapor as regards pressure and temperature. Adiabatic expansion will then be represented by a vertical line $A''E$, the final point $E$ being at lower temperature. Adiabatic compression will be shown by a vertical line $A''G$. With a saturation curve of the form shown, it appears that during adiabatic expansion some of the vapor condenses, while adiabatic compression results in superheating. If the state-point is originally at $M$ so that $x$ is somewhat less than 1 (say 0.7 or 0.8), then adiabatic expansion is accompanied by a decrease in $x$, adiabatic compression by an increase of $x$.

If the saturation curve slopes in the other direction, as in the case of ether, the conditions just stated will, of course, be reversed.

Adiabatic expansion of the liquid is represented by the line $A'F$; evidently some of the liquid is vaporized during the



FIG. 64.

process. If the mixture is originally mostly liquid, as indicated by a point $N$ near the curve $s'$, then adiabatic expansion results in an increase of $x$, adiabatic compression in a decrease of $x$.

For a given pressure there is some value of $x$ for which an indefinitely small adiabatic change produces no change in $x$; in other words, at this point the constant-$x$ curve has a vertical tangent. For this point we have evidently $dq = 0$ and $dx = 0$, and the general equation (1), Art. 123, becomes

$$[c'(1-x) + c''x]dT = 0, \qquad (1)$$

whence

$$\frac{x}{x-1} = \frac{c'}{c''}, \qquad (2)$$

or

$$x = \frac{c'}{c'-c''}. \qquad (3)$$

The locus of the points determined by (3) is a curve $n$ (Fig. 64),
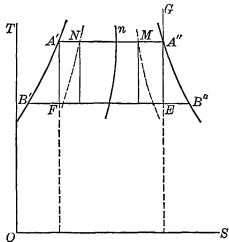
$$dq = rdx ; \qquad (4)$$

that is, all the heat entering the mixture is expended in vaporizing the liquid. The zero curve is of little practical importance.

The change of the quality $x$ during the adiabatic expansion of a mixture is readily calculated by means of the entropy equation. In the initial state, the entropy of the mixture is

$$s_1 = s_1' + \frac{x_1 r_1}{T_1},$$

and in the final state it is

$$s_2 = s_2' + \frac{x_2 r_2}{T_2}.$$

But for an adiabatic change $s_2 = s_1$; therefore, we have the relation $\qquad s_1' + \dfrac{x_1 r_1}{T_1} = s_2' + \dfrac{x_2 r_2}{T_2}, \qquad (5)$

in which $x_2$ is the only unknown quantity.

**125. Special Curves on the TS-plane.** — The region between the liquid and saturation curves may be covered with series of curves in such a way that the position of the point representing a mixture indicates at once the various properties of the mixture.

In the first place, horizontal lines intercepted between the curves $s'$ and $s''$ are lines of constant temperature, also lines of constant pressure; while vertical lines are lines of constant entropy.

Lines of constant quality, $x_1, x_2, x_3, \ldots$ may be drawn as explained in Art. 121.

Curves of constant volume may be drawn as follows: The volume of a unit weight of mixture whose quality is $x$ is given by the equation

$$v = x(v'' - v') + v', \qquad (1)$$

whence $\qquad x = \dfrac{v - v'}{v'' - v'}. \qquad (2)$

Suppose that the curve for some definite volume (say $v = 5$ cu. ft.) is to be located. For different pressures $p_1, p_2, p_3, \ldots$ the saturation volumes $v_1'', v_2'', v_3'', \ldots$ are known from the

tables. Substituting successively these values of $v''$ in (2), values of $x$, as $x_1$, $x_2$, $x_3$, . . . corresponding to the pressures $p_1$, $p_2$, $p_3$, . . . will be found. The value of $v'$ may be taken as constant for all pressures. The value of $x_1$ locates a definite point on the $p_1$ line, that of $x_2$ a point on the $p_2$ line, etc. The locus of these points is evidently a curve, any point of which represents a mixture having the given volume $v$; hence it is a constant-volume curve.

In a similar manner curves of constant energy $u$ may be located. Since

$$u = q' + x\rho, \qquad (3)$$

we have

$$x = \frac{u - q'}{\rho}. \qquad (4)$$

For given pressures $p_1$, $p_2$, · · ·

$$x_1 = \frac{u - q_1'}{\rho_1}, \quad x_2 = \frac{u - q_2'}{\rho_2}, \text{ etc.}$$

Values of $q'$ and $\rho$ for different pressure are given in the table, and therefore for a given $u$, values of $x_1$, $x_2$, . . . are readily calculated. These locate points on the corresponding $p$-lines, and the locus of the points is the desired constant-$u$ curve.

By the same process may be drawn curves of constant total heat,

$$q = q' + xr = \text{const.}$$

or curves of constant heat content

$$i = i' + xr = \text{const.}$$



FIG. 65.

In Fig. 65, the various curves are shown drawn through the same point $P$. From the general course of the curves the behavior of the mixture during a given change of state may be traced. Thus: (1) If a mixture expands adiabatically, $v$ increases but $p$, $T$, $u$, and $i$ decrease. The quality $x$ decreases as long as the state-point lies to the right of the zero curve. (2) If a mixture expands isodynamically ($u = \text{const.}$), $v$, $s$, and $x$ increase, $p$, $T$, and $i$ decrease.
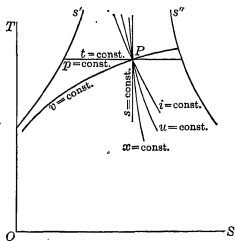
for water vapor, taking values of $s'$ and $s''$ from the steam table. Then draw the curves $v = 2$, $v = 10$, $v = 40$ cu. ft. Also draw the curves $u = 600$ B. t. u., $u = 800$ B. t. u.

## 126. Special Changes of State.

Certain of the curves described in preceding articles represent important changes of state of the mixture of saturated vapor and liquid. The principal relations governing some of these changes will be developed in this article. It is assumed that the system remains a mixture during the change, that is, that the path of the state-point is limited by the curves $s'$ and $s''$.

(a) *Isothermal, or Constant Pressure, Change of State.* — Let $x_1$ denote the initial quality, $x_2$ the final quality. Then the initial volume is

$$v_1 = x_1(v'' - v') + v'$$

and the final volume is

$$v_2 = x_2(v'' - v') + v'.$$

The change in volume is therefore

$$v_2 - v_1 = (x_2 - x_1)(v'' - v'), \qquad (1)$$

and the external work is

$$W = p(v_2 - v_1) = p(v'' - v')(x_2 - x_1). \qquad (2)$$

The change of energy is

$$u_2 - u_1 = J\rho(x_2 - x_1), \qquad (3)$$

and the heat absorbed is

$$q = r(x_2 - x_1). \qquad (4)$$

These equations refer to a unit weight of mixture.

EXAMPLE. At a pressure of 140 lb., absolute, the volume of one pound of a mixture of steam and water is increased by 0.8 cu. ft. The change of quality is $\dfrac{v_2 - v_1}{v'' - v'} = \dfrac{0.8}{3.199 - 0.017} = 0.2514$. The external work is

$$140 \times 144 \times 0.8 = 16{,}128 \text{ ft.-lb.}$$

The increase of energy is $J\rho(x_2 - x_1) = 778 \times 786.1 \times 0.2514 = 153850$ ft.-lb.; and the heat absorbed is $r(x_2 - x_1) = 869 \times 0.2514 = 218.5$ B. t. u.

(b) *Change of State at Constant Volume.* — Since the volumes $v_1$ and $v_2$ are equal, we have

$$x_1(v_1'' - v') = x_2(v_2'' - v'), \qquad (5)$$

where $v_1''$ and $v_2''$ are the saturation volumes corresponding to the pressures $p_1$ and $p_2$, respectively. From (5) the quality $x_2$ in the final state may be determined. The external work $W$ is zero; hence we have for the heat absorbed

$$q = A(u_2 - u_1) = (q_2' + x_2\rho_2) - (q_1' - x_1\rho_1) . \qquad (6)$$

EXAMPLE. A pound of a mixture of steam and water at 120 lb. pressure, quality 0.8, is cooled at constant volume to a pressure of 4 in. of mercury. Required the final quality and the heat taken from the mixture.

From (5)

$$x_2 = \frac{x_1(v_1'' - v')}{v_2'' - v'} = \frac{0.8(3.724 - 0.017)}{176.6} = 0.0167.$$

Therefore

$$q = 311.9 + 0.8 \times 795.8 - (93.4 + 0.0167 \times 959.5) = 839.2 \text{ B. t. u.}$$

(c) *Adiabatic Change of State.* For a reversible adiabatic change the entropy of the mixture remains constant; hence we have

$$s_1' + \frac{x_1 r_1}{T_1} = s_2' + \frac{x_2 r_2}{T_2}, \qquad (7)$$

from which equation the final quality $x_2$ can be found. Having $x_2$, the final volume $v_2$ per unit weight is

$$v = x_2(v_2'' - v') + v'. \qquad (8)$$

Since the heat added is zero, the external work is equal to the decrease in the intrinsic energy of the mixture. That is,

$$W = u_1 - u_2 = J[(q_1' + x_1\rho_1) - (q_2' + x_2\rho_2)]. \qquad (9)$$

EXAMPLE. Three cubic feet of a mixture of steam and water, quality 0.89, and having a pressure of 80 lb. per square inch, absolute, expands adiabatically to a pressure of 5 in. Hg. The final quality, final volume, and the external work are required.

From the steam tables we find the following values:

|  | $q$ | $\rho$ | $s'$ | $\dfrac{r}{T}$ | $v''$ |
|---|---|---|---|---|---|
| For $p = 80$ lb. | 281.8 | 819.6 | 0.4533 | 1.1667 | 5.464 |
| For $p = 5$ in. Hg. | 101.7 | 953.7 | 0.1880 | 1.7170 | 143.2 |

The weight of the mixture is

$$M = \frac{3}{x_1(v'' - v') + v'} = \frac{3}{0.89(5.464 - 0.017) + 0.017} = 0.6167 \text{ lb.}$$

From (7), the quality $x_2$ in the second state is given by the relation

$$0.4533 + 0.89 \times 1.1667 = 0.1880 + 1.7170\, x_2,$$

whence

$$x_2 = 0.759.$$

The volume in the second state, neglecting the insignificant volume of the liquid, is

$$V_2 = 0.6167 \times 0.759 \times 143.2 = 67.02 \text{ cu. ft.}$$

Finally, the external work is

$$W = 778 \times 0.6167\,[(281.8 + 0.89 \times 819.6) - (101.7 + 0.759 \times 953.7)] = 89{,}086 \text{ ft.-lb.}$$

(d) *Isodynamic Change of State.* If the energy of the mixture remains constant, we have

$$u_1 = u_2,$$

or

$$q_1' + x_1\rho_1 = q_2' + x_2\rho_2. \tag{10}$$

From (10) the final value of $x$ is determined, and the final volume is then found from (8).

For the isodynamic change, the heat added to the mixture is evidently equal to the external work. There is no simple way of finding the work. As an approximation, an exponential curve

$$p_1 v_1{}^n = p v^n \tag{11}$$

may be passed through the points $p_1$, $v_1$, and $p_2$, $v_2$, and the value of $n$ can be found. This curve will approximate to the true isodynamic on the $pv$-plane, and the external work will then be approximately

$$W = \frac{p_1 v_1 - p_2 v_2}{n - 1}. \tag{12}$$

In practice the isodynamic of vapor mixtures is of little importance.

127. **Approximate Equation for the Adiabatic of a Vapor Mixture.** — In certain investigations, especially those relating to the flow of steam, it is convenient to represent the relation between $p$ and $v$ during an adiabatic change by an equation of the form

$$p V^n = C. \tag{1}$$

The value of the exponent $n$ is not constant, but varies with the initial pressure, the initial quality, and also with the final ressure; and at best the equation is an approximation. Rankine assumed for $n$ the value $\frac{10}{9}$ for all initial conditions. Zeuner, neglecting the influence of initial pressure, gave the formula

$$n = 1.035 + 0.1\,x. \qquad (2)$$

Mr. E. H. Stone,* using the tables of Marks and Davis, has derived the relation

$$n = 1.059 - 0.000315\,p + (0.0706 + 0.000376\,p)x. \qquad (3)$$

The following table gives values of $n$ calculated from (3).

| Initial Quali-ty | INITIAL PRESSURE IN POUNDS PER SQUARE INCH, ABSOLUTE | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 20 | 40 | 60 | 80 | 100 | 120 | 140 | 160 | 180 | 200 | 220 | 240 |
| 1.00 | 1.131 | 1.132 | 1.133 | 1.134 | 1.136 | 1.137 | 1.138 | 1.139 | 1.141 | 1.142 | 1.143 | 1.145 |
| 0.95 | 1.127 | 1.128 | 1.128 | 1.130 | 1.131 | 1.131 | 1.132 | 1.133 | 1.134 | 1.135 | 1.136 | 1.137 |
| 0.90 | 1.123 | 1.123 | 1.124 | 1.124 | 1.125 | 1.125 | 1.126 | 1.126 | 1.127 | 1.127 | 1.128 | 1.129 |
| 0.85 | 1.119 | 1.119 | 1.119 | 1.119 | 1.120 | 1.120 | 1.120 | 1.120 | 1.120 | 1.120 | 1.120 | 1.121 |
| 0.80 | 1.115 | 1.115 | 1.114 | 1.114 | 1.114 | 1.114 | 1.113 | 1.113 | 1.113 | 1.113 | 1.112 | 1.112 |
| 0.75 | 1.111 | 1.110 | 1.110 | 1.109 | 1.109 | 1.108 | 1.107 | 1.106 | 1.106 | 1.105 | 1.104 | 1.104 |
| 0.70 | 1.108 | 1.106 | 1.105 | 1.104 | 1.103 | 1.102 | 1.101 | 1.100 | 1.099 | 1.098 | 1.097 | 1.096 |
| 0.65 | 1.104 | 1.102 | 1.101 | 1.099 | 1.098 | 1.096 | 1.095 | 1.093 | 1.092 | 1.091 | 1.089 | 1.088 |
| 0.60 | 1.100 | 1.098 | 1.096 | 1.094 | 1.093 | 1.091 | 1.089 | 1.087 | 1.085 | 1.083 | 1.081 | 1.080 |
| 0.55 | 1.096 | 1.093 | 1.092 | 1.089 | 1.087 | 1.085 | 1.083 | 1.080 | 1.078 | 1.076 | 1.074 | 1.072 |
| 0.50 | 1.092 | 1.089 | 1.087 | 1.084 | 1.082 | 1.079 | 1.077 | 1.074 | 1.071 | 1.069 | 1.066 | 1.064 |

Having the initial values $p_1$, $V_1$, and $x_1$, and the final pressure $p_2$, the final volume $V_2$ is found approximately from (1), the appropriate value of $n$ being taken from the table. The external work is found approximately by the usual formula for the change represented by (1), namely,

$$W = \frac{p_1 V_1 - p_2 V_2}{n - 1}. \qquad (4)$$

EXAMPLE. Taking the data of the example of Art. 126 (c), we have = 80, $V$ = 3, $x$ = 0.89, whence $n$ = 1.123. The final pressure is 5 in. Hg.

and $\qquad W = 144 \times \dfrac{60 \times 9 - 80.10 \times 2.100}{0.123} = 88{,}074$ ft.-lb.

Comparing these results with the results obtained by the exact method, it appears that the volume $V_2$ is about 0.36 per cent smaller and the work $W$ about 0.13 per cent smaller. Hence the approximation is sufficiently close for all practical purposes.

## EXERCISES

**1.** From Bertrand's equation calculate the pressure of steam corresponding to the following temperatures: 60°, 250°, 400° F.

**2.** Find the values of the derivative $\dfrac{dp}{dt}$ for the same temperatures.

**3.** Using the results of Ex. 1 and 2, find the specific volumes for the given temperatures.

**4.** Find (a) the latent heat, (b) the total heat of saturated steam, at a temperature of 324° F.

**5.** Calculate the latent heat of steam, (a) by the quadratic formula (2), Art. 114; (b) by the exponential formula (see footnote, p. 176) for the temperatures 220° F. and 380° F. Compare the results.

In the following examples take required values from the steam table, p. 315.

**6.** Find the entropy, energy, heat content, and volume of 4.5 lb. of a mixture of steam and water at a pressure of 120 lb. per square inch, quality 0.87.

**7.** Find the quality and volume of the mixture after adiabatic expansion to a pressure of 16 lb. per square inch.

**8.** Find the external work of the expansion.

**9.** Using the data of the preceding examples, calculate the volume and work by means of the approximate exponential equation $pV^n = C$.

**10.** A mixture, initial quality 0.97, expands adiabatically in a 12 in. by 12 in. cylinder from a pressure of 100 lb. per square inch, gauge, to a pressure of 10 lb. per square inch, gauge. Find the point of cut-off.

**11.** The volume of 6.3 lb. of mixture at a pressure of 140 lb. per square inch is 17.2 cu. ft. Find the quality of the mixture; also the entropy and energy of the mixture.

**12.** The mixture in Ex. 11 is cooled at constant volume to a pressure of 20 lb. per square inch. Find the final value of $x$ and the heat abstracted.

**13.** At a pressure of 180 lb. per square inch the volume of 2 lb. of a mixture of steam and water is increased by 0.9 cu. ft. Find the increase of quality, increase of energy, heat added, and external work.

**14.** A mixture of steam and water, quality 0.85, at a pressure of 18 lb. per square inch, is compressed adiabatically. Find the pressure at which

the water is completely vaporized. Find also the work of compression per pound of mixture.

**15.** Steam at a pressure of 80 lb. per square inch expands, remaining saturated until the pressure drops to 50 lb. per square inch. Find approximately the heat that must be added to keep the steam in the saturated condition.

**16.** Water at a temperature of 352° F. and under the corresponding pressure expands adiabatically until the pressure drops to 30 lb. per square inch. Find the per cent of water vaporized during the process. Find the work of expansion per pound of water.

**17.** Two vessels, one containing $M_1$ lb. of mixture at a pressure $p_1$ and quality $x_1$, the other $M_2$ lb. at a pressure $p_2$ and quality $x_2$, are placed in communication. No heat enters or leaves while the contents of the vessels are mixing. Derive equations by means of which the final pressure $p_3$ and final quality $x_3$ may be calculated.

**18.** Let 1 lb. of mixture at a pressure of 20 lb. per square inch, quality 0.96, enter a condenser which contains 20 lb. of mixture at a pressure of 3 in. Hg., quality 0.05. Assuming that no heat leaves the condenser during the process, find the pressure and quality after mixing.

## REFERENCES

### PRESSURE AND TEMPERATURE OF SATURATED VAPORS

Regnault: Mém. de l'Inst. de France **21**, 465. 1847. Rel. des expér. **2**.

Henning: Wied. Ann. (4) **22**, 609. 1907.

Holborn and Henning: Wied. Ann. (4) **25**, 833. 1908.

Holborn and Baumann: Wied. Ann. (4) **31**, 945. 1910.

Risteen: The Locomotive **26**, 85, 183, 246; **27**, 54; **28**, 88.

    These articles contain a very complete account of the experiments of Regnault, Holborn and Henning, and Thiesen.

Chwolson: Lehrbuch der Physik **3**, 730.

    Gives comprehensive discussion of the many formulas proposed for the relation between the pressure and temperature of various vapors.

Preston: Theory of Heat, 330.

Marks and Davis: Steam Tables and Diagrams, 93.

Peabody: Steam and Entropy Tables, 8th ed., 8.

Marks: Jour. Am. Soc. Mech. Engrs. **33**, 563. 1911.

### PROPERTIES OF SATURATED STEAM

#### (a) Specific Heat of Water. Heat of Liquid

Regnault: Mém. de l'Inst. de France **21**, 729. 1847.

Dieterici: Wied. Ann. (4) **16**, 593. 1905.

Barnes: Phil. Trans. **199 A**, 149. 1902.

Rowland: Proc. Amer. Acad. of Arts and Sciences **15**, 75; **16**, 38. 1880-1881.

Day: Phil. Mag. **46**, 1. 1898.

Griffiths: Thermal Measurement of Energy.

Marks and Davis: Steam Tables and Diagrams, 88.


### (b) Latent Heat

Regnault: Mém. de l'Inst. de France **21**, 635. 1847.

Griffiths: Phil. Trans. **186 A**, 261. 1895.

Henning: Wied. Ann. (4) **21**, 849, 1906; (4) **29**, 441, 1909.

Dieterici: Wied. Ann. (4) **16**, 593. 1905.

Smith: Phys. Rev. **25** 145. 1907.


### (c) Total Heat

Davis: Proc. Am. Soc. of Mech. Engrs. **30**, 1419. 1908. Proc. Amer. Acad. **45**, 265.

Marks and Davis: Steam Tables and Diagrams, 98.


### (d) Specific Volume

Fairbairn and Tate: Phil. Trans. (1860), 185.

Knoblauch, Linde, and Klebe: Mitteil. über Forschungsarbeit. **21**, 33. 1905

Peabody: Proc. Am. Soc. Mech. Engrs. **31**, 595. 1909.

Peabody: Steam and Entropy Tables, 8th ed., 12.

Marks and Davis: Steam Tables and Diagrams, 102.

Davis: Proc. Am. Soc. Mech. Engrs. **30**, 1429.


## PROPERTIES OF REFRIGERATING FLUIDS

### (a) Ammonia

Dieterici: Zeitschrift für Kälteindustrie. 1904.

Jacobus: Trans. Am. Soc. Mech. Engrs. **12**, 307.

Wood: Trans. Am. Soc. Mech. Engrs. **10**, 627.

Peabody: Steam and Entropy Tables, 8th ed., 27.

Zeuner: Technical Thermodynamics (Klein) **2**, 252.

Lorenz: Technische Wärmelehre, 333.


### (b) Sulphur Dioxide

Cailletet and Mathias: Comptes rendus **104**, 1563. 1887.

Lange: Zeitschrift für Kälteindustrie 1899, 82.

Mathias: Comptes rendus **119**, 404. 1894.

Miller: Trans. Am. Soc. Mech. Engrs. **25**, 176.

Wood: Trans. Am. Soc. Mech. Engrs. **12**, 137.

Zeuner: Technical Thermodynamics **2**, 256.

<div style="text-align: center;">(c) Carbon Dioxide</div>

nagat: Comptes rendus **114**, 1093. 1892.
llier: Zeit. für Kälteindustrie 1895, 66, 85.
aner: Technical Thermodynamics **2**, 262.

## GENERAL EQUATIONS FOR VAPORS. CHANGES OF STATE

aner: Technical Thermodynamics **2**, 53.
yrauch: Grundriss der Wärme-Theorie **2**, 33.
ston: Theory of Heat, 650.
rry: Temperature Entropy Diagram, 43.

# CHAPTER XI

## SUPERHEATED VAPORS

**128. General Characteristics of Superheated Vapors.** — The nature of a superheated vapor has been indicated in Art. 106, describing the process of vaporization. So long as a vapor is in immediate contact with the liquid from which it is formed it remains saturated, and its temperature is fixed by the pressure according to the relation $t = f(p)$. When vaporization is completed, or when the saturated vapor is removed from contact with the liquid, further addition of heat at constant pressure results in a rise in temperature. If $t_s$ denotes the saturation temperature given by $t_s = f(p)$ and $t$ the temperature after superheating, the difference $t - t_s$ is the **degree of superheat**. Thus for steam at a pressure of 120 lb. per square inch, $t_s = 341.3°F$; hence if at this pressure the steam has a temperature of 460°, the degree of superheat is $460° - 341.3° = 118.7°$.

As soon, therefore, as a vapor passes into the superheated state, the character of the relation between the coördinates $p$, $v$, and $t$ changes. The temperature is freed from the rigid connection with the pressure that obtains in the saturated state, and $p$ and $t$ may be varied independently. The volume $v$ of the superheated vapor depends upon both $p$ and $t$ thus taken as independent variables; that is,

$$v = \phi(p, t), \tag{1}$$

as in the case of a perfect gas. The form of the characteristic equation (1) for a superheated vapor is, however, less simple than that of the gas equation $pv = BT$.

The state described by the term "superheated vapor" lies between two limiting states; the saturated vapor on the one hand, and the perfect gas, obeying the laws of Boyle and Joule, on the other. The characteristic equation therefore should

196

be of such form as to reduce to the equation of the perfect gas, as the upper limit is approached and to give the proper values of $p$, $v$, and $t$ of saturated vapor when the lower limit is reached. In the case of compound substances like water or ammonia, however, one disturbing element is introduced at very high temperatures. The vapor may to some extent dissociate; thus steam may in part split up into its components hydrogen and oxygen, ammonia into nitrogen and hydrogen. Nernst has found for example that at a pressure of one atmosphere 3.4 per cent of water vapor is dissociated at a temperature of 2500° C. Manifestly the existence of dissociation must influence the relation between the variables $p$, $v$, and $t$. However, at the temperatures and pressures with which we are concerned in the technical applications of thermodynamics, the amount of dissociation is entirely negligible, and the characteristic equation may be assumed to hold for all temperatures within the range of ordinary practice.

**129. Critical States.** — The region between the limit curves $v'$, $v''$ (Fig. 60) or $s'$, $s''$ (Fig. 62) is the region of mixtures of saturated vapor and liquid. The fact that these two curves approach each other as the temperature is increased suggests that a temperature may be reached above which it is impossible for a mixture of liquid and vapor to exist. Let it be assumed that the two limit curves merge into each other at the point $H$ (Fig. 66), and thus constitute a single curve, of which the liquid and saturation curves, as we have previously called them, are merely two branches. The significance of this assumption may be gathered from the following considerations.
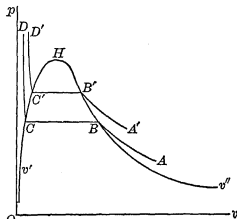


FIG. 66.

Let superheated vapor in the initial state represented by point $A$ (Fig. 66 and 67) be compressed isothermally. Under usual conditions, the pressure will rise until it reaches the pres-

sure of saturated vapor corresponding to the given constant temperature $t$, and the state of the vapor will then be represented by point $B$ on the saturation curve. Further compression at constant temperature results in condensation of the saturated vapor, as indicated by the line $BC$. If the liquid be compressed isothermally, the volume will be decreased slightly as the pressure rises, and the process will be represented by curve $CD$. The isothermal has therefore three distinct parts: along $AB$ the fluid is superheated vapor, along $BC$ a mixture, and along $CD$ a liquid. If the initial temperature be taken at a higher value $t'$, the result will be similar except that the segment $B'C'$ will be shorter. If the limit curves meet at point $H$, it is evident that the temperature may be chosen so high that this horizontal segment of the isothermal disappears; in other words, the isothermal lies entirely outside of the single limit curve.
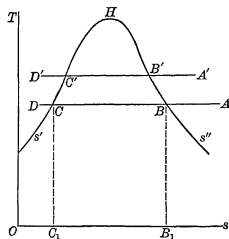


FIG. 67.

In Fig. 66 the segment $BC$ represents the difference $v'' - v'$ between the volume $v''$ of saturated vapor and the volume $v'$ of the liquid; and in Fig. 67, the area $B_1 B C C_1$ represents the latent heat $r$ of vaporization. For the isothermal $t_c$ that passes through $H$, the segment $BC$ reduces to zero; hence, for this temperature and all higher temperatures, we have

$$v'' - v' = 0, \text{ or } v'' = v',$$

and

$$r = 0.$$

The second result also follows from the first when we consider the Clapeyron equation

$$v'' - v' = \frac{Jr}{T} \frac{1}{\dfrac{dp}{dT}}.$$

The experiments of Andrews show that the condition just described may be actually attained. The isothermals for carbon

dioxide as determined by Andrews are shown in Fig. 68. For $t = 13.1°$ and $21.5°$C. the horizontal segments corresponding to condensation are clearly marked. For $t = 31.1°$ the horizontal segment disappears and there is merely a point of inflexion in the curve. At $48.1°$ the point of inflexion disappeared, and the isothermal has the general form of the isothermal for a perfect gas.
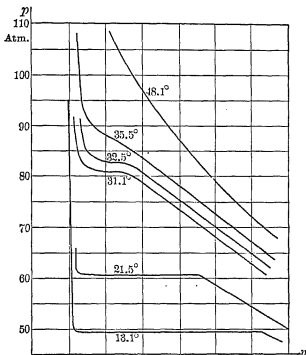
The temperature $t_c$ was called by Andrews the **critical temperature**. It has a definite value for any liquid. The pressure $p_c$ and



FIG. 68.

volume $v_c$ indicated by the point $H$ are called respectively the **critical pressure** and **critical volume**. Values of $t_c$ and $p_c$ for various substances are given in the following table:

| SUBSTANCE | $t_c$, DEGREES C. | $p_c$, ATMOSPHERES |
|---|---|---|
| Water . . . . . . . . . | 365.0 * | 200.5 |
| Ammonia . . . . . . . . | 130.0 | 115.0 |
| Ether . . . . . . . . | 197.0 | 35.77 |
| Sulphur dioxide . . . . . . | 155.4 | 78.9 |
| Carbon dioxide . . . . . . | 30.92 | 77.0 |
| Carbon disulphide . . . . . | 277.7 | 78.1 |
| Nitrogen . . . . . . . . | −146.0 | 35.0 |
| Oxygen . . . . . . . . | −118.0 | 50.0 |
| Hydrogen . . . . . . . | −220.0 | 20.0 |
| Air . . . . . . . . . | −140.0 | 30.0 |

* According to the recent experiments of Holborn and Baumann, the critical temperature of water is 706.1° F (374.5° C) and the critical pressure is 3200 lb. per square inch. See article by Prof. Marks, Jour. A. S. M. E., Vol. 33, p. 563.

Although at sufficiently high pressure the fluid may be in the liquid state, the closest observation fails to show where the gaseous state ceases and the liquid state begins. As stated by Andrews, the gaseous and liquid states are to be regarded as widely separated forms of the same state of aggregation.

It has been proposed to make the critical temperature the basis of a distinction between gases and vapors. Thus, air, nitrogen, oxygen, nitric oxide, etc., whose critical temperatures are far below ordinary temperature, are designated as gases, while steam, chloroform, ether, etc., whose critical temperatures are above ordinary temperature are designated as vapors.

The determination of the critical values $t_c$, $p_c$, and $v_c$ by thermodynamic principles is a problem of great theoretical interest, but lies beyond the scope of this book.

**130. Equations of van der Waals and Clausius.** — Many attempts have been made to deduce rationally a single characteristic equation, which with appropriate change of constants will represent the properties of various fluids in all states from the gaseous condition above the critical temperature to the liquid condition. Such a general equation is that of van der Waals, namely,

$$p = \frac{BT}{v - a} - \frac{C}{v^2}, \tag{1}$$

which was deduced from certain considerations derived from the kinetic theory of gases. As van der Waals' equation does not accurately represent the results of Andrew's experiments on carbon dioxide, Clausius suggested a modification of the last term of the equation and ultimately arrived at an equation of the form

$$p = \frac{BT}{v - a} - \frac{f(T)}{(v+c)^2}, \tag{2}$$

where $f(T)$ is a function of the absolute temperature that takes the value 1 at the critical temperature.

The equations of van der Waals and Clausius are constructed with special reference to the behavior of fluids in the vicinity of the critical state; hence they apply more particularly to such fluids as carbon dioxide, the critical temperature of which is within the range of temperature encountered in the practical applications of heat media. The critical temperatures of most important fluids, as water, ammonia, and sulphur dioxide are, however, far above the ordinary range, and for these media the general equations do not give as good results as certain purely empirical equations deduced from experiments covering a relatively small region. For some fluids, notably ammonia, there is unfortunately a lack of experimental data; for the most important fluid, water, we have, however, reliable data furnished by the recent experiments at Munich.

**131. Experiments of Knoblauch, Linde, and Klebe.** — The experiments made at the Munich laboratory were so conducted that three important relations could be obtained simultaneously. These were :

1. Relation between pressure and temperature of saturated steam.

2. Relation between specific volume and temperature of saturated steam.

3. Relation between pressure and temperature of superheated steam with the volume remaining constant.

The experiment covered the range 100° to 180° C. The apparatus employed is shown diagrammatically in Fig. 69. An iron vessel $a$ contains a smaller glass vessel $b$ to which is attached a glass tube $c$. A similar glass tube $d$ leads
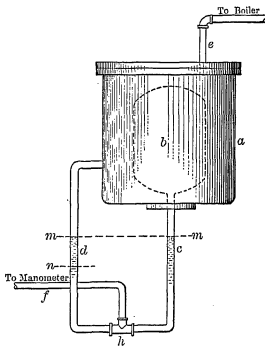


FIG. 69.

a tube $f$ leading to a mercury manometer. Steam is introduced into vessel $a$ from a boiler, and suitable provision is made for returning the condensed steam to the boiler.

A given weight of water is put into the glass vessel $b$ and is evaporated gradually by the heat absorbed from the steam surrounding it. As long as vessel $b$ contains a saturated mixture, the pressure within $b$ must be the same as that within $a$, since the temperature is the same throughout. Hence the mercury levels $m$, $m$ in tubes $c$ and $d$ will be at the same height. When the water in $b$ is all vaporized and the pressure and temperature of the steam in $a$ is further increased, the steam in $b$ becomes superheated. While the temperature is still the same in vessels $a$ and $b$, the pressures in the two vessels are not equal. This may be shown by the $Ts$-diagram (Fig. 70). Let point $A$ on the saturation curve $s''$ denote the state of the steam in vessel $b$ just at the end of vaporization; it also represents the state of the saturated steam in the outer vessel $a$. As the temperature rises from $t_1$ to $t_2$ the state of the steam in $a$ changes as represented by the curve $AC$; that is, the steam in $a$ is saturated at the pressure $p_2$. The apparatus is so manipulated, however, that the mercury level $m$ in tube $c$ is held constant, thus keeping a constant volume of steam in vessel $b$. The point representing the state of the steam in $b$ moves along the constant volume curve $AB$ in the superheated region, and the final pressure $p_3$ given by the point $B$ is smaller than the pressure $p_2$ of the saturated steam in $a$. As a result the mercury level in the tube $d$ will be depressed to the level $n$. A comparison of the mercury level in the manometer with the level $m$ gives the relation between the pressure and temperature of superheated steam at the given constant volume $v$; and a comparison with the level $n$ gives the relation between the pressure and temperature of saturated steam.
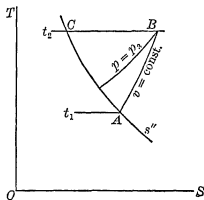
**132. Equations for Superheated Steam.** — To represent the results of the Munich experiments, Linde deduced the empirical equation

$$pv = BT - p(1 + ap)\left[C\left(\frac{373}{T}\right)^n - D\right].\qquad(1)$$

n metric units with $p$ in kilogram per square *meter*, the constants have the following values:

$$B = 47.10 \qquad\qquad C = 0.031 \qquad\qquad n = 3.$$
$$a = 0.0000002 \qquad D = 0.0052$$

With English units and pressures in pounds per square *inch*, the equation becomes:

$$pv = 0.5962\, T - p(1 + 0.0014\, p)\left(\frac{150300000}{T^3} - 0.0833\right).\quad(2)$$

The form of Eq. (1) is such as to make it inconvenient for the purpose of computation; and the constant $D$ in the last term leads to complication in the working out of a general heory. A modified form of the equation, namely,

$$v + c = \frac{BT}{p} - (1 + ap)\frac{m}{T^n}\qquad(3)$$

s free from these objections and with constants properly chosen represents the results of the Munich experiments as accurately as Linde's equation. The constants are as follows:

| Metric Units | English Units |
|---|---|
| $B = 47.113$ | $B = 85.87$, $p$ in pounds per square foot |
| | $= 0.5963$, $p$ in pounds per square inch |
| $\log m = 11.19839$ | $\log m = 13.67938$ |
| $n = 5$ | $n = 5$ |
| $c = 0.0055$ | $c = 0.088$ |
| $a = 0.00000085$ | $a = 0.0006$, $p$ in pounds per square inch. |

The final equation with constants inserted is therefore

$$v + 0.088 = 0.5962\,\frac{T}{p} - (1 + 0.0006\, p)\frac{47795 \times 10^9}{}\qquad(4)$$

An equation of the simple form

$$v + c = \frac{BT}{p} \qquad (5)$$

has been proposed by Tumlirz on the strength of Battelli's experiments. Linde has shown that this equation may be made to represent with fair accuracy the results of the Munich experiments. For English units and with $p$ in pounds per square *inch*, the equation becomes

$$v + 0.256 = 0.5962 \frac{T}{p}. \qquad (6)$$

For moderate pressure this formula is quite accurate, but at high pressures and superheat the volumes given by it are considerably smaller than those indicated by the experiments.

Two other characteristic equations deserve mention. For many years Zeuner's empirical equation

$$pv = BT - Cp^n \qquad (7)$$

has been extensively used. The results of the Munich experiments have shown that the form of this equation is defective, and that it cannot accurately represent the behavior of superheated steam over a wide range. Callendar, from certain theoretical considerations, has deduced the equation,

$$v - b = \frac{BT}{p} - C_0\left(\frac{273}{T}\right)^n \qquad (8)$$

which in form resembles Eq. (3), but lacks the factor $p$ in the last term. While this equation is somewhat simpler than Eq. (3), it is less accurate.

**133. Specific Heat of Superheated Steam.** — The experimental evidence on the specific heat of superheated steam may be classified as follows :

1. The early experiments of Regnault at a pressure of one atmosphere and at temperatures relatively close to saturation.

2. The experiments of Mallard and Le Chatelier, Langen, and others at very high temperatures.

3. The experiments of Holborn and Henning at atmospheric pressure and at temperatures varying from 110° to 1400° C.

4. Recent experiments with steam at various pressures and with temperatures close to the saturation limit. Of these, the experiments of Knoblauch and Jakob are considered the most reliable.

Regnault concluded from his experiments that at a pressure of one atmosphere the specific heat of superheated steam has the constant value 0.48 for all temperatures. This value has been largely used for all temperatures and for all pressures as well.

Experiments by Mallard and Le Chatelier and by Langen at high temperatures agree in making the specific heat a linear function of the temperature. Thus, according to Langen,

$$c_p = 0.439 + 0.000239\, t, \qquad (1)$$

where $t$ is the temperature on the C. scale.

The earlier experiments of Holborn and Henning at much lower temperatures than those of Langen lead to the formula

$$c_p = 0.446 + 0.0000856\, t. \qquad (2)$$

This is again a linear relation, but the coefficient of $t$ is smaller than that in Langen's formula. Equations (1) and (2) show that the specific heat varies with the temperature at least, and that the convenient assumption of the constant value 0.48 is not permissible.

Finally, the experiments of Knoblauch and Mollier show conclusively that $c_p$ depends also upon the pressure. In these experiments, steam was run through a first superheater in which all traces of moisture were removed. It was then run through a second superheater consisting of coils immersed in an oil bath. The heat was applied by means of an electric current and could be measured quite accurately, and a comparison of the heat supplied with the rise of the temperature of the steam gave a means of calculating the mean specific heat over the temperature range involved. Experiments were conducted at pressures of 2, 4, 6, and 8 kg. per square centimeter. The

results are shown by the points in Fig. 71. From these results the following conclusions may be drawn: (1) The specific heat varies with the pressure, being higher the higher the pressure at the same temperature. (2) With the pressure constant, the specific heat falls gradually from the saturation limit, reaches a minimum value, and then rises again.

Starting with the characteristic equation (3), Art. 132, it is possible to deduce a general equation for the specific heat $c_p$ that will give results substantially in accord with the experimental results of Knoblauch and Mollier. For this purpose we make use of the general relation

$$\left(\frac{\partial c_p}{\partial p}\right)_T = -AT\frac{\partial^2 v}{\partial T^2} \text{ (Art. 57).} \qquad (3)$$

From the characteristic equation,

$$v + c = \frac{BT}{p} - (1 + ap)\frac{m}{T^n}, \qquad (4)$$

we obtain by successive differentiation

$$\frac{\partial v}{\partial T} = \frac{B}{p} + \frac{mn}{T^{n+1}}(1 + ap), \qquad (5)$$

$$\frac{\partial^2 v}{\partial T^2} = -\frac{mn(n+1)}{T^{n+2}}(1 + ap). \qquad (6)$$

Substituting in (3), the result is

$$\left(\frac{\partial c_p}{\partial p}\right)_T = \frac{Amn(n+1)}{T^{n+1}}(1 + ap). \qquad (7)$$

Taking $T$ as constant and integrating (7) with $p$ as the independent variable, the result is

$$c_p = \frac{Amn(n+1)}{T^{n+1}}p\left(1 + \frac{a}{2}p\right) + \text{const. of integration.}$$

Now since $T$ was taken as constant, the constant of integration may be some function of $T$; hence we may write

$$c_p = \phi(T) + \frac{Amn(n+1)}{T^{n+1}}p\left(1 + \frac{a}{2}p\right). \qquad (8)$$
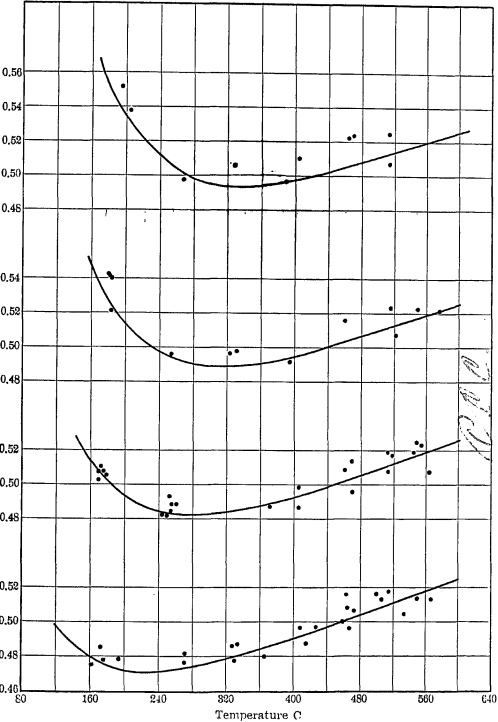
The groups of points represent the results of experiments at 2, 4, 6, and 8 kg. per sq. cm., respectively, beginning with the lowest group.

Fig. 71.

increased. From Langen's experiments, it is seen that at very high temperatures $c_p$ is given by an equation of the form

$$c_p = a + bT;$$

hence we are justified in assuming that

$$\phi(T) = \alpha + \beta T,$$

where $\alpha$ and $\beta$ are constants to be determined from experimental evidence. Equation (8) thus becomes

$$c_p = \alpha + \beta T + \frac{Amn(n+1)}{T^{n+1}}p\left(1 + \frac{a}{2}p\right). \qquad (9)$$

This is the general equation for the specific heat of superheated steam at constant pressure.

It may be seen at once that this equation gives results agreeing in a general way with those of Knoblauch and Mollier. At a given temperature $T$ the specific heat increases with the pressure; furthermore for a given pressure, $c_p$ has a minimum value as appears by equating to zero the derivative

$$\frac{\partial c_p}{\partial T} = \beta - \frac{Amn(n+1)^2}{T^{n+2}}p\left(1 + \frac{a}{2}p\right).$$

The following values of the constants have been found to make Eq. (9) fit fairly well the experimental results of Knoblauch and Mollier:

$$\alpha = 0.367$$
$$\beta = 0.00018 \text{ for the C. scale.}$$
$$\beta = 0.0001 \text{ for the F. scale}$$

Replacing the product $Amn(n+1)$ by a single constant $C$, we have as the final formula for the specific heat

$$c_p = 0.367 + 0.0001\ T + p(1 + 0.0003\ p)\ \frac{C}{T^6}, \qquad (10)$$

where $\log C = 14.42408$ (pressure in pounds per square inch).

Figure 71 shows the curves representing this formula for the pressures of the Knoblauch and Mollier experiments. The agreement between the points and curves is satisfactory, considering the difficulty of the experiments. In Fig. 72 the $c_p$-curves for various pressures in pounds per square inch are
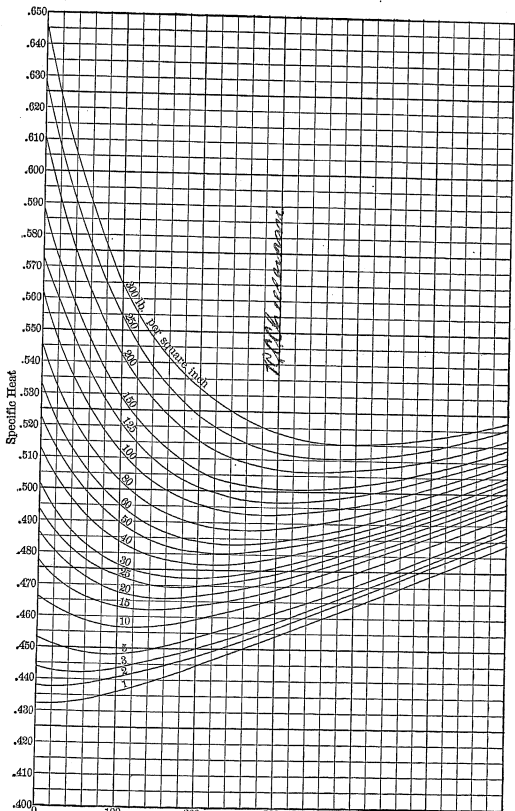
**134. Mean Specific Heat.** — Formula (10), Art. 133, gives the specific heat at a given pressure and temperature. For some purposes it is desirable to have the mean specific heat between two temperatures, the pressure remaining constant. This is readily calculated by the mean value theorem; thus denoting by $(c_p)_m$ the mean specific heat, we have

$$(c_p)_m = \frac{\int_{T_1}^{T_2} c_p \, dT}{T_2 - T_1}. \tag{1}$$

Using the general expression for $c_p$, we have, therefore,

$$(c_p)_m = \frac{1}{T_2 - T_1} \int_{T_1}^{T_2} \left[ \alpha + \beta T + \frac{Amn(n+1)}{T^{m+1}} p \left(1 + \frac{a}{2} p\right) \right] dT$$

$$= \alpha + \frac{\beta}{2}(T_1 + T_2)$$

$$+ \frac{Amp(n+1)\left(1 + \frac{a}{2} p\right)\left(\frac{1}{T_1^{\,n}} - \frac{1}{T_2^{\,n}}\right)}{T_2 - T_1}. \tag{2}$$

The calculation, while straightforward is rather long, and if $p$-curves are available, it is usually preferable to determine the mean $c_p$ by Simpson's rule or by the planimeter.

Curves of mean specific heat are shown in Fig. 73. For any degree of superheat the mean specific heat between the saturation state and the given state is given by the ordinate corresponding to the given degree of superheat and the given pressure. For example, at a pressure of 150 lb. per square inch the mean specific heat for 240° superheat is 0.529.

**135. Heat Content. Total Heat.** — Having a formula for the specific heat at constant pressure, equations for the heat content and the intrinsic energy of a unit weight of superheated steam at a given pressure and temperature are readily derived. For this purpose the general equation

$$dq = c_p \, dT - AT \left(\frac{\partial v}{\partial T}\right)_p dp \quad \text{(see Art. 54)} \tag{1}$$

Mean Specific Heat

Superheat, Deg. F.

300 lb. per square inch
275
250
175
150
100
80
60
50
40
30
25
20
15
10
5
3
2
1
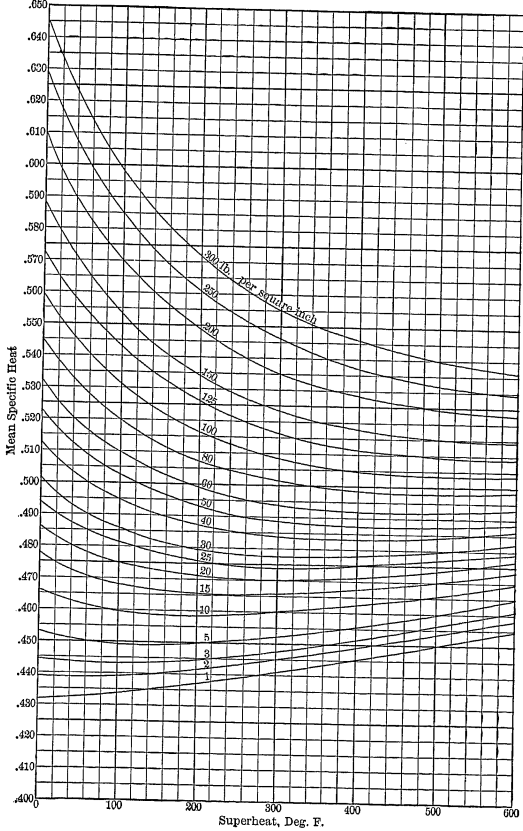
$$i = A(u + pv),$$

we have
$$di = A[du + d(pv)],$$

or
$$di = dq + Av\,dp. \tag{2}$$

Hence, making use of (1),
$$di = c_p dT - A\left(T\frac{\partial v}{\partial T} - v\right)dp. \tag{3}$$

From the characteristic equation we have
$$\frac{\partial v}{\partial T} = \frac{B}{p} + n(1 + ap)\frac{m}{T^{n+1}},$$

whence
$$T\frac{\partial v}{\partial T} - v = (n+1)(1 + ap)\frac{m}{T^n} + c.$$

Introducing in (3) this expression for $T\dfrac{\partial v}{\partial T} - v$ and the general expression for $c_p$, the result is

$$di = (\alpha + \beta T)\,dT + Amn(n+1)\,p\left(1 + \frac{a}{2}p\right)\frac{dT}{T^{n+1}}$$
$$- \frac{Am(n+1)}{T^n}(1 + ap)\,dp - Ac\,dp. \tag{4}$$

Since $i$ depends upon the state of the subtance only, the second member of (4) must be an exact differential. The integral is readily found to be

$$i = \alpha T + \frac{\beta}{2}T^2 - A(n+1)p\left(1 + \frac{a}{2}p\right)\frac{m}{T^n} - Acp + i_0. \tag{5}$$

The constant of integration $i_0$ is determined by applying Eq. (5) to the saturation state. For a given pressure and corresponding saturation temperature the second member of (5) exclusive of $i_0$ can be calculated. The first member is the value of $i$ for the assumed pressure as given in the steam table. Hence $i_0$ is found by subtraction. By this method the mean value $i_0 = 886.7$ is obtained.

Introducing known constants, Eq. (5) becomes

$$i = T(0.367 + 0.00005\,T) - p(1 + 0.0003\,p)\frac{C}{T^5}$$
$$- 0.0163\,p + 886.7. \tag{6}$$

Here log $C = 13.72511$ when $p$ is taken in pounds per square inch.

The **total heat** of a unit weight of superheated vapor is the heat required to raise the temperature of the liquid to the boiling point at the given constant pressure, evaporate it, and then superheat, it still at constant pressure, to the temperature under consideration. On the $TS$-plane, the process is shown by the line $ABCD$ (Fig. 74). The area $OABCC_1$ represents the total heat of the saturated vapor, which has been denoted by $q''$. The area



FIG. 74.

$C_1CDD_1$ represents the heat added to superheat the vapor. This heat is evidently given by the integral
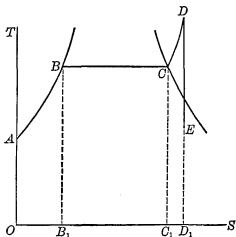
$$\int c_p dT = \int \left[ \alpha + \beta T + \frac{C}{T^{n+1}} p \left( 1 + \frac{a}{2} p \right) \right] dT$$

taken between the saturation temperature $T_s$ at point $C$ and the final temperature $T$ at point $D$. This integral is, in fact, the product $(c_p)_m (T - T_s)$, where $(c_p)_m$ is the mean specific heat for the temperature range $T - T_s$. The total heat of a unit weight of superheated steam is given therefore by the expression

$$q = q'' + (c_p)_m (T - T_s). \tag{7}$$

The term $(c_p)_m (T - T_s)$ is easily found from the mean specific heat curves (Fig. 73), and $q'' (= i'')$ is given in the steam table. Hence with the aid of the curves, an approximate value for the heat content may be calculated.

EXAMPLE. Find the heat content of one pound of steam at a pressure of 150 lb. per square inch superheated 200°.

From the steam table $i'' (= q'')$ for this pressure is 1194.6 B.t.u.; and from Fig. 73 the mean specific heat from saturation to 200° superheat is 0.534.

Hence $\qquad i = 1194.6 + 200 \times 0.534 = 1301.4$ B.t.u.

The result given by formula (6) is 1301.7 B.t.u.

**136. Intrinsic Energy.** — For the intrinsic energy we have from the defining equation $i = A(u + pv)$,

$$Au = i - Apv. \tag{1}$$

Using the expressions for $i$ and $v$ heretofore derived, we obtain the equation

$$Au = T(\alpha + \tfrac{1}{2}\beta T - AB) - \frac{Amp}{T^n}\Big[ n + (n-1)\frac{\alpha}{2}p \Big] + i_0. \tag{2}$$

This expression gives the intrinsic energy in B. t. u. of a unit weight of superheated steam. Introducing the proper constants, we have, when $p$ is taken in pounds per square *inch*,

$$Au = T(0.2566 + 0.00005\,T) - \frac{Cp}{T^6}(1 + 0.00024\,p) + 886.7, \tag{3}$$

where $\log C = 13.64593$.

The intrinsic energy may also be found quite exactly by the following method. For the given pressure $p$ the energy of one pound of saturated steam is

$$Au'' = q' + \rho,$$

and the increase of energy due to the superheat is

$$\int_{T_s}^{T} c_v\,dT = (c_v)_m (T - T_s),$$

where $(c_v)_m$ denotes the mean specific heat at constant volume. The difference $(c_p)_m - (c_v)_m$ varies somewhat with the pressure and superheat, but 0.13 may be taken as a mean value. Hence the energy of one pound of superheated steam is given by the equation

$$Au = q' + \rho + [(c_p)_m - 0.13](T - T_s). \tag{4}$$

Values of $q'$ and $\rho$ are given in the steam table and the proper value of $(c_p)_m$ may be found from the curves of Fig. 73.

EXAMPLE. Find the intrinsic energy of one pound of steam at a pres-

**137. Entropy.** — From the general equation

$$dq = c_p dT - AT\left(\frac{\partial v}{\partial T}\right)_p dp,$$

we have

$$ds = \frac{dq}{T} = c_p \frac{dT}{T} - A\left(\frac{\partial v}{\partial T}\right)_p dp. \qquad (1)$$

Introducing in this equation the expressions previously derived for $c_p$ and $\left(\frac{\partial v}{\partial T}\right)_p$ (see Art. 133), the result is

$$ds = \left(\frac{\alpha}{T} + \beta\right)dT + Amnp(n+1)\left(1 + \frac{\alpha}{2}p\right)\frac{dT}{T^{n+2}} - AB\frac{dp}{p}$$
$$- \frac{Amn}{T^{n+1}}(1 + \alpha p)dp. \qquad (2)$$

This is necessarily an exact differential since $s$ is a function of the state only. The integral is found to be

$$s = \alpha \log_e T + \beta T - AB \log_e p - Anp\left(1 + \frac{\alpha}{2}p\right)\frac{m}{T^{n+1}} + s_0. \qquad (3)$$

Inserting the known constants and passing to common logarithms, (3) becomes

$$s = 0.8451 \log T + 0.0001 T - 0.2542 \log p$$
$$- p(1 + 0.0003 p)\frac{C}{T^6} - 0.3964. \qquad (4)$$

In using (4), $p$ is taken in pounds per square *inch*, and log $C = 13.64593$. The constant $0.3964$ is determined by passing to the saturation limit, as was done in finding the value of $i_0$.

Equation (4) gives the entropy of one pound of superheated steam at any given pressure and temperature.

The entropy may also be found as follows. Let the point $D$ (Fig. 74) represent the state of the fluid and assume $CD$ to be a constant pressure line cutting the saturation curve at $C$. Then $OC_1$ gives the entropy $s''$ of saturated steam at the same pressure as the superheated steam, and $C_1 D_1$

entropy is

$$\int_{T_0}^{T} \frac{dT}{T} \quad \int_{T_0}^{T} \left[ \frac{a}{T} + \beta + \frac{Amn}{T^{n+1}} p'\left(1 + \frac{a}{x}p\right) \right] dT$$

$$\left[ a \log_e T + \beta T \quad \frac{Amn}{T^n} p'\left(1 + \frac{a}{x}p\right) \right]$$

Hence the entropy of the steam in the state $D$ is

$$s = s'' + \left[ a \log_e T + \beta T \quad \frac{Amn}{T^n} p'\left(1 + \frac{a}{x}p\right) \right] \qquad (5)$$

Equation (3) is preferable, however, as it does not contain the saturation entropy $s''$.

### EXERCISES

**1.** Find the entropy, energy, and heat content of 1 lb. of superheated steam at a pressure of 80 lb. per square inch absolute and a temperature of 410° F.

**2.** Saturated steam at a pressure of 140 lb. per square inch absolute is superheated to a temperature of 450 F. at constant pressure. Find (a) heat added; (b) change of energy; (c) change of entropy per pound of steam.

**3.** Assume data and compare the results obtained by using (6) and (7) of Art. 135.

**4.** Assume data and calculate entropy by both (3) and (5), Art. 137. Compare results.

**138. Special Changes of State.** By means of characteristic equation (3), Art. 132, and the general equations that have been deduced for the heat content, energy, and entropy, most problems that arise in connection with the changes of state of superheated steam may be solved with comparative ease. On account, however, of the fact that the specific heat of steam is given by a somewhat complicated formula, it cannot be expected that the relations here derived will have the simple form of those for perfect gases. In the following discussions of special changes of state, we shall give merely an outline of the processes involved, leaving the details to be filled in by the student.

1. *Constant Pressure.* Let superheated steam change state
at constant pressure from an initial temperature $t_1$ to a final
temperature $t_2$. For the heat added we have

$$q = i_2 - i_1 = \alpha(T_2 - T_1) + \frac{\beta}{2}(T_2^2 - T_1^2)$$
$$- Amp\,(n+1)\left(1 + \frac{a}{2}p\right)\left(\frac{1}{T_2^n} - \frac{1}{T_1^n}\right). \quad (1)$$

The external work is given by the relation

$$W = p(v_2 - v_1) = B(T_2 - T_1) - mp\,(1+ap)\left[\frac{1}{T_2^n} - \frac{1}{T_1^n}\right]. \quad (2)$$

The change of energy may be found from the energy equation

$$u_2 - u_1 = Jq - W,$$

or independently by calculating from the general formula the
energies in the initial and final states.

The change of entropy may be obtained, likewise, from the
general equation for entropy or from the relation

$$s_2 - s_1 = \int_{T_1}^{T_2} c_p \frac{dT}{T} = \alpha \log_e \frac{T_2}{T_1} + \beta(T_2 - T_1)$$
$$- Amnp\left(1 + \frac{a}{2}p\right)\left(\frac{1}{T_2^{n+1}} - \frac{1}{T_1^{n+1}}\right). \quad (3)$$

The preceding equations apply to a unit weight of the
fluid.

2. *Constant Volume.* If $T_1$ and $T_2$ denote, as before, the
initial and final temperatures, respectively, we have from the
characteristic equation

$$v + c = \frac{BT_2}{p_2} - (1 + ap_2)\frac{m}{T_2^n}, \quad (4)$$

from which $p_2$ may be found. Having $T_1$, $p_1$, and $T_2$, $p_2$, the
initial and final values of the energy and entropy may be de-
termined from the general formulas. Since the external work is
zero, the heat added is equal to the increase of energy.

3. *Isothermal Expansion.* Let the initial and final pressures

characteristic equation.  For the change of entropy per unit weight we have from the general equation for entropy

$$s_2 - s_1 = AB \log_e \frac{p_1}{p_2} + \frac{Amn}{T^{n+1}}\left[p_1\left(1 + \frac{a}{2}p_1\right) - p_2\left(1 + \frac{a}{2}p_2\right)\right]. \quad (5)$$

The heat added during the expansion per unit weight is therefore

$$q = T(s_2 - s_1) = ABT \log_e \frac{p_1}{p_2}$$

$$+ \frac{Amn}{T^n}\left[p_1\left(1 + \frac{a}{2}p_1\right) - p_2\left(1 + \frac{a}{2}p_2\right)\right]. \quad (6)$$

For the external work, taking $dv$ from the characteristic equation, we have

$$W = \int_1^2 p\,dv = \int_{p_1}^{p_2}\left(-\frac{BT}{p} - \frac{m}{T^n}ap\right)dp$$

$$= BT \log \frac{p_1}{p_2} + \frac{ma}{2\,T^n}(p_1{}^2 - p_2{}^2). \quad (7)$$

The change of energy may be found by combining (6) and (7) or from the general equation of energy.  It is found to be

$$u_2 - u_1 = \frac{m}{T^n}\left[n(p_1 - p_2) + \frac{a}{2}(n-1)(p_1{}^2 - p_2{}^2)\right]. \quad (8)$$

It should be noted that in the case of superheated steam constant temperature does *not*, as with perfect gases, indicate constant intrinsic energy.

4. *Adiabatic Change of State.*  For an adiabatic change the entropy remains constant; hence, for the relation between the final pressure $p_2$ and temperature $T_2$, we have from the general equation for entropy

$$\alpha \log_e T_2 + \beta T_2 - AB \log_e p_2 - Anp_2\left(1 + \frac{a}{2}p_2\right)\frac{m}{T_2{}^{n+1}} = C,$$

where $C$ is a constant determined from the initial state.  The pressure $p_2$ is generally given; therefore, we have the transcendental equation

$$\alpha \log_e T_2 + \beta T_2 - p_2\left(1 + \frac{a}{2}p_2\right)\frac{Amn}{T^{n+1}} = C + AB \log_e p_2 = C', \quad (9)$$

Having the initial and final values of $p$ and $T$, the initial and final values $u_1$ and $u_2$ of the intrinsic energy may be calculated. The external work per unit weight is then

$$W = u_1 - u_2. \qquad (10)$$

In problems connected with the flow of steam the change of heat content resulting from an adiabatic expansion is required. This difference is found by calculating from the general equation for the heat content the initial and final values $i_1$ and $i_2$.

If the adiabatic expansion is carried far enough, the expansion line, as $DE$ (Fig. 74), will cross the saturation curve $s''$, and the state-point will enter the region between the curves $s'$ and $s''$. This means that at the end of the expansion the fluid is a mixture of liquid and vapor. The investigation of this case presents no difficulties. The entropy and energy at the initial point $D$ are calculated from the general equation. Knowing the pressure for the final state $E$, the quality $x$ is readily determined from the equation

$$s_1 = s_2' + \frac{x r_2}{T_2}, \qquad (11)$$

where $s_1$ denotes the entropy in the initial state. Having $x$, the energy in the final state is calculated from the equation

$$u_2 = J(q_2' + x \rho_2). \qquad (12)$$

Then the external work per unit weight is given by the equation

$$W = u_1 - u_2 = u_1 - J(q_2' + x_2 \rho_2). \qquad (13)$$

EXAMPLE. Steam at a pressure of 150 lb. per square inch absolute and superheated 100° F. expands adiabatically to a pressure of 5 in. of mercury. Required the final condition of the fluid and the external work per pound; also the pressure at which the steam becomes saturated.

From the general equation the entropy in the initial state is found to be 1.6346. From the steam table we obtain for the final pressure $s' = 0.1880$, $\frac{r}{T} = 1.7170$; hence

$$1.6346 = 0.1880 + 1.7170\,x,$$

or

$$x = 0.8425.$$

In the initial state the energy in B. t. u. is

$$A u_1 = 918.1(0.2566 + 0.00005 \times 918.1) - \frac{150\,C}{918.1^5}(1 + 0.00024 \times 150) + 886.7$$

$$= 1153.9 \text{ B. t. u.}$$

In the final state the energy is

$$Au_2 = q_2' + x_2\rho_2 = 101.7 + 0.8425 \times 953.7 = 905.2.$$

Hence, the external work per pound of steam is

$$W = u_1 - u_2 = 778(1153.9 - 905.2) = 193,490 \text{ ft.-lb.}$$

The initial entropy 1.6346 is the entropy of saturated steam at a pressure of 66.6 lb. per square inch. Hence the steam becomes saturated at this pressure.

## 139. Approximate Equations for Adiabatic Change of State. —
Exact calculations that involve adiabatic changes of superheated steam are tedious on account of the transcendental form of the equation for entropy; and it is therefore desirable to introduce simplifying approximations, provided the results obtained by them are sufficiently accurate. An investigation of a number of cases covering the range of values ordinarily used in the technical applications of superheated steam shows that a set of equations similar in form to the equations for a perfect gas may be obtained, and that the error involved in using these approximate equations does not in general exceed one or two per cent.

The relation between pressure and volume during an adiabatic change may be represented approximately by the equation

$$p(v + c)^n = \text{const.} \tag{1}$$

The value of $c$ is taken the same as in formula (4), Art. 131, namely, $c = 0.088$.

The value of $n$ probably varies slightly with the initial pressure and with the degree of superheat; however, it appears that the value $n = 1.31$ gives quite accurate results for the range of pressure and superheat found in practice. If now we take the approximate characteristic equation

$$p(v + c) = BT, \quad (\text{Art. 132}) \tag{2}$$

we get by combining (1) and (2),

$$T = \frac{C}{B} \, p^{\frac{n-1}{n}}, \tag{3}$$

or

$$\frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)^{\frac{n-1}{n}}. \tag{4}$$

$$W = \int_{v_1}^{v_2} p\,dv = \int_{v_1}^{v_2} \frac{dv}{(v+c)^n} = \frac{p_1(v_1+c) - p_2(v_2+c)}{n-1}. \quad (5)$$

Given the initial state of the fluid, the volume in the final state may be found from (1), the final temperature from (4), and the external work from (5).

EXAMPLE. A pound of superheated steam at a pressure of 200 lb. per square inch and superheated 200° expands adiabatically to a pressure of 50 lb. per square inch. Required the final condition and the external work.

The initial volume is found to be 2.973 cu. ft., and the initial entropy 1.6657. Using the formula for $s$ (Art. 137), the final temperature is found by trial to be 752.5° absolute; and taking this value of $T_2$, the exact value of the final volume is found to be 8.681 cu. ft.

From (3), Art. 136, the energy in the initial state is found to be 1200.57 B. t. u., that in the final state 1098.82 B. t. u.; hence the external work is 778 (1200.57 − 1098.82) = 79,262 ft.-lb.

Taking the approximate formulas, we have

$$v_2 + c = (v_1 + c)\left(\frac{p_1}{p_2}\right)^{\frac{1}{n}} = (2.973 + 0.088)\left(\frac{200}{50}\right)^{\frac{1}{1.31}} = 8.819;$$

hence $v_2 = 8.819 - 0.088 = 8.731$ cu. ft.

$$T_2 = T_1\left(\frac{p_2}{p_1}\right)^{\frac{n-1}{n}} = 1041.4\left(\frac{50}{200}\right)^{0.237} = 749.8°.$$

$$W = \frac{p_1(v_1+c) - p_2(v_2+c)}{n-1} = \frac{144}{0.31}(200 \times 3.061 - 50 \times 8.819) = 79,550 \text{ ft.-lb.}$$

It will be seen that for practical purposes the results obtained from the approximate equations are satisfactory as regards accuracy.

**140. Tables and Diagrams for Superheated Steam.** — The leading properties of superheated steam — volume, entropy, and total heat — for various pressures and degrees of superheat have been calculated and tabulated by Marks and Davis and by Peabody. The values in the Marks and Davis tables are derived from specific heat curves that differ somewhat from the curves of Fig. 72, and they therefore differ from the values obtained from the equations of Arts. 135–137. However, throughout the range of ordinary practice, the difference does not exceed one half of one per cent.

The Marks and Davis tables are accompanied by graphical charts that may be used to great advantage in the approximate

olution of numerical problems. The principal chart has the

eat content $i$ as ordinate and the entropy $s$ as abscissa. The
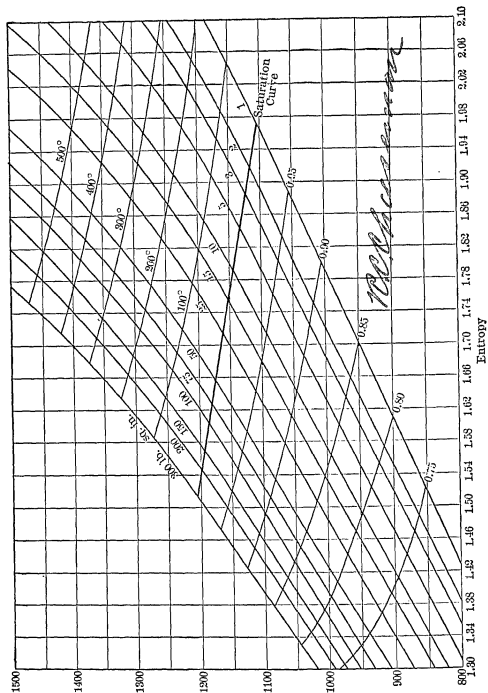
turated steam at various pressures. The region above this
rve is the region of superheat, and the lines running approxi-
ately parallel to the saturation curve are lines of constant
gree of superheat. Below the saturation curve is the region
wet steam, and the lines running parallel to the saturation
rve are lines of constant quality. The lines that cross the
turation curve obliquely are lines of constant pressure.

The first conception of the heat content-entropy chart is
e to Dr. R. Mollier of Dresden, hence we shall refer to it as
e **Mollier chart**. In addition to the chart published by
arks and Davis, one is contained in Stodola's *Steam Turbines*
d one in Thomas' *Steam Turbines*. In the light of the
cently acquired knowledge of the properties of saturated and
perheated steam, the Marks and Davis chart must be regarded
 the most accurate.

The Mollier chart may be used for the approximate solution
 many problems that involve the properties of saturated and
perheated steam, and it is specially valuable in problems on
e flow of steam. The following examples illustrate some of
e uses of the chart:

Ex. 1. Steam at a pressure of 150 lb. per square inch superheated 200° F.
pands adiabatically to a pressure of 3 lb. per square inch.

The point representing the initial condition lies at the intersection of the
nstant-pressure line marked 150 and the line of 200° superheat. Locating
is point on the chart, it is found at the intersection of the lines $i = 1300$
d $s = 1.687$. The heat content and entropy in the initial state are thus
termined. The line $s = 1.687$ intersects the constant-pressure curve $p = 3$
 the line $i = 1002$; hence the heat content after adiabatic expansion is
02 B. t. u. The quality in the final state is found to be 0.88.

Ex. 2. When steam is *wire-drawn* by flowing through a valve from a
gion of higher pressure $p_1$ to a region of lower pressure $p_2$, the heat content
mains constant. Steam at a pressure of 200 lb. per square inch and
ality 0.95 flows into the atmosphere; required the final condition of the
eam.

Drawing a line of constant-heat content from the initial point to the
rve $p = 14.7$, it is found that the final point lies above the saturation curve
d that the steam is superheated about 12° at exit. The entropy increases
om $s = 1.498$ to $s = 1.766$.

**141. Superheated Ammonia and Sulphur Dioxide.** — Experi-

other than that of water is very scant, and our knowledge of such properties is accordingly imperfect. For superheated ammonia Ledoux has proposed the characteristic equation

$$pv = BT - Cp^m, \qquad (1)$$

and this form has been accepted by Peabody, who derives the following values of the constants (English units):

$$B = 99, \quad C = 710, \quad m = \tfrac{1}{4}.$$

For sulphur dioxide Peabody uses the same equation with the constants:

$$B = 26.4, \quad C = 184, \quad m = 0.22.$$

According to Regnault the specific heat of superheated ammonia has the constant value 0.52. It is very likely that this specific heat is no more constant than that of superheated steam and that it varies with pressure and temperature. However, experimental evidence on this point is lacking. Lorenz finds that for superheated sulphur dioxide $c_p = 0.329$.

The problem that most frequently arises in connection with the use of these fluids as refrigerating media is the determination of the state of the superheated vapor after adiabatic compression. It may be assumed that the relation between pressures and temperatures for an adiabatic change follows approximately the law for perfect gases, namely:

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{p_2}{p_1}\right)^{\frac{n-1}{n}}. \qquad (2)$$

Zeuner found that for superheated steam the exponent $\frac{n-1}{n}$ in (2) is equal to the exponent $m$ in the characteristic equation (1). Hence, using the values of $m$ assumed by Peabody, we have:

For ammonia $\qquad n = \dfrac{1}{1-m} = \dfrac{1}{1-0.25} = 1.333.$

For sulphur dioxide $n = \dfrac{1}{1 - 0.22} = 1.282.$

ttrated vapor. Let $A$ (Fig. 76) represent the initial state, nd $B$ the final state after adiabatic compression. $EA$ and $EB$ are constant-pressure curves. Denoting by $T_s'$ the saturaon temperature correspond-
ng to the pressure $p_1$, the ncrease of entropy from $E$ 
o $A$ is $c_p \log_e \dfrac{T_1}{T_s'}$, and the 
tal entropy in the state $A$ is

$$s_1'' + c_p \log_e \frac{T_1}{T_s'}.$$

ikewise, the entropy in the ate $B$ is

$$s_2'' + c_p \log_e \frac{T_2}{T_s''}.$$



Fig. 76.

ince $AB$ is an adiabatic, the entropies at $A$ and $B$ are equal, nd therefore

$$s_1'' + c_p \log_e \frac{T_1}{T_s'} = s_2'' + c_p \log_e \frac{T_2}{T_s''}. \qquad (3)$$

n this equation $s_1''$, $s_2''$, $T_s'$, and $T_s''$ are tabular values corresponding to the given pressures $p_1$ and $p_2$, and $T_1$ is given. ence, $T_2$ is the only unknown quantity.

### EXERCISES

**1.** Calculate by Eq. (2), (4), and (6), respectively, of Art. 132 the volme of one pound of superheated steam at a pressure of 180 lb. per square ch and a temperature of 430° F. Compare the results.

**2.** If the products $pv$ are plotted as ordinates with the pressures $p$ as bscissas, show the general form of the isothermals $T = C$ when Eq. (3), rt. 132 is used; when Eq. (6) is used.

**3.** For ammonia, Peabody gives the following equations for the latent eat of vaporization: $r = 540 - 0.8\ (t - 32)$. If at the critical temperature = 0, find $t_c$ for ammonia by means of this formula and compare with the lue of $t_c$ given in Art. 129. Explain the discrepancy.

**4.** Following the method of Art. 133, deduce an equation for $c_p$, using e approximate equation (5), Art. 132; also using Callendar's equation (8).

**5.** By means of Eq. (3), Art. 132, calculate the specific volume of satuted steam at the following pressures : 5 in. Hg., 20, 50, 150 lb. per square
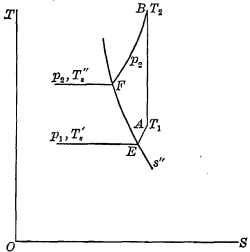
**6.** Calculate the mean specific heat of superheated steam at a pressure of 140 lb. per square inch between saturation and 250° superheat. Compare the result with the curves of Fig. 73.

**7.** Using the mean specific heat curves, Fig. 73, find the heat content and energy of one pound of superheated steam at a pressure of 85 lb. per square inch and a temperature of 430° F.

**8.** A pound of saturated steam at a pressure of 120 lb. per square inch is superheated at constant pressure to a temperature of 386° F. Find the heat added, the external work, and the increase of energy.

**9.** The steam after superheating expands adiabatically until it again becomes saturated. Find the pressure at the end of expansion and the external work.

**10.** The following empirical equation has been proposed for the value of $c_p$ very close to the saturation limit:

$$(c_p)_{\text{sat}} = 0.41 + \frac{C}{(t_c - t_s)^4},$$

in which $t_c$ is the critical temperature, 689° F., and $t_s$ is the saturation temperature corresponding to an assumed pressure. Using the curves of Fig. 72, calculate the value $C$ for several assumed pressures, and thus test the validity of the formula for these curves.

**11.** The following equation has also been proposed for the value of $c_p$ at saturation: $(c_p)_{\text{sat}} = a + bt_s$. Test this equation, and if it holds good within reasonable limits determine the constants $a$ and $b$.

**12.** In the initial state 6.4 cu. ft. of superheated steam has a temperature of 420° F. and is at a pressure of 160 lb. per square inch. By the approximate equations of Art. 139 find the temperature and volume after adiabatic expansion to a pressure of 80 lb. per square inch; also the work of expansion.

**13.** Assume for the initial state of superheated steam $p_1 = 80$ lb. per square inch, $v_1 = 20$ cu. ft., $t_1 = 350°$ F. Plot the successive pressures and volumes for an isothermal expansion to a pressure of 30 lb. per square inch. Compare the expansion curve with the isothermal of air under the same conditions.

**14.** With the data of Ex. 13 find the external work, heat added, and change of energy (a) for the superheated steam; (b) for air.

## REFERENCES

THE CRITICAL STATE. EQUATIONS OF VAN DER WAALS AND CLAUSIUS

The literature on these subjects is very extensive. For comprehensive discussions, reference may be made to the following works:

Preston: Theory of Heat, Chap. V, Sections 6 and 7.

euner: Technical Thermodynamics (Klein) **2**, 202–229.
hwolson: Lehrbuch de Physik **3**, 791–841.

## CHARACTERISTIC EQUATIONS

allendar: Proc. of the Royal Soc. **67**, 266.   1900.
inde: Mitteilungen über Forschungsarbeiten **21**, 20, 35.   1905.
euner: Technical Thermodynamics **2**, 223.
/eyrauch: Grundriss der Wärme-Theorie **2**, 70, 87.

## SPECIFIC HEAT OF SUPERHEATED STEAM

allard and Le Chatelier: Annales des Mines **4**, 528.   1883.
angen: Zeit. d. Ver. deutsch. Ing., 622.   1903.
olborn and Henning: Wied. Annalen **18**, 739.   1905. **23**, 809.   1907.
egnault: Mem. Inst. de France **26**, 167.   1862.
noblauch and Jakob: Mitteilungungen über Forschungsarbeiten **35**, 109.
noblauch and Mollier: Zeit. des Ver. deutsch. Ing. **55**, 665.   1911.
homas: Proc. Am. Soc. Mech. Engrs. **29**, 633.   1907.
A most complete discussion of the work of various investigators is given
/ Dr. H. N. Davis, Proc. Am. Acad. of Arts and Sciences **45**, 267.   1910.

## GENERAL THEORY OF SUPERHEATED VAPORS

allendar: Proc. of the Royal Soc. **67**, 266.
/eyrauch: Grundriss der Wärme-Theorie **2**, 117.
euner: Technical Thermodynamics **2**, 243.

# CHAPTER XII

## MIXTURES OF GASES AND VAPORS

**142. Moisture in the Atmosphere.** — Because of evaporation of water from the earth's surface, atmospheric air always contains a certain amount of water vapor mixed with it. The weight of the vapor relative to the weight of the air is slight even when the vapor is saturated. Nevertheless, the moisture in air influences in a considerable degree the performance of air compressors, air refrigerating machines, and internal combustion motors; and in an accurate investigation of these machines the medium must be considered not dry air but rather a mixture of air and vapor. The study of air and vapor mixtures is also important in meteorology and especially in problems relating to heating and ventilation. Finally, it has been proposed to use a mixture of air with high-pressure steam as the working medium for heat engines, and the analysis of the action of an engine working under this condition demands a special investigation of air and steam mixtures.

Experiment has shown that Dalton's law holds good within permissible limits for a mixture of gas and vapor. The gas has the pressure $p'$ that it would have if the vapor were not present, and the vapor has the pressure $p''$ that it would have if the gas were not present. The pressure of the mixture is

$$p = p' + p''. \tag{1}$$

If the vapor is saturated, the temperature $t$ of the mixture must be the saturation temperature corresponding to the pressure $p''$. If the temperature is higher than this, the vapor must be superheated.

The water vapor in the atmosphere is usually superheated. Let point $A$, Fig. 77, represent the state of the vapor, and let $AB$ be a constant pressure curve cutting the saturation curve

t $B$. Further, let $m$ denote the weight per cubic foot of the
apor in the state $A$, and $m_1$, the weight per cubic foot of *satu-
ated* vapor at the same temperature, that is, in the state $C$.

he ratio $\dfrac{m}{m_1}$ is called the **humidity** of the air under the given

onditions. If the mixture of air and vapor is cooled at constant
ressure, the vapor will follow the
ath $AB$ and at $B$ it will become
turated. Upon further cooling
ome of the vapor will condense.
he temperature $T_0$ at which con-
ensation begins is called the **dew
oint** corresponding to the state $A$.

The humidity may be expressed
pproximately in terms of pressures.
et $p_a''$ denote the pressure of the
apor in the state $A$ and $p_c''$ the
ressure of saturated vapor at the
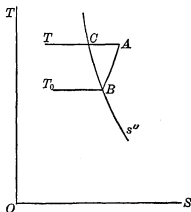


FIG. 77.

ame temperature, hence in the state represented by $C$. At the
ow pressures under consideration we may assume that the vapor
ollows the gas law $pV = MBT$. Hence, taking $V = 1$, we have

$$p_a'' = p_b'' = mBT,$$

nd
$$p_c'' = m_1 BT.$$

herefore, denoting the humidity by $\phi$, we have

$$\phi = \frac{m}{m_1} = \frac{p_b''}{p_c''}. \qquad (2)$$

hat is, the humidity is the ratio of the pressure corresponding
o the dew point to the saturation pressure corresponding to
ne temperature of the mixture.

For investigations that involve hygrometric conditions, the
ata ordinarily required may be found in table II, page 319.

At 70° the saturation pressure is, from table II, 0.738 inches of Hg, while at 52° the saturation pressure is 0.3905 inches of Hg. The humidity is therefore

$$\phi = \frac{0.3905}{0.738} = 0.529.$$

If the air were saturated at 70°, it would contain 8.017 grains of vapor per cubic foot. Hence with 52.9 per cent humidity the weight of vapor per cubic foot is

$$8.017 \times 0.529 = 4.241 \text{ grains.}$$

EXAMPLE 2. Atmospheric air has a temperature of 90° F. and a humidity of 80 per cent. It is required that air be furnished to a building at 70° F. and with 40 per cent humidity.

From table II, the pressure of saturated vapor at 70° is 0.738 inches of Hg; hence from (2) the pressure corresponding to the dew point is $0.40 \times 0.738 = 0.2952$ inches of Hg, and the dew point is 44.5°. In the initial state one cubic foot of air contains $0.80 \times 14.85 = 11.88$ grains of vapor. The air is cooled to 44.5° by proper refrigerating apparatus and in this state contains $3.39 \times \dfrac{459.6 + 44.5}{459.6 + 90} = 3.11$ grains, the difference $11.88 - 3.11 = 8.77$ grains being condensed. The air freed from the condensed vapor is now heated to the required temperature, 70°.

**143. Constants for Moist Air.** — The constants $B$, $c_p$, $c_v$, etc., given in Chapter VII apply only to dry air. For air containing water vapor the constants must be changed somewhat, the magnitude of the change depending, of course, upon the relative weight of vapor present.

An expression for the constant $B$ of the mixture may be obtained by the following method. Let the volume $V$ contain $M_1$ lb. of air at the pressure $p'$ and $M_2$ lb. of water vapor at the pressure $p''$. Then assuming that the gas law may be applied to the vapor, we have

$$p'V = M_1 B_1 T, \tag{1}$$

$$p''V = M_2 B_2 T, \tag{2}$$

whence

$$\frac{p''}{p'} = \frac{M_2}{M_1} \cdot \frac{B_2}{B_1}. \tag{3}$$

Let $\dfrac{M_2}{M_1} = z$, and $\dfrac{B_2}{B_1} = e$; then from (3)

$$\frac{p''}{p'} = ez = \frac{p''}{p - p''}, \tag{4}$$

hence
$$p'' = p\,\frac{ez}{1+ez}, \quad p' = p\,\frac{1}{1+ez}. \tag{5}$$

Adding the members of (1) and (2), we obtain
$$\begin{aligned}
pV &= (M_1 B_1 + M_2 B_2)\,T \\
&= M_1 B_1 (1+ez)\,T \\
&= \frac{M_1 B_1}{M_1 + M_2}(1+ez)(M_1 + M_2)\,T. \tag{6}
\end{aligned}$$

The constant $B_m$ of the mixture is, however, given by the equation
$$pV = (M_1 + M_2)B_m T. \tag{7}$$

Hence, comparing (6) and (7), we have
$$B_m = B_1 \frac{M_1}{M_1 + M_2}(1+ez) = B_1 \frac{1+ez}{1+z}. \tag{8}$$

Taking the molecular weight of water vapor as 18, we have
$$B_2 = \frac{1543}{18} = 85.72,$$

and
$$e = \frac{B_2}{B_1} = \frac{85.72}{53.34} = 1.61.$$

EXAMPLE. Find the value of $B$ for air at 90° F. completely saturated with water vapor. The pressure of the mixture is 14.7 lb. per square inch. From the table the pressure $p''$ of the vapor is 0.691 lb. per square inch; therefore the pressure $p'$ of the air is $14.7 - 0.691 = 14.009$ lb. per square inch. From (5), $1 + ez = \dfrac{p}{p'} = \dfrac{14.7}{14.009} = 1.0493$, $ez = 0.0493$, and $z = \dfrac{0.0493}{1.61}$
$= 0.0306$. Therefore, $B_m = 53.34 \times \dfrac{1.0493}{1.0306} = 54.31.$

The specific heat of the mixture is found by applying the law deduced in Art. 83. If $c_p'$ and $c_p''$ denote respectively the specific heats of the air and steam, then the specific heat of the mixture is given by the equation
$$c_p = \frac{c_p' + zc_p''}{1+z}. \tag{9}$$

EXAMPLE. Taking $c_p$ for air as 0.24, and for steam at 90° as 0.43, the specific heat of the mixture given in the preceding example is
$$\frac{0.24 + 0.0306 \times 0.43}{1 + 0.0306} = 0.2456.$$

**144. Mixture of Wet Steam and Air.** — In a given volume $V$ let there be $M_1$ lb. of air and $M_2$ lb. of saturated vapor mixture of quality $x$. The absolute temperature of the entire mixture is $T$, and the total pressure $p$. The pressure $p$ is the sum of the partial pressures $p'$ and $p''$ of the air and steam, respectively. This follows from Dalton's law, which within reasonable limits holds good for the case under consideration. We have then

$$p' + p'' = p, \tag{1}$$

$$p'V = M_1 BT, \tag{2}$$

$$V = M_2 [x(v'' - v') + v'], \tag{3}$$

where, as usual, $v''$ and $v'$ denote, respectively, the specific volumes of steam and water at the saturation temperature $T$.

The energy of the mixture is the sum of the energies of the two constituents; hence, we have

$$AU = M_1 c_v T + M_2(q + x\rho) + U_0. \tag{4}$$

Likewise, the entropy of the mixture is

$$S = M_1 [c_v \log_e T + (c_p - c_v) \log_e V] + M_2 \left( s' + \frac{xr}{T} \right) + S_0. \tag{5}$$

By means of these equations various changes of state may be investigated.

**145. Isothermal Change of State.** — Since $T$ remains constant, we have from (4)

$$A(U_2 - U_1) = M_2 \rho (x_2 - x_1), \tag{1}$$

and from (5)

$$S_2 - S_1 = M_1 AB \log_e \frac{V_2}{V_1} + M_2 \frac{r}{T}(x_2 - x_1). \tag{2}$$

Hence, the heat added is given by the equation

$$Q = T(S_2 - S_1) = M_1 ABT \log_e \frac{V_2}{V_1} + M_2 r(x_2 - x_1). \tag{3}$$

The external work is

$$W = JQ - (U_2 - U_1) = M_1 BT \log_e \frac{V_2}{V_1} + JM_2(r - \rho)(x_2 - x_1)$$

$$= p_1' V_1 \log_e \frac{V_2}{V_1} + p_1''(V_2 - V_1). \tag{4}$$

$$V_2 = M_2 [x_2(v'' - v') + v'],$$

neglecting the small water volume $v'$,

$$V_2 = M_2 x_2 v'', \tag{5}$$

hile in the initial state

$$V_1 = M_2 x_1 v''. \tag{6}$$

ence, combining (5) and (6),

$$x_2 = \frac{V_2}{V_1} x_1. \tag{7}$$

From (7) it appears that isothermal expansion is accompanied
 an increase of the quality $x$, that is, by evaporation, while
othermal compression involves condensation.

**146. Adiabatic Change of State.** — In the case of an adiabatic
ange the final total pressure $p_2$ is usually given. Assuming
at the steam in the mixture does not become superheated,
e final temperature $T_2$ of the mixture must be the saturation
mperature corresponding to the partial pressure $p_2''$ of the
eam. The determination of the final state of the mixture
volves the determination of two unknown quantities; namely,
e partial pressure $p_2''$ and the quality $x_2$ of the saturated
por. Hence two relations are required. One is given by
e condition that the entropy of the mixture shall remain
nstant during the change, the other by the condition that
e final volume $V_2$ may be considered as occupied by each
nstituent of the mixture independently of the other.

In the application of the first condition it is convenient to
e an expression for the entropy of the mixture of a form
fferent from that given by (5), Art. 144. In terms of the
mperature and pressure, the entropy of a unit weight of air
given by the expression

$$s = c_p \log_e T - AB \log_e p + s_0 ;$$

nce for the mixture we have

$$S = M_1(c_p \log_e T - AB \log_e p') + M_2 \left( s' + \frac{xr}{T} \right) + S_0. \tag{1}$$

As the constant $S_0$ disappears when the difference of entropy between two states is taken, it may be ignored in the calculation.

Let $S_1$ denote the entropy in the initial state. Then since the entropy remains constant, we have

$$S_1 = M_1 \left( c_p \log_e T_2 - AB \log_e p_2' \right) + M_2 \left( s_2' + \frac{x_2 r_2}{T_2} \right). \quad (2)$$

In Eq. (2), $S_1$, $M_1$, $M_2$, and the coefficients $c_p$ and $AB$ are known, as is the final total pressure $p_2$. The partial pressures $p_2'$ and $p_2''$, the quality $x_2$, and temperature $T_2$ are unknown. However, $T_2$ depends upon $p_2''$, and $p_2'$ is found from the relation $p_2' + p_2'' = p_2$ when $p_2''$ is determined. Denoting the final volume by $V_2$, we have

$$V_2 = \frac{M_1 B T_2}{p_2'} = M_2 x_2 v_2'',$$

whence

$$x_2 = \frac{M_1 B T_2}{M_2 p_2' v_2''}. \quad (3)$$

Inserting this expression for $x_2$ in (2), we have finally

$$S_1 = M_1 \left( c_p \log_e T_2 - AB \log_e p_2' \right) + M_2 \left( s_2' + \frac{M_1}{M_2} \frac{B r_2}{p_2' v_2''} \right). \quad (4)$$

In this equation $p_2'$ is the only unknown. The solution is most easily effected by assuming several values of $p_2''$ and calculating for these the values of the second member. These calculated values are then plotted as ordinates with the corresponding values of $p_2''$ as abscissas and the intersection of the curve thus obtained with the line $S_1 = \text{const.}$ gives the desired value of $p_2''$.

The external work of expansion or compression is equal to the change of energy. Hence, using the general expression for the energy of the mixture, we have

$$AW = M_1 c_v (T_1 - T_2) + M_2 (q_1 - q_2 + x_1 \rho_1 - x_2 \rho_2). \quad (5)$$

EXAMPLE. In a compressor cylinder suppose water to be injected at the beginning of compression in such a manner that the weight of water and water vapor is just equal to the weight of the air. Let the pressure of the mixture be normal atmospheric pressure 29.92 in. of mercury, and let the temperature be 79.1° F. The mixture is compressed to a pressure of 120 lb.

ing to 79.1° rise is 1 in. Hg, hence the partial pressure of the air is 28.92 in. Hg. The initial quality $x_1$ is found from the relation

$$V_1 = \frac{M_1 B T_1}{p_1'} = M_2 x_1 v_1''$$

whence

$$x_1 = \frac{M_1 B T_1}{M_2 p_1' v_1''} = \frac{53.34 \times 538.7}{28.92 \times 0.4912 \times 144 \times 656.7} = 0.0214.$$

The factor $0.4912 \times 144$ is used to reduce pressure in inches of mercury to pounds per square foot.

For the entropy of the mixture we obtain from (1) (neglecting the constant $S_0$)

$$S_1 = 0.24 \log_e 538.7 - 0.0686 \log_e (28.92 \times 0.4912) + 0.0916 + 0.0214 \times 1.9482 = 1.4587.$$

Since the ratio of the final to the initial pressure of the mixture is $\frac{120}{14.7} = 8.2$, we assume that the pressure $p_2''$ of the vapor after compression will be approximately 8 times the initial pressure $p_1''$. Hence we assume $p_2'' = 7$, 8, and 9 in. of mercury, respectively, and calculate the corresponding values of the second member of (2). Some of the details of the calculation are given.

<table>
<tr><th></th><th></th><th></th><th colspan="6">FROM STEAM TABLE</th></tr>
<tr><th>$p_2''$ (in. Hg)</th><th>$p_2'' \frac{\text{lb.}}{\text{sq. in.}}$</th><th>$p_2'$</th><th>$t_2$</th><th>$T_2$</th><th>$s_2'$</th><th>$r_2$</th><th>$v_2''$</th><th></th></tr>
<tr><td>7</td><td>3.43</td><td>116.57</td><td>146.9</td><td>606.5</td><td>0.2097</td><td>1011.1</td><td>104.4</td><td rowspan="3">} Data</td></tr>
<tr><td>8</td><td>3.92</td><td>116.08</td><td>152.3</td><td>611.9</td><td>0.2186</td><td>1007.9</td><td>92.18</td></tr>
<tr><td>9</td><td>4.41</td><td>115.59</td><td>157.1</td><td>616.7</td><td>0.2265</td><td>1005.0</td><td>82.57</td></tr>
</table>

<table>
<tr><th>$p_2''$</th><th>$c_p \log T_2$</th><th>$AB \log p_2'$</th><th>$\dfrac{Br_2}{p_2' v_2''}$</th><th>$S$</th><th></th></tr>
<tr><td>7</td><td>1.5378</td><td>0.3264</td><td>0.0308</td><td>1.4519</td><td rowspan="3">} Results</td></tr>
<tr><td>8</td><td>1.5400</td><td>0.3262</td><td>0.0349</td><td>1.4673</td></tr>
<tr><td>9</td><td>1.5418</td><td>0.3259</td><td>0.0390</td><td>1.4814</td></tr>
</table>

The pressure $p_2''$ that gives the value $S = 1.4587$ lies between 7 and 8 in. Hg and by the graphical method or by interpolation we find $p_2'' = 7.44$ in. Hg, or $p_2'' = 3.65$ lb. per square inch. Therefore $p_2' = 120 - 3.65 = 116.35$ lb. per square inch. From the steam table the following values are found for the pressure $p_2'' = 7.44$ in. Hg: $t_2 = 149.3$, $T_2 = 608.9$, $q_2' = 117.3$, $r_2 = 1009.4$, $\rho_2 = 942.8$, $v_2'' = 99$. The final quality is

$$x_2 = \frac{B T_2}{p_2' v_2''} = \frac{53.34 \times 608.9}{116.35 \times 144 \times 99} = 0.01958.$$

The external work per pound of air is

$$W = J[0.17(149.3 - 79.1) + 117.3 - 47.2 + 0.0214 \times 989.8 - 0.01958 \times 942.8]$$
$$= 61566 \text{ ft. lb.}$$

The volume of the mixture at the end of compression is

$$V = \frac{BT_2}{p_2'} = \frac{53.34 \times 608.9}{116.35 \times 144} = 1.9836 \text{ cu. ft.,}$$

and the work of expulsion is therefore

$$1.9836 \times 120 \times 144 = 33498 \text{ ft. lb.}$$

Hence, the work of compression and expulsion is 95064 ft. lb.

The effect of injecting water into a compressor cylinder may be shown by a comparison of the result just obtained with the work of compressing and expelling 1 lb. of dry air under the same conditions.

The initial volume of 1 lb. of air is $\dfrac{53.34 \times 538.7}{14.7 \times 144} = 13.574$ cu. ft.

The final volume after adiabatic compression to 120 lb. per square inch is

$$13.574 \left( \frac{14.7}{120} \right)^{\frac{1}{1.4}} = 3.0296 \text{ cu. ft.}$$

The work of compression is

$$\frac{1.44}{0.4} (14.7 \times 13.574 - 120 \times 3.0296) = 59044 \text{ ft. lb.,}$$

the work of expulsion is $3.0296 \times 120 \times 144 = 52350$ ft. lb., and the sum is 111394 ft. lb. The effect of water injection is therefore to reduce the volume and temperature at the end of compression and the work of compression and expulsion. The reduction of work in this case is about 17 per cent.

## 147. Mixture of Air with High-pressure Steam. — In the preceding articles, we have dealt with mixtures of steam and air in which the pressure of the vapor content was small. The suggestion has been made that a mixture of air at relatively high temperature and pressure mixed with steam either superheated, saturated, or with a slight amount of moisture be used as a medium for heat engines. An analysis of the action of such a medium in a motor demands in the first place a discussion of the process of mixing, afterwards a discussion of the change of state of the mixture.

Let $M_1$ lb. of air compressed to a pressure $p_1$ and having a temperature $T_1$ be mixed with $M_2$ lb. of wet steam having a pressure $p_2$ and quality $x_2$. The temperature $T_2$ of the steam

g the air into a receiver which contains steam, or vice versa. nce under these conditions the pressure of the mixture can- t be raised above the pressure of the constituents, the volume the mixture cannot be taken as the original volume $V_1$ of e air. We assume, on the other hand, that the conditions e such that the volume of the resulting mixture is the sum the volumes of the constituents; that is,

$$V = V_1 + V_2. \tag{1}$$

s a second condition, the internal energy of the mixture is ual to the sum of the energies of the constitutents; hence e have the equation of condition

$$U = U_1 + U_2. \tag{2}$$

Let $T$ denote the temperature after mixing $p'$ the partial pres- re of the air and $p''$ the partial pressure of the steam. When ovided the steam does not become superheated, the tempera- re $T$ must be the saturation temperature corresponding to the essure $p''$.

The following relations are readily obtained.

$$V_1 = \frac{M_1 B T_1}{p_1}. \tag{3}$$

$$V_2 = M_2 [x_2(v_2'' - v') + v'],$$

since the quality $x_2$ is nearly 1,

$$V_2 = M_2 x_2 v_2''. \tag{4}$$

$$V = \frac{M_1 B T}{p'} = M_2 x v'', \tag{5}$$

here $x$ denotes the quality after mixing, and $v''$ is the specific lume of steam corresponding to the pressure $p''$.

$$U_1 = M_1 c_v T_1. \tag{6}$$

$$U_2 = M_2(q_2' + x_2\rho_2). \tag{7}$$

$$U = M_1 c_v T + M_2(q' + x\rho). \tag{8}$$

rom (2) we have

$$M_1 c_v T + M_2(q' + x\rho) = M_1 c_v T_1 + M_2(q_2' + x_2\rho_2). \tag{9}$$

From (1),

$$V = \frac{M_1 B T_1}{p_1} + M_2 x_2 v''. \qquad (10)$$

Having $V$ calculated from (10), we obtain from (5)

$$x = \frac{V}{M_2 v''}, \qquad (11)$$

and this expression for $x$ substituted in (9) gives finally

$$M_1 c_v T + M_2\left(q' + \frac{\rho V}{M_2 v''}\right) = M_1 c_v T_1 + M_2(q_2' + x_2 \rho_2). \qquad (12)$$

In (12) the second member is known from the initial conditions. In the first member $q'$, $\rho$, and $v''$ are dependent on $T$; hence $T$ is the one unknown. As usual, the solution is obtained by taking various values of $T$ and plotting the resulting values of the first member of (12).

EXAMPLE. Let 1 lb. of wet steam, quality 0.85, at a pressure of 200 lb. per square inch, be mixed with 2 lb. of air at a pressure of 220 lb. per square inch and a temperature of 400°. Required the condition of the mixture.

From the data given, the following values are readily found:

$V_1 = 2.895$ cu. ft.; $V_2 = 1.948$ cu. ft.; $V = 2.895 + 1.948 = 4.843$ cu. ft.
$U = U_1 + U_2 = 1273.8$ B. t. u.

Equation (12) becomes

$$0.34\, T + q' + 4.843\, \frac{\rho}{v''} = 1273.8.$$

We now assume for $p''$ the values 50, 75, and 100 lb. per square inch; from the tables we find the corresponding values of $q'$, $\rho$, $v''$, and $T$, and calculate the values of the first member. The results are:

For
$$p'' = 50, \quad 981 \text{ B. t. u.}$$
$$p'' = 75, \quad 1222.3 \text{ B. t. u.}$$
$$p'' = 100, \quad 1451 \text{ B. t. u.}$$

Plotting these results, we find $p'' = 81$ lb. per square inch very nearly. The temperature of the mixture is therefore 313° F. and the quality of the steam is $x = \dfrac{4.843}{5.4} = 0.897$. (5.4 is the specific volume $v''$ corresponding to a pressure of 81 lb.) The partial pressure $p'$ of the air is found from (5) to be 130 lb. per square inch. Hence the pressure of the mixture is $130 + 81 = 211$ lb. per square inch.

It is seen that, as the result of mixing, the temperature is considerably vered, the pressure takes a value between $p_1$ and $p_2$, and the quality of e steam is increased.

If the steam is initially superheated, the preceding equations ust be modified by inserting for $V_2$ and $U_2$ the appropriate pressions for the volume and energy, respectively, of super-ated steam. To reduce as far as possible the complication the formulas we shall take the approximate equation (5), rt. 132, for the volume. We have then

$$V_2 = M_2 v_2 = M_2 \left( \frac{B'T_2}{p_2} - c \right). \tag{13}$$

ne constant $B$ is written with a prime merely to distinguish from the constant for air. The intrinsic energy of the steam given by Eq. (2), Art. 136. This equation can be simplified ith a small sacrifice of accuracy by dropping the term con-ining $a$. The modified equation then takes the form

$$Au = T(e + fT) - \frac{Cp}{T^5} + 886.7, \tag{14}$$

which $e = 0.2566$, $f = 0.00005$, and $\log C = 13.64593$.

From (6) and (14) the energies of the constituents before ixing can be calculated, and the sum of these gives the nergy $U$ of the mixture. We have then as one equation of ndition

$$M_1 c_v T + M_2 \left[ T(e + fT) - \frac{Cp''}{T^5} + 886.7 \right] = A U. \tag{15}$$

nce $p''$ and $T$ are here independent, there are two unknowns d a second condition is required. From (3) and (13) the itial volumes $V_1$ and $V_2$ are found and the sum gives the lume $V$ of the mixture. Then

$$V = M_2 \left( \frac{B'T}{p''} - c \right),$$

$$p'' = \frac{B'T}{\dfrac{V}{M_2} + c}. \tag{16}$$

om (15) and (16) the unknowns $p''$ and $T$ can be found.

EXAMPLE. Let 5 lb. of air at 60° F. be compressed adiabatically from atmospheric pressure to a pressure of 200 lb. per square inch and mixed with 1 lb. of steam at 200 lb. per square inch superheated 100°. The condition of the mixture is required.

The temperature of the air after compression

$$T_1 = 519.6 \left(\frac{200}{14.7}\right)^{\frac{1}{1.40}} = 1095°.$$

The saturation temperature of steam at 200 lb. per square inch is 381.8° F; hence $T_2 = 381.8 + 100 + 459.6 = 941.4°$. The energy of the air is

$$5 \times 0.17 \times 1095 = 930.75 \text{ B. t. u.}$$

and that of the steam is, from (14),

$$941.4 \ (0.2566 + 0.00005 \times 941.4) - C\frac{200}{941.4^6} + 886.7 = 1160.6 \text{ B. t. u.}$$

Hence        $A(U_1 + U_2) = AU = 930.75 + 1160.6 = 2091.35.$ B. t. u.

We have then from (15).

$$0.85 \, T + T(0.2566 + 0.00005 \, T) - \frac{Cp''}{T^6} = 1204.65.$$

To derive an expression for the partial pressure $p''$ the total volume $V$ must be found. Before mixing, the volume of the air is

$$V_1 = \frac{M_1 B T_1}{p_1} = \frac{5 \times 53.34 \times 1095}{144 \times 200} = 10.14 \text{ cu. ft.,}$$

and the volume of the steam is

$$V_2 = \frac{B' T_2}{p_2} - c = \frac{0.5962 \times 941.4}{200} - 0.256 = 2.55 \text{ cu. ft.}$$

Hence        $V = 10.14 + 2.55 = 12.69$ cu. ft.

After mixing the superheated steam at the partial pressure $p''$ and temperature $T$ occupies this volume; hence, we have (since $M_2 = 1$)

$$p'' = \frac{B' T}{V + c} = \frac{0.5962 \, T}{12.69 + 0.256}.$$

Introducing this expression for $p''$ in the term $\frac{Cp''}{T^6}$, that term becomes $\frac{C'}{T^4}$, where log $C' = 12.30919$. The equation in $T$ then becomes

$$1.1066 \, T + 0.00005 \, T^2 - \frac{C'}{T^4} = 1204.65.$$

| $T$ | $1.1066\,T$ | $0.00005\,T^2$ | $\dfrac{C'}{T^4}$ | Sum |
|---|---|---|---|---|
| 1000 | 1106.6 | 50. | 2.04 | 1154.56 |
| 1050 | 1161.93 | 55.13 | 1.68 | 1215.38 |
| 1100 | 1217.26 | 60.5 | 1.39 | 1276.37 |

By interpolation it is readily found that $T = 1041°$. The pressure of the
[ste]am is

$$p'' = \frac{0.5962 \times 1041}{12.946} = 47.94 \text{ lb. per square inch,}$$

[wh]ile the pressure of the air is

$$p' = \frac{53.34 \times 1041 \times 5}{144 \times 12.69} = 151.93 \text{ lb. per square inch.}$$

[Th]erefore $\qquad p = p' + p'' = 199.9$ lb. per square inch.

The total pressure $p$ should evidently be 200 lb. per square inch; hence
[th]e result may be regarded as a check on the calculation.

Having now the initial condition of the mixture, the condi-
[tio]n after adiabatic expansion to any assumed lower pressure
[an]d the work of expansion may be found by the methods of
[Ar]t. 146.

The discussions of Arts. 146 and 147 furnish the necessary
[eq]uations for the analysis of the action of a motor that uses a
[mi]xture of air and steam as its working fluid.

### EXERCISES

**1.** Find the humidity and the weight of vapor per cubic foot when the
[tem]perature is 85° and the dew point is 70°.

**2.** The humidity is 0.60 when the atmospheric temperature is 74° F.
[Fi]nd the dew point.

**3.** Find the value of $B$ for air at 80° with 70 per cent humidity. Find
[als]o the specified heat $c_p$ of the mixture.

**4.** A mixture of air and wet steam has a volume of 3 cu. ft. and the
[tem]perature is 240° F. The weight of the air present is 1 lb., that of the
[ste]am and water 0.4 lb. Find the partial pressures of the air and vapor, the
[tot]al pressure of the mixture, and the quality of the steam.

**5.** Let the mixture in Ex. 4 expand isothermally to a volume of 5 cu. ft.
[Fin]d the external work, the heat added, the change of entropy, and the
[cha]nge of energy.

**6.** Let the mixture expand adiabatically to a volume of 5 cu. ft. Find
[the] condition of the mixture after expansion, and the external work.

**7.** Let 1 lb. of steam, quality 0.87, at a pressure of 150 lb. per square inch, be mixed with 4 lb. of air at a pressure of 160 lb. per square inch and a temperature of 340° F. Find the condition of the mixture.

**8.** Let the mixture in Ex. 7 expand adiabatically to a pressure of 40 lb. per square inch. Determine the final state of the mixture and calculate the work of expansion.

**9.** Let 1 lb. of steam at a pressure of 150 lb. per square inch and superheated 140° be mixed with 6 lb. of air at a pressure of 160 lb. per square inch and a temperature of 340° F. Find the condition of the mixture.

**10.** Let the mixture in Ex. 9 expand adiabatically until the pressure drops to 14.7 lb. per square inch. Required the final state of the mixture and the work of expansion.

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

Berry: The Temperature Entropy Diagram, 136.
Zeuner: Technical Thermodynamics, 320.
Lorenz: Technische Wärmelehre, 366.

## THE FLOW OF FLUIDS

**148. Preliminary Statement.** — Under the title "flow of fluids" are included all motions of fluids that progress continuously in one direction, as distinguished from the oscillating motions that characterize waves of various kinds. Important examples of the flow of elastic fluids are the following: (1) The flow in long pipes or mains, as in the transmission of illuminating gas or of compressed air. (2) The flow through moving channels, as in the centrifugal fan. (3) The flow through orifices and tubes or nozzles. The recent development of the steam turbine has made especially important a study of the last case, namely, the flow of steam through orifices and nozzles, and it is with this problem that we shall be chiefly concerned in the present chapter.

Of the early investigators in the field under discussion, mention may be made of Daniel Bernoulli (1738), Navier (1829), and of de Saint Venant and Wantzel (1839). The latter deduced the rational formulas that to-day lie at the foundation of the theory of flow; they further stated correctly conditions for maximum discharge, and advanced certain hypotheses regarding the pressure in the flowing jet which were at the time disputed but which have since been proved valid.

Extensive and important experiments on the flow of air were made by Weisbach (1855), Zeuner (1871), Fleigner (1874 and 1877), and Hirn (1844). These served to verify theory and afforded data for the determination of friction coefficients. In 1897 Zeuner made another series of experiments on the flow of air through well-rounded orifices.

Experiments on the flow of steam were made by Napier (1866), Zeuner (1870), Rosenhain (1900), Rateau (1900), Gutermuth and Blaess (1902, 1904).

243

Most of the experimental work here noted relates to the flow of fluids through simple orifices or through short convergent tubes. The more complicated relations between velocity, pressure, and sectional area that obtain for flow through relatively long diverging nozzles have been investigated experimentally by Stodola, while the theory has been developed by H. Lorenz and Prandtl. The flow of steam through turbine nozzles has also been discussed by Zeuner.

**149. Assumptions.** — In order to simplify the analysis of fluid flow and render possible the derivation of fundamental equations, certain assumptions and hypotheses must necessarily be made.

1. It is assumed that the fluid particles move in non-intersecting curves — stream lines — which in the case of a prismatic



FIG. 78.

channel may be considered parallel to the axis of the channel. We may imagine surfaces stretched across the channel, as $F$, $F'$, $F''$, etc., Fig. 78, to which the stream lines are normal. These are the cross sections of the channel. They are not necessarily plane surfaces, but they may usually be so assumed with sufficient accuracy.

2. The fluid, being elastic, is assumed to fill the channel completely. From this assumption follows the *equation of continuity*, namely :

$$Fw = Mv, \tag{1}$$

in which $F$ denotes the area of cross section, $w$ the mean velocity of flow across the section, $M$ the weight of fluid passing in a unit of time, and $v$ the specific volume.

3. It is assumed that the motion is steady. The variables $p$, $v$, $T$ giving the state of the fluid and also the mean velocity $w$ remain constant at any cross section $F$; in other words, these variables are independent of the time and depend only upon the position of the cross section.

**150. Fundamental Equations.** — The general theory of flow of elastic fluids is based upon two fundamental equations, which are derived by applying the principle of conservation of
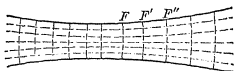
energy to an elementary mass of fluid moving in the tube or channel.

Let $w_1$ denote the velocity with which the fluid crosses a section $F_1$ of a horizontal tube, Fig. 79, and $w$ the velocity at some second section $F$. A unit weight of the fluid at section $F_1$ has the kinetic energy of motion $\frac{w_1^2}{2\,g}$ due to the velocity $w_1$; hence if $u_1$ is the intrinsic energy of the fluid at this section, the total energy is $u_1 + \frac{w_1^2}{2\,g}$. Likewise, the energy of a unit weight of fluid at section $F$ is $u + \frac{w^2}{2\,g}$. In general, the total energy at section $F$ is different from that at section $F_1$ and the change of energy between the sections must arise: (1) from energy entering or leaving the fluid in the form of heat during the passage from $F_1$ to $F$; (2) from work done on or by the fluid. The heat entering the fluid per unit of weight between the two
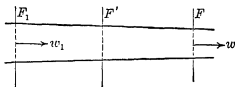


FIG. 79.

sections we will denote by $q$. Evidently work must be done against the frictional resistance between the fluid and tube; let this work per unit weight of fluid be denoted by $z$. The heat equivalent $Az$ necessarily enters the flowing fluid along with the heat $q$ from the outside. Aside from the friction work, the only source of external work is at the sections $F_1$ and $F$. As a unit weight of fluid passes section $F_1$, a unit weight also passes section $F$. Denoting by $p_1$ and $v_1$ the pressure and specific volume, respectively, at $F_1$, the work done on a unit weight of fluid in forcing it across section $F_1$ is the product $p_1 v_1$; similarly, the product $pv$ gives the work done by a unit weight of fluid at section $F$ on the fluid preceding it. For each unit weight flowing the net work *received* at the section $F_1$ and $F$ is, therefore,

$$p_1 v_1 - pv.$$

Equating the change of energy between $F_1$ and $F$ to the energy received from external sources, we obtain

$$\left(u + \frac{w^2}{2\,g}\right) - \left(u_1 + \frac{w_1^2}{2\,g}\right) = J(q + Az) - z + p_1 v_1 - pv,$$

or
$$\frac{w^2 - w_1{}^2}{2g} = J_q + (u_1 + p_1 v_1) - (u + pv). \qquad (1)$$

This is the first fundamental equation.

It will be observed that the friction work $z$ drops out of the equation; the effect of friction is to alter the distribution between internal energy $u$ and kinetic energy $\frac{w^2}{2g}$ at section $F$, leaving the sum total unchanged.

Differentiation of (1) gives

$$\frac{w \, dw}{g} + du + d(pv) = J \, dq, \qquad (2)$$

a form of the fundamental equation that is useful in subsequent analysis.

Equation (1), as is apparent, takes account only of initial conditions at section $F_1$ and final conditions at section $F$, and gives no information of anything that occurs between these sections. A second fundamental equation taking account of internal phenomena between the two sections is derived as follows. Consider a lamina of the fluid moving along the channel. This element receives from external sources the heat $dq$ and also the heat $A \, dz$, the equivalent of the work done against frictional resistances. Independently of its motion, the lamina of fluid may increase in volume and thereby do external work against the surrounding fluid, and its internal energy may increase. According to the first law we have, therefore,

$$J(dq + A \, dz) = du + p \, dv. \qquad (3)$$

The first member represents the energy entering the lamina during the passage from $F_1$ to $F$, $du$ is the increase of energy, and $p \, dv$ the external work done. Combining (3) with (2), we get

$$\frac{w \, dw}{g} + v \, dp + dz = 0, \qquad (4)$$

whence by integration we obtain

$$\frac{w^2 - w_1{}^2}{} = -\int^{v} v \, dp - z. \qquad (5)$$

The fundamental equations (1) and (5), or the equivalent differential equations (2) and (4), are perfectly general and hold equally well for gases, vapors, and liquids.

**151. Special Forms of the Fundamental Equation.** — In nearly all cases of flow the heat entering or leaving the fluid is so small as to be negligible, and we may, therefore, assume that $q = 0$. The sum $u + pv$ will be recognized as the work equivalent of the heat content $i$; that is,

$$u + pv = Ji. \quad \text{(See Art. 52.)}$$

Equation (1) of Art. 150 may, therefore, be written in the form

$$\frac{w^2 - w_1^2}{2\,g} = J(i_1 - i). \quad (1)$$

For a perfect gas

$$Ji = u + pv = \frac{k}{k-1}\,pv, \quad (2)$$

whence,

$$\frac{w^2 - w_1^2}{2\,g} = \frac{k}{k-1}\,(p_1v_1 - pv). \quad (3)$$

If the fluid is a mixture of liquid and saturated vapor, the heat content $i$ is practically equal to the total heat. (See Art. 86.)   Hence we may put

$$i = q' + xr, \quad (4)$$

and (1) becomes

$$\frac{w^2 - w_1^2}{2\,g} = J[q_1' + x_1r_1 - (q' + xr)]. \quad (5)$$

For a superheated vapor, the general form (1) is used, the values of $i_1$ and $i$ being calculated from formula (6), Art. 135.

Equations (3) and (5) being derived from the first fundamental equation hold equally well for frictionless flow and for flow with friction.

**152. Graphical Representation.** — A consideration of the fundamental equations developed in Art. 150 leads to several convenient and instructive graphical representations, in which
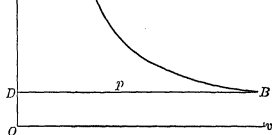
FIG. 80.

$p$-axis is given by

$$\int_{p_1}^{p} v\,dp = -\int_{p_1}^{p} v\,dp.$$

In the case of frictionless flow, however, the second fundamental equation [(5), Art. 150] becomes

$$\frac{w^2 - w_1{}^2}{2\,g} = -\int_{p_1}^{p} v\,dp. \qquad (1)$$

Hence for frictionless flow, the increase of kinetic energy is given by the area between the $p$-axis and the curve representing the expansion.

2. If the flowing fluid is a saturated vapor of given quality, the representation just given applies but the equation of the expansion line $AB$ must be expressed in the form $pv^n =$ const. It is, therefore, more convenient to use the temperature $T$ and entropy $S$ as coördinates. If the flow is frictionless and adiabatic, the expansion curve $AB$ is the vertical isentropic, Fig. 81. The area $OHCAA_1$ represents the total heat of the mixture in the initial state $A$, and the area $OHDBA_1$ the total heat in the final state $B$;

FIG. 81.

hence the difference of these areas, namely, the area $ABDC$, represents the difference $q_1' + x_1 r_1 - (q' + xr)$, and from (5),
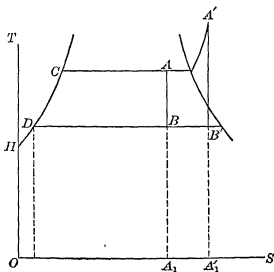
Art. 151, this area, therefore, represents the increase of energy

$$\frac{w^2 - w_1^2}{2\,g}.$$

If the initial point is at $A'$ in the superheated region, we have

$$i_1 = \text{area } OHCAA'A_1',$$
$$i = \text{area } OHDB'A_1',$$
$$i_1 - i = \text{area } A'B'DCAA'.$$

3. The work $z$ expended in overcoming friction may be shown on either the $pv$- or the $TS$-plane. When friction is taken into account, the heat $Az$, the equivalent of the friction work $z$, reënters the fluid, and consequently the heat content $i$ and the volume $v$ are both greater at the lower pressure $p$ than they would be were there no friction. Hence the expansion curve $AB'$, Fig. 82 and 83, for flow with friction must lie to the right of the curve $AB$ for flow without friction. This statement applies to both figures.

Let $i_1$ denote the heat content in the initial state $A$, $i$ the heat content in the state $B$, and $i'$ the heat content in the final state $B'$ when friction enters into consideration. Then

$$i' > i,$$

whence

$$i_1 - i' < i_1 - i.$$

It follows from (1) Art. 151, that the change of kinetic energy $\dfrac{w'^2 - w_1^2}{2\,g}$ for flow with friction is less than the change $\dfrac{w^2 - w_1^2}{2\,g}$ in the case of frictionless flow. Friction, therefore, causes a loss of kinetic energy given by the relation

$$\frac{w^2 - w'^2}{2\,g} = J(i' - i). \tag{2}$$

On the $TS$-plane, Fig. 83, this loss is represented by the area $A_1BB'B_1'$; for

$$i' = \text{area } OHDB'B_1',$$
$$i = \text{area } OHDBA_1,$$
$$i' - i = \text{area } A_1BB'B_1'.$$

fluid; hence as explained in Art. 50, the increase of entropy is $A \int_{T_2}^{T_1} \frac{dz}{T}$, and the area $A_1 A B' B_1$ under the curve $AB'$ represents (in heat units) the friction work $z$.

On the $pv$-plane let a constant $i$ line be drawn from point $B'$, Fig. 82, cutting the frictionless expansion line in the point $G$.
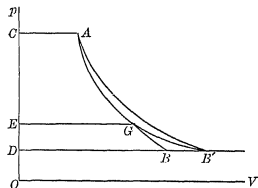


FIG. 82.

Then since the heat content $i'$ is the same at $G$ as at $B'$, the difference $i_1 - i'$ in passing from $A$ to $B'$ along the actual curve is the same as in passing from $A$ to $G$ along the ideal frictionless expansion curve $AB$. But the change of $i$ between the states represented by points $A$ and $G$, which in work units represents the increase of kinetic energy between $A$ and $G$, is given by the area $A G E C$. Hence we have:

For frictionless flow, $\dfrac{w^2 - w_1^2}{2 g} = $ area $ABDC$.

For the actual flow, $\dfrac{w'^2 - w_1^2}{2 g} = $ area $A G E C$.

Hence the loss of kinetic energy due to friction is given by the area $BDEG$.

From the fundamental equation (5), Art. 150, we have

$$z = \int_p^{p_1} v\,dp - \frac{w^2 - w_1^2}{2 g}, \qquad (3)$$

in which the integral refers to the actual expansion curve. Referring to Fig. 82, $\int_p^{p_1} v\,dp$ is given by the area $AB'DC$

while the change of energy for the actual flow is, as just shown, given by the area $AGEC$; hence the difference, the area $AB'DEGA$, represents the work of friction $z$.

The friction work $z$ (area $A_1AB'B_1'$, Fig. 83) is greater than the loss of kinetic energy (area $A_1BB'B_1'$). The reason for this lies in the fact that part of the heat $Az$ entering the moving fluid is capable of being transformed back into mechanical energy. As shown in Chapter IV, the loss of available energy, represented by area $A_1BB'B_1'$, is the increase of entropy multiplied by the lower temperature. The triangular area $ABB'$ represents, therefore, the part of the friction work that is recovered.
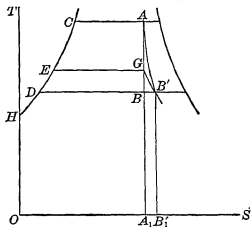


FIG. 83.

4. The most convenient graphical representation for practical purposes is obtained by taking the heat content $i$ and entropy $s$ as coördinates. On this $is$-plane a series of constant pressure lines are drawn, Fig. 84; then a vertical segment $AB$ represents a frictionless adiabatic change from pressure $p_1$ to a lower pressure $p$, while a curve $AB'$ between the same pressure limits represents an expansion with increasing entropy, that is, one with friction. The segment $AB$, therefore, represents the increase of jet energy $\dfrac{w^2 - w_1^2}{2g}$ without
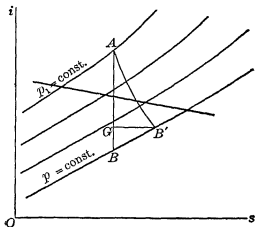


FIG. 84.

friction, the segment $AG$, the smaller increase $\dfrac{w'^2 - w_1^2}{2g}$ with

which the pressure is $p_1$ through an orifice or short tube, Fig. 85, into a region in which exists a pressure $p_2$ lower than $p_1$. If we take the section $F_1$ in the reservoir, the velocity $w_1$ will be small and may be assumed to be zero. The second section $F$ will be taken at the end of the tube, and the pressure at this section will be denoted by $p$. Assuming the flow to be frictionless and adiabatic, we have, since $w_1 = 0$,
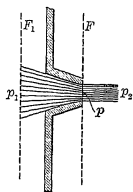
$$\frac{w^2}{2g} = \int_p^{p_1} v\,dp. \tag{1}$$

The law of the expansion is given by the equation

$$p_1 v_1{}^n = p v^n, \tag{2}$$

where for air $n = k$, while for saturated or

FIG. 85.

superheated vapor it has a value depending on the conditions existing. In any case, $n$ can be determined, at least approximately. Making use of (2) to evaluate the definite integral of (1), we get

$$\frac{w^2}{2g} = \frac{n}{n-1} p_1 v_1 \left[ 1 - \left( \frac{p}{p_1} \right)^{\frac{n-1}{n}} \right]. \tag{3}$$

If $F$ denotes the area of the orifice or tube, and $M$ the weight of fluid discharged per second, the law of continuity is expressed by the equation

$$M v = F w, \tag{4}$$

whence eliminating $w$ between (3) and (4), we obtain

$$M = \frac{F}{v} \sqrt{ 2 g p_1 v_1 \frac{n}{n-1} \left[ 1 - \left( \frac{p}{p_1} \right)^{\frac{n-1}{n}} \right] }. \tag{5}$$

From (2), we have

$$v = v_1 \left( \frac{p_1}{p} \right)^{\frac{1}{n}},$$

which substituted in (5) gives

$$M = F \sqrt{ 2 g \frac{n}{n-1} \frac{p_1}{v_1} \left[ \left( \frac{p}{p_1} \right)^{\frac{2}{n}} - \left( \frac{p}{p_1} \right)^{\frac{n+1}{n}} \right] }. \tag{6}$$

If now various values be assigned to the lower pressure $p$
and the values of $w$ and $M$ be found from (3) and (6), respec-
tively, the relations be-
tween $p$, $w$, and $M$ will be
as shown in Fig. 86. The
initial pressure $p_1$ is rep-
resented by the ordinate
$OG$, the lower pressure $p$
by the ordinate $OH$, and
the curve $AB$ represents
the change of state of the
moving fluid starting from
the initial state $A$. The
shaded area $GABH$ rep-



FIG. 86.

resents the integral $\int_p^{p_1} v\,dp$ and, therefore, the kinetic energy

of the jet $\dfrac{w^2}{2g}$ at the section $F$. The abscissa $HE$ represents

the velocity $w$ found from the equation

$$w = \sqrt{2g \times \text{area } \overline{GABH} \text{ (in ft. lb.)}},$$

while the abscissa $HD$ represents to some chosen scale the
weight of fluid discharged per second, as found from (4) or
directly from (6). Inspection of (6) shows that the discharge
$M$ reduces to zero when $p = p_1$ and also when $p = 0$. It fol-
lows that the curve $GDO$ must have the general form shown
in the figure and that the discharge $M$ must have a maximum
value for some value of $p$ between $p = 0$ and $p = p_2$. Let
this value of $p$ be denoted by $p_m$. Evidently from (6), $M$ is a
maximum when

$$\left(\frac{p}{p_1}\right)^{\frac{2}{n}} - \left(\frac{p}{p_1}\right)^{\frac{n+1}{n}}$$

is a maximum. Placing the first derivative of this expression

This ratio is called the **critical** ratio, and $p_m$ is called the **critical** value of the lower pressure $p$. For air, taking $n = k = 1.4$, this ratio is 0.5283 or approximately 0.53; for saturated or slightly wet steam, taking $n = 1.135$, the ratio is 0.5744.

The question now arises as to the relation between the pressure $p$ in the jet at section $F$ and the pressure $p_2$ of the region into which the jet discharges. If it is assumed that $p$ and $p_2$ are always equal, then $p = 0$ when $p_2 = 0$, and from (6) $M = 0$. This can only mean that no fluid can be discharged into a perfect vacuum, a result manifestly absurd. It follows that under certain conditions, $p$ must be different from $p_2$. Saint Venant
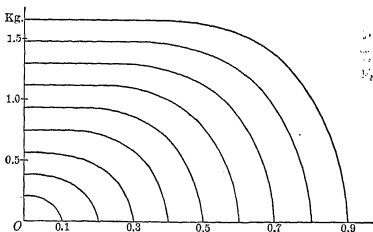


FIG. 87.

and Wantzel, to whom equations (3) and (6) are due, asserted that the discharge into a vacuum must be a maximum and advanced the hypothesis that for all values of $p_2$ lower than the critical pressure $p_m$ the discharge is the same. We have, therefore, two distinct cases: (1) If $p_2$ is greater than $p_m$, the pressure $p$ in the jet takes the value $p_2$, and $w$ and $M$ are found from (3) and (6), respectively. (2) If $p_2$ is equal to or less than $p_m$ the pressure $p$ assumes the constant value $p_m$ given by (7), and the velocity and discharge remain the same for all values of $p_2$ between $p_2 = p_m$ and $p_2 = 0$.

The hypothesis of Saint Venant has been fully confirmed by the experiments of Fleigner, Zeuner, and Gutermuth. Figure 87 shows the results of Gutermuth's experiments on the flow of steam through a short tube with rounded entrance, using dif-

ferent initial pressures $p_1$. In each case the discharge becomes constant when the lower pressure reaches a definite value $p_m$.

**154. Formulas for Discharge.** — Since for all values of $p_2$ less than $p_m$ the discharge remains constant and the pressure at the plane of the orifice or tube takes the value $p_m$, we may obtain the maximum velocity and discharge by substituting for $\dfrac{p}{p_1}$ in (3) and (6) of Art. 153 the critical value $\left(\dfrac{2}{n+1}\right)^{\frac{n}{n-1}}$. The resulting equations are:

$$w = \sqrt{2\,g\,\frac{n}{n+1}\,p_1 v_1},\qquad (1)$$

and

$$M = F\left(\frac{2}{n+1}\right)^{\frac{1}{n-1}}\sqrt{2\,g\,\frac{n}{n+1}\,\frac{p_1}{v_1}}.\qquad (2)$$

These equations give $w$ and $M$ for $p_2 < p_m$; if $p_2 > p_m$ the ratio $\dfrac{p_2}{p_1}$ must be substituted for $\dfrac{p}{p_1}$ in the original equations.

By easy transformations (1) and (2) may be given simpler forms. The following are some of the well-known formulas that have been thus derived.

1. *Fliegner's Equation for Air.* From the general equation

$$p_1 v_1 = BT,$$

which applies to the air in the reservoir from which the flow proceeds, we have

$$\frac{p_1}{v_1} = \frac{p_1{}^2}{BT}.$$

Substituting this expression for $\dfrac{p_1}{v_1}$ in (2), and taking $n = k$, the result is

$$M = \left(\frac{2}{k+1}\right)^{\frac{1}{k-1}}\left[\frac{2\,gk}{B(k+1)}\right]^{\frac{1}{2}} F\,\frac{p_1}{\sqrt{T_1}}.\qquad (3)$$

Inserting the numerical values of $k$ and $B$ for air, we get in English units

$$M = 0.53\ F\,\frac{p_1}{\sqrt{T}}.\qquad (4)$$

This is the equation given by Fliegner as representing the results of his experiments on the flow of air from a reservoir into the atmosphere. It holds good when the pressure in the reservoir is greater than twice the pressure of the atmosphere.

When the pressure in the reservoir is less than twice the atmosphere pressure the following empirical equation is given by Fliegner:

$$M = 1.06 \, F \sqrt{\frac{p_a(p_1 - p_a)}{T_1}}. \tag{5}$$

2. *Grashof's Equation for Steam.* In formula (2), $p_1$ and $v_1$ refer to the fluid in the reservoir. If this fluid is saturated steam, then $p_1$ and $v_1$ are connected by an approximate relation

$$p_1 v_1{}^m = C, \tag{6}$$

in which for English units, $m = 1.0631$ and $C = 144 \times 484.2$. From (6) we readily obtain

$$\sqrt{\frac{p_1}{v_1}} = \frac{p_1{}^{\frac{m+1}{2m}}}{C^{\frac{1}{2m}}}$$

and substituting this in (2), the resulting equation is

$$M = \left(\frac{2}{n+1}\right)^{\frac{1}{n-1}} \sqrt{\frac{2\,gn}{(n+1)\,C^{\frac{1}{m}}}} \; F p_1{}^{\frac{m+1}{2m}}. \tag{7}$$

If now we take for steam the value $n = 1.135$, (7) reduces to the simple form

$$M = 0.01911 \, F p^{0.97}. \tag{8}$$

In this formula, $F$ is taken in square feet and $p$ in pounds per square foot. When the area is taken in square inches and the pressure in pounds per square inch, (8) becomes

$$M = 0.0165 \, F p^{0.97}. \tag{9}$$

This formula is applicable for values of $p_2$ below the critical back pressure $p_m$.

3. *Rateau's Formula.* Rateau has modified the Grashof formula and gives the following as more nearly agreeing with the results of his experiments:

$$M = \frac{F p}{}$$

4. *Napier's equations.* The following simple, though some-what inaccurate, equations based upon the experiments of Mr. R. D. Napier, are due to Rankine.

When the pressure in the reservoir exceeds $\frac{5}{3}$ of the back pressure

$$M = \frac{Fp}{70}; \tag{11}$$

when it is less than $\frac{5}{3}$ of the back pressure

$$M = \frac{Fp_2}{42} \sqrt{\frac{3(p_1 - p_2)}{2\,p_2}}. \tag{12}$$

EXAMPLE.  Find the discharge in pounds per minute of saturated steam at 100 lb. pressure (absolute) through an orifice having an area of 0.4 sq. in. The back pressure is less than the critical pressure, 57 lb. per square inch.

1. By Grashof's formula

$$M = 60 \times 0.0165 \times 0.4 \times 100^{0.97} = 34.493 \text{ lb.}$$

2. By Rateau's formula

$$M = \frac{60 \times 0.4 \times 100}{1000}\,(16.367 - 0.96 \times 2) = 34.673 \text{ lb.}$$

3. By Napier's formula

$$M = \frac{0.4 \times 100}{70} \times 60 = 34.286 \text{ lb.}$$

4. The discharge may be found from the two fundamental formulas

$$w = \sqrt{2\,gJ\,(i_1 - i_2)} = 223.7\,\sqrt{i_1 - i_2},$$

and

$$M = \frac{Fw}{v}.$$

The critical pressure $p_m$ is 57.44 lb. per square inch.  From the steam table (or more conveniently, and with sufficient accuracy, from the *is*-chart) we find:

$$i_1 \text{ (for 100 lb.)} = 1186.5 \text{ B. t. u.}$$

$$i_m \text{ (for 57.44 lb.)} = 1142.7 \text{ B. t. u.}$$

$$x_m = 0.964.$$

$$v_m = x_m\,(v_m'' - v_m') + v_m' = 7.07 \text{ cu. ft.}$$

Then      $w = 223.7\sqrt{1186.5 - 1142.7} = 1480$ ft. per second,

and       $M = 60 \times \dfrac{0.4}{144} \times \dfrac{1480}{7.07} = 34.89$ lb.

$k$ the ratio $\frac{c_p}{c_v}$ of the specific heats. Then the velocity of sound in the medium is given by the relation

$$w = \sqrt{gkpv}. \quad \text{(See any textbook in Physics)}. \qquad (1)$$

If we denote by $p_m$ the critical back pressure, we have

$$\frac{p_m}{p_1} = \left(\frac{2}{k+1}\right)^{\frac{k}{k-1}}, \qquad (2)$$

which combined with the adiabatic equation

$$\frac{p_m}{p_1} = \left(\frac{v_1}{v_m}\right)^k, \qquad (3)$$

gives

$$\frac{v_1}{v_m} = \left(\frac{2}{k+1}\right)^{\frac{1}{k-1}}. \qquad (4)$$

Combining (2) and (4), we have

$$\frac{p_1 v_1}{p_m v_m} = \frac{k+1}{2}. \qquad (5)$$

The velocity through the orifice is

$$w = \sqrt{2\,g\,\frac{k}{k+1}\,p_1 v_1},$$

and by the use of (5) this becomes

$$w = \sqrt{gk p_m v_m}. \qquad (6)$$

Comparing (6) with (1), it appears that *the maximum velocity of flow from a short convergent tube is the same as the velocity of sound in the fluid in the state it has at the critical section.*

This result is due to Holtzmann (1861).

**156. The de Laval Nozzle.** — The character of the flow through a simple orifice depends largely upon the pressure $p_2$ in the region into which the jet passes. There are two cases to be discussed:

1. When $p_2$ is equal to or greater than the critical pressure $p_m$ given by the ratio

$$\frac{p_m}{p_1} = \left(\frac{2}{k+1}\right)^{\frac{k}{k-1}}.$$

2. When $p_2$ is less than $p_m$.

In the first case the pressure at the cross section $a$, Fig. 88, as we have seen, takes the value $p_2$ of the surrounding region, and, therefore, the jet experiences no change of pressure as it passes into the region beyond the nozzle. There is no tendency, consequently, for the jet to spread laterally, and for some distance beyond the orifice it will have practically constant cross section. Furthermore, since there is no drop in pressure along the axis of the jet, the velocity remains practically constant at successive cross sections.



This velocity is given by (1), Art. 151.
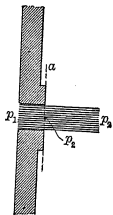
FIG. 88.
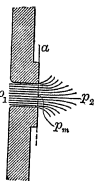
In the second case the pressure at section $a$ takes the critical value $p_m$, which is greater than the pressure of the surroundings. As a result of the pressure difference $p_m - p_2$, the jet will expand laterally, as shown in Fig. 89. Furthermore, along the axis of the jet the pressure drops continuously from its initial value $p_m$ until at some distance from the orifice it attains the pressure [$p_2$]. Hence, due to this pressure drop, the velocity of the jet in the direction of the axis will increase [as] successive sections are passed. The initial velocity at section $a$ is



FIG. 89.

$$w_s = \sqrt{gkp_m v_m},$$

[th]at is, the acoustic velocity.

The lateral spreading of the jet may [be] prevented by adding to the orifice [a] properly proportional tube, as shown [in] Fig. 90. The orifice and tube to-[get]her constitute a de Laval nozzle. The tube must diverge [so] as to permit the expansion of the fluid required by the drop [in] pressure from $p_m$ at section $a$ to $p_2$ at section $b$. The area [of] the end section $b$ depends upon the final pressure $p_2$. At [sec]tion $a$ the jet has the acoustic velocity $w_s$ as if the added
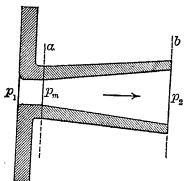


FIG. 90.

its velocity increases and at the end section $b$ takes the value $w_2$ given by the relation

$$\frac{w_2{}^2 - w_s{}^2}{2\,g} = J(i_m - i_2).$$ (1)

The general character of the flow through the de Laval nozzle may be seen from the following analysis.

Assuming frictionless adiabatic flow, the fundamental equations (6) and (7), Art. 150, become, respectively,

$$du + pdv = 0,$$ (2)

$$\frac{wdw}{g} = -vdp.$$ (3)

We have also the equation of continuity

$$Fw = Mv,$$ (4)

from which by differentiation we obtain

$$\frac{dw}{w} + \frac{dF}{F} = \frac{dv}{v}.$$ (5)

For perfect gases,

$$u = \frac{pv}{k-1},$$

while for superheated or saturated vapors,

$$u = \frac{pv}{n-1}.$$

Therefore, (2) becomes

$$\frac{d(pv)}{k-1} + pdv = 0,$$

or

$$kpdv + vdp = 0,$$ (6)

whence

$$\frac{dv}{v} = -\frac{dp}{kp}.$$

Combining this relation with (5), we obtain

$$\frac{dw}{w} + \frac{dF}{F} + \frac{dp}{kp} = 0.$$ (7)

Now from (3),

$$\frac{dw}{w} = -\frac{gv}{w^2}\,dp;$$

hence (7) becomes

$$\left(\frac{1}{kp} - \frac{gv}{w^2}\right)dp + \frac{1}{F}\,dF = 0. \tag{8}$$

By introducing the equation for the acoustic velocity

$$w_s^2 = kgpv, \tag{9}$$

(8) may be readily reduced to the form

$$\frac{1}{p}\frac{dp}{dx} = -\frac{kw^2}{w^2 - w_s^2}\frac{1}{F}\frac{dF}{dx}. \tag{10}$$

The variable $x$ may be used to denote the distance of a nozzle section from some fixed origin, Fig. 90. For vapors, $k$ may be replaced by $n$.

The nozzle has two distinct parts: the rounded orifice extending from $O$ to $A$, Fig. 91, and the diverging tube extending from $A$ to $B$. As the cross sections decrease in area from $O$ to $A$, the derivative $\frac{dF}{dx}$ is negative for this part; for the diverging part from $A$ to $B$, $\frac{dF}{dx}$ is positive; for the throat $A$ it has the value zero. The pressure drops continuously from $O$ to $B$ as shown by the curve
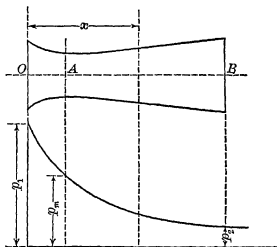


Fig. 91.

of pressure; hence $\frac{dp}{dx}$ is negative throughout. Referring to (10) we have the following results:

For orifice $OA$, $\frac{dF}{dx}$ is $-$; $\frac{dp}{dx}$ is $-$; $\frac{kw^2}{w^2 - w_s^2}$ is $-$; $w < w_s$.

For tube $AB$, $\frac{dF}{dx}$ is $+$; $\frac{dp}{dx}$ is $-$; $\frac{kw^2}{w^2 - w_s^2}$ is $+$; $w > w_s$.

For throat $A$, $\frac{dF}{dx} = 0$; $\frac{kw^2}{w^2 - w_s^2} = \infty$; $w = w_s$.

Hence the velocity steadily increases until at the throat it attains the acoustic velocity; then in the diverging tube it further increases. Inspection of (10) shows that divergence is necessary if the velocity $w$ is to exceed the acoustic velocity $w_s$.

**157. Friction in nozzles.** In the case of flow through a simple orifice or through a short convergent tube with rounded entrance, the friction between the jet and orifice, or tube, is small and scarcely demands attention. With the divergent de Laval nozzle, on the contrary, the friction may be considerable and must be taken into account. As explained in Art. 152, the effect of friction is to produce a decrease in the jet energy $\dfrac{w^2}{2g}$ at the end section. Referring back to Fig. 83, suppose $A$ to denote the initial state of the fluid entering the nozzle, $B'$ the final state at exit, and $B$ the final state that would have been attained with frictionless flow; then the area $A_1BB'B_1'$ represents the increase in the final heat content $i_2$ due to friction and it likewise represents the decrease in jet energy at exit.

Let $i_1$, $i_2$, and $i_2'$ denote, respectively, the heat content of the fluid in the states represented by the points $A$, $B$, and $B'$. Without friction, we have

$$\frac{w_2^2}{2g} = J(i_1 - i_2),$$

while with friction

$$\frac{w_2'^2}{2g} = J(i_1 - i_2').$$

The loss of kinetic energy due to friction is, therefore,

$$\frac{w_2^2}{2g} - \frac{w_2'^2}{2g} = J(i_2' - i_2).$$

It is customary to take as a friction coefficient the ratio of the loss of energy to the kinetic energy without friction. Denoting this ratio by $y$ we have, therefore,

$$y = \frac{w_2^2 - w_2'^2}{w_2^2} = \frac{i_2' - i_2}{i_1 - i_2}, \tag{1}$$

whence

$$\frac{w_2'}{2\,g} = J(1 - y)(i_1 - i_2). \tag{2}$$

The experiments that have been made on the flow of steam through nozzles indicate that the value of $y$ may lie between 0.08 and 0.20.

EXAMPLE. Steam in the dry saturated state flows from a boiler in which the pressure is 120 lb. per square inch absolute into a turbine cell in which the pressure is 35 lb. absolute. A de Laval nozzle is used, and the value of $y$ is 0.12. Find the velocity of the jet, and the loss of kinetic energy; also the final quality of the steam.

For the given initial state, $i = 1190.1$ B. t. u. At the end of adiabatic expansion to the lower pressure, $x_2$ is found to be 0.925, and $i_2$ is found to be 1095.8 B. t. u. The exit velocity on the assumption of frictionless flow is, therefore,

$$w = 223.7\sqrt{1190.1 - 1095.8} = 2172 \text{ ft. per second,}$$

while the actual velocity is

$$w' = 223.7\sqrt{(1 - 0.12)(1190.1 - 1095.8)} = 2038 \text{ ft. per second.}$$

The loss of kinetic energy is,

$$0.12 \times 778 \times 94.3 = 8804 \text{ ft.-lb.,}$$

or in B. t. u.,

$$0.12 \times 94.3 = 11.3 \text{ B. t. u.}$$

This heat is represented by the rectangle $A_1BB'B_1'$, Fig. 83. Hence, for the quality $x_2'$ in the actual final condition $B'$, we have

$$x_2' - x_2 = \frac{y(i_1 - i_2)}{r_2} = \frac{11.3}{938.4} = 0.012;$$

and, therefore, $x_2' = 0.925 + 0.012 = 0.937$.

The effects of friction are: (1) to decrease the velocity of flow at a given section; (2) to increase the specific volume $v$ of the fluid passing the section. The latter effect is seen in the case of steam in the increased quality or increased degree of superheat due to the heat generated through friction reëntering the moving fluid. From the equation of continuity

$$F = M\frac{v}{w}, \tag{3}$$

it appears that the effect of friction is to increase the numerator $v$ and decrease the denominator $w$ of the fraction of the

second member; hence for a given discharge $M$, the cross section $F$ must be larger the greater the friction, that is, for the same lower pressure $p_2$.

The effect of friction may be viewed from another aspect. In Fig. 92, let the curve $CMAE$ represent the pressures along the axis of a de Laval nozzle on the assumption of no friction. This curve is readily found for a given value of $p_1$ by finding for various lower pressures $p$ the proper cross section $F$ by means of the two equations,

$$\frac{w^2}{2g} = J(i_1 - i), \text{ and } F = \frac{Mv}{w}.$$



FIG. 92.

Let $A$ be a point on the pressure curve obtained in this manner. If now friction is taken into account, the section $F'$ associated with the lower pressure $p$ has a larger area than the section $F$ calculated on the assumption of no friction; therefore, the point $A$ is shifted by friction to a new position $A'$ underneath the new section $F'$. Similarly the end section $F_e$ must be increased in area to $F_e'$, and the point $E$ on the frictionless pressure curve is shifted to a new position $E'$. The effect of friction, therefore, is to raise the pressure curve as a whole, that is, to increase the pressure at any point in the axis of the nozzle.
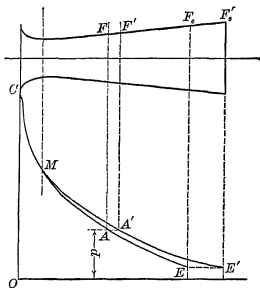
**158. Design of Nozzles.** — The data required in the design of a nozzle are the initial and final pressures, the weight of steam that must be delivered per hour or per minute, and the coefficient $y$. Two cross section areas must be calculated, that at the throat, and that at the end of the nozzle. The following example illustrates the method.

EXAMPLE. Required the dimension of a nozzle to deliver 450 lb. of steam per hour, initially dry and saturated, with an initial pressure of 175 lb. absolute and final pressure of 15 lb. absolute. Let $y = 0.13$.

The critical pressure in the throat is $175 \times 0.57 = 100$ lb. approx. Then for frictionless adiabatic flow

$$i_1 = 1196.4 \text{ B. t. u.},$$

$$i_m \text{ (at throat)} = q_m' + x_m r_m = 298.1 + 0.962 \times 888.4 = 1152.9,$$

$$i_2 = q_2' + x_2 r_2 = 181.1 + 0.863 \times 969.7 = 1017.5,$$

$$i_1 - i_m = 43.5; \quad i_1 - i_2 = 178.9.$$

Since the throat is near the entrance, the effect of friction between entrance and throat is practically negligible; hence the velocity at the throat is

$$w_m = 223.7\sqrt{43.5} = 1475 \text{ ft. per second.}$$

Taking account of the loss of energy $(y = 0.13)$, the velocity of exit is

$$w_2 = 223.7\sqrt{0.87 \times 178.9} = 2791 \text{ ft. per second.}$$

The quality of steam at the throat was found to be 0.962, and that at exit, without friction, 0.863. Because of friction, the quality at exit is increased by the amount $178.9 \times 0.13 \div 969.7 = 0.024$, thus giving a final quality $363 + 0.024 = 0.887$. Neglecting the volume $v'$ of a unit weight of water, since $x$ is large, the specific volumes at throat and exit are respectively

$$4.42 \times 0.962 = 4.252 \text{ cu. ft.}$$

and

$$26.23 \times 0.887 = 23.26 \text{ cu. ft.}$$

From the equation of continuity $Fw = Mv$, we have, since

$$M = \frac{450}{60 \times 60} = 0.125 \text{ lb. per second,}$$

$$F_m = \frac{0.125 \times 4.252}{1475} = 0.00036 \text{ sq. ft.}$$

$$= 0.0519 \text{ sq. in.}$$

the area of the cross section at the throat. The area at exit is

$$F_2 = \frac{0.125 \times 23.26}{2791} = 0.001042 \text{ sq. ft.} = 0.15 \text{ sq. in.}$$

If the cross section of the nozzle is made circular, the diameters at throat and exit are respectively

$$d_m = 0.251 \text{ in.}, \quad d_2 = 0.437 \text{ in.};$$

and taking the taper of the nozzle as 1 to 10, the length of the conical part is

$$10(0.437 - 0.257) = 1.8 \text{ in.}$$

## EXERCISES

**1.** Find the weight of air discharged per minute through an orifice inch in diameter from a reservoir in which the pressure is maintained at

orifice having an area of 0.4 sq. in. into a region in which the pressure is 55 lb. per square inch. Find (a) the velocity; (b) the weight discharged per minute. Compare the results obtained by using Grashof's, Napier's, and Rateau's formulas, respectively.

**3.** If in Ex. 2 the back pressure is 80 lb. per square inch, what is the weight discharged? Assume the steam to be initially dry and saturated.

**4.** If for superheated steam the exponent $n$ in the adiabatic equation $pv^n = \text{const.}$ is taken as 1.30, find the critical ratio $\dfrac{p_m}{p_1}$.

**5.** A de Laval nozzle is required to deliver 630 lb. of steam per hour. The steam is initially dry and saturated at a pressure of 110 lb. per square inch and the final pressure is 8 in. of mercury. Find the necessary areas of the throat section and end section of nozzle, assuming frictionless flow.

**6.** In Ex. 5 find the areas of the two sections when the loss of kinetic energy is 0.15 of the available energy.

**7.** Find the area of an orifice that will discharge 1000 lb. of dry steam per hour, the initial pressure being 150 lb. per square inch and the back pressure 105 lb. per square inch.

**8.** In an injector, steam flows through a diverging nozzle into a combining chamber in which a partial vacuum is maintained, due to the condensation of the steam in a jet of water. If the initial pressure is 80 lb. per square inch and the pressure in the combining chamber is 8 lb. per square inch, find the velocity of the steam jet. Assume $y = 0.08$.

**9.** Steam at 160 lb. pressure superheated 100° flows through a nozzle into a turbine cell in which the pressure is 70 lb per square inch. Find the area of the throat of the nozzle for a discharge of 36 lb. per minute.

**10.** Let steam at 160 lb. pressure, superheated 100°, expand adiabatically without friction. Take values of the back pressure $p_2$ as abscissas, and plot curves showing (a) the available drop in heat content $i_1 - i_2$; (b) the velocity of the jet; (c) the area of cross section required for a discharge of one pound per second.

SUGGESTION. Find $i_2$ for the following pressures: 140, 120, 100, 80, 60, 40, 20, 10, 5 lb. per square inch. Then find $w$ from the formula $w = 223.7\sqrt{i_1 - i_2}$, and the cross section from the equation of continuity.

**11.** Steam at 160 lb. pressure superheated 100° is discharged into a region in which the pressure is $p_2$ through an orifice having an area of 0.25 sq. in. Take the values of $p_2$ given in Ex. 10 and plot a curve showing the weight discharged for different values of $p_2$.

**12.** Show that if the loss of kinetic energy is $y$ per cent of the available energy, the decrease in the velocity of the jet is approximately $\frac{1}{2}y$ per cent of the ideal velocity.

# REFERENCES

## GENERAL THEORY OF FLOW OF FLUIDS

Zeuner: Technical Thermodynamics **1**, 225; **2**, 153.
Lorenz: Technische Wärmelehre, 99, 122.
Weyrauch: Grundriss der Wärme-Theorie **2**, 303.
Peabody: Thermodynamics, 5th ed., 423.
Stodola: Steam Turbines, 4, 45.
Rateau: Flow of Steam through Nozzles.


## ORIGINAL PAPERS GIVING EXPERIMENTAL RESULTS OR DISCUSSIONS

Weisbach: Civilingeineur **12**, 1, 77.  1866.
Fliegner: Civilingenieur **20**, 13 (1874); **23**, 443 (1877).
De Saint Venant and Wantzel: Journal de l'École polytechnique **16**.  183
    Comptes rendus **8**, 294 (1839); **17**, 140 (1843); **21**, 366 (1845).
Gutermuth: Zeit. des Verein. deutsch. Ing. **48**, 75.  1904.
Emden : Wied. Annallen **69**, 433.  1899.
Lorenz: Zeit. des Verein. deutsch. Ing. **47**, 1600.  1903.
Prandtl and Proell: Zeit. des Verein. deutsch. Ing. **48**, 348.  1904.
Büchner: Zeit. des Verein. deutsch. Ing. **49**, 1024.  1904.
Rateau: Annales des Mines, 1.  1902.
Rosenhain: Proc. Inst. C. E. **140**.  1899.
Wilson: London Engineering **13**.  1872.

## THROTTLING PROCESSES

**159. Wiredrawing.** — The flow of a fluid from a region of higher pressure into a region of much lower pressure through a valve or constricted passage gives rise to the phenomenon known as **wiredrawing** or **throttling**. Examples are seen in the passage of steam through pressure-reducing valves, in the throttling calorimeter, in the passage of ammonia through the



FIG. 93.

expansion valve in a refrigerating machine, and in the flow through ports and valves in the ordinary steam engine. Wire-drawing is evidently an irreversible process, and as such, is always accompanied by a loss of available energy.

The fluid in the region of higher pressure is moving with a velocity $w_1$, Fig. 93. As it passes through the orifice into the region of lower pressure $p_2$, the velocity increases to $w_2$ according to the general equation for flow, viz:

$$\frac{w_2{}^2 - w_1{}^2}{2\,g} = J\,(i_1 - i_2). \tag{1}$$

The increased velocity is not maintained, however, because the energy of the jet is dissipated as the fluid passing through the orifice enters and mixes with the fluid in the second region. Eddies are produced, and the increase of energy $\dfrac{w_2{}^2 - w_1{}^2}{2\,g}$ is returned to the fluid in the form of heat generated through internal friction. Utimately, the velocity $w_2$ is sensibly equal to the original velocity $w_1$; therefore from (1), we obtain

$$i_1 = i_2, \tag{2}$$

as the general equation for a wiredrawing process. The initial and final points lie, therefore, on a curve of constant heat content.

**160. Loss due to Throttling.** — Let steam in the initial state denoted by point $A$, Fig. 94, be throttled to a lower pressure, the final state being denoted by



point $B$ on the constant-$i$ curve $AB$. Also let $T_0$ denote the lowest available temperature. The increase of entropy during the change $AB$ is represented by $A_1B_1$, and this increase multiplied by the lowest available temperature $T_0$ gives the loss of available energy. Evidently this loss is represented by the area $A_1DCB_1$.
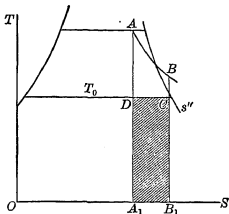
Fig. 94.

EXAMPLE. In a steam engine the pressure is reduced by a throttling valve from 160 lb. per square inch to 90 lb. per square inch absolute. The initial quality is $x = 0.99$ and the absolute back pressure is 4 in. of mercury. Required the loss of available energy per pound of steam.

From the steam table the initial heat content is 1187.2 B. t. u. At a pressure of 90 lb. the heat content of saturated steam is 1184.5 B. t. u., therefore in the second state the steam is superheated. As the degree of superheat is evidently small, it may be determined with sufficient accuracy from the curves of mean specific heat. At a pressure of 90 lb. the mean specific heat near saturation is 0.55; hence the superheat is $\dfrac{1187.2 - 1184.5}{0.55} = 5°$, nearly.

The entropy in the second state is the sum of the entropy at saturation 1.6107 for a pressure of 90 lb., and the entropy due to superheat, which is approximately.

$$0.55 \log_e \frac{T_s + 5}{T_s} = 0.55 \log_e \frac{785}{780} = 0.0035.$$

Hence, $s_2 = 1.6107 + 0.0035 = 1.6142$. The entropy in the initial state

replaced by a corresponding reversible change with the condition that the heat content $i$ remains constant. The general equation

$$di = Tds + Avdp,$$

then becomes,

$$0 = Tds + Avdp,$$

and approximately we have, therefore,

$$\Delta s = -\frac{Av}{T}\Delta p, \qquad (1)$$

in which $\Delta s$ is the increase of entropy corresponding to the change of pressure $\Delta p$. Since $\Delta p$ is intrinsically negative, it follows that $\Delta s$ must be positive. Equation (1) may be written in the more convenient form

$$\Delta s = -\frac{Apv}{T}\frac{\Delta p}{p}. \qquad (2)$$

For perfect gases (2) reduces to the simple form

$$\Delta s = -AB\frac{\Delta p}{p}. \qquad (3)$$

For steam having the quality $x$, we have

$$v = x(v'' - v') + v',$$

and

$$Apv = Apx(v'' - v') + Apv';$$

or neglecting the small specific volume $v'$ of the water,

$$Apv = x\psi.$$

Eq. (2) therefore takes the form

$$\Delta s = -\frac{x\psi}{T}\frac{\Delta p}{p}. \qquad (4)$$

Mean values for $p$, $T$, and $\psi$ should be taken.

EXAMPLE. If in passing into the engine cylinder the pressure of steam is reduced by wiredrawing from 125 lb. to 120 lb. per square inch, what is the loss of available energy? The initial value of $x$ is 0.98 and the pressure at exhaust is 16 lb. per square inch.

Taking the two pressures 125 and 120, the following mean values are found from the table:

$$p = 122.5, \ T = 802.4, \ \psi = 82.5. \ \text{Also, } \Delta p = -5.$$

Hence, $\quad \Delta s = \dfrac{0.95 \times 82.5}{802.4} \times \dfrac{5}{122.5} = 0.00398.$

For $T_0$ we take the temperature corresponding to the 16 lb., namely, 675.9°. Therefore the loss of available energy is

$$675.9 \times 0.00398 = 2.7 \text{ B. t. u. approx.}$$

**161. The Throttling Calorimeter.** — A valuable application of the throttling process is seen in the calorimeter devised by Professor Peabody for determining the quality of steam. In the operation of the calorimeter steam from the main is led into a small vessel in which the pressure is maintained at a value slightly above atmospheric pressure. The steam is thus wiredrawn in passing through the valve in the pipe that connects the main and the vessel. For successful operation the amount of moisture in the steam must be small so that, as the result of throttling, the steam in the vessel is superheated.

In Fig. 94, let point $A$ represent the state of the steam in the main and point $B$ the observed state of the steam in the calorimeter ; then

$$i_A = i_B. \qquad (1)$$

But

$$i_A = i_1' + x r_1, \qquad (2)$$

where $i_1'$ and $r_1$ refer to the pressure $p_1$ in the main ;

and

$$i_B = i_2'' + c_p(t_2' - t_2), \qquad (3)$$

where $t_2'$ is the observed temperature of the steam in the calorimeter, $t_2$ is the saturation temperature corresponding to the pressure $p_2$ in the calorimeter, $i_2''$ is the saturation heat content corresponding to the pressure $p_2$, and $c_p$ is the mean specific heat of superheated steam for the temperature range $t_2' - t_2$. Combining the preceding equations, we obtain

$$x = \frac{i_2'' + c_p(t_2' - t_2) - i_1'}{r_1}. \qquad (4)$$

EXAMPLE. The initial pressure of the steam is 140 lb. per square inch, the observed pressure in the calorimeter 17 lb. per square inch, and the temperature in the calorimeter 258° F. Required the initial quality.

The temperature of saturated steam at 17 lb. pressure is 219.4° F.; hence the steam in the calorimeter is superheated $258 - 219.4 = 38.6°$. From the curves of mean specific heat the value 0.477 is found for the pressure 17 lb.

and the degree of superheat in question; and from the steam table we have $i_2'' = 1153$, $i_1' = 324.2$, $r_1 = 869$. Hence,

$$x = \frac{1153 + 0.477 \times 38.6 - 324.2}{869} = 0.975.$$

The Mollier chart, Fig. 75, may be used conveniently in the solution of problems that involve the throttling of steam. Since the heat content remains constant during a throttling process, the points representing the initial and final states lie on the same horizontal line. In the preceding example the final point is located from the observed superheat 38.6° and the observed pressure 17 lb. in the calorimeter. A horizontal line drawn through this point intersects the constant pressure line $p = 140$ lb., and from this point of intersection the quality $x = 0.975$ is read directly.

**162. The Expansion Valve.** — In the compression refrigerating machine the working fluid after compression is condensed and the liquid under the higher pressure $p_1$ is permitted to flow through the so-called expansion valve into coils in which exists a much lower pressure $p_2$. Let point $A$, Fig. 95, on the liquid curve represent the initial state of the liquid. The point that represents the final state must lie at the intersection of a constant -$i$ curve through $A$ and line of constant pressure $p_2$. Evidently we have



Fig. 95.

$$i_a = i_1',$$

and

$$i_b = i_2' + x_2 r_2,$$

where $x_2$ denotes the quality of the mixture in the final state. Therefore

$$i_1' = i_2' + x_2 r_2, \qquad (1)$$

or

$$x_2 = \frac{i_1' - i_2'}{r_2}. \qquad (2)$$

The increase of entropy (represented by $A_1 B_1$) is

$$\Delta s = s_2' + \frac{x_2 r_2}{T} - s_1', \qquad (3)$$
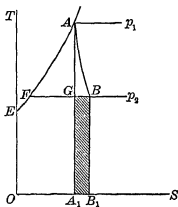
and the loss of refrigerating effect due to the expansion valve, which is represented by the area $A_1 GBB_1$, is

$$T_2 \Delta s = x_2 r_2 - T_2(s_1' - s_2')$$
$$= i_1' - i_2' - T_2(s_1' - s_2'). \quad (4)$$

The following equalities between the areas of Fig. 95 are evident:

$$\text{area } OEAA_1 = \text{area } OEFBB_1,$$
$$\text{area } FGA = \text{area } A_1 GBB_1.$$

**163. Throttling Curves.** — If steam initially dry and saturated be wiredrawn by passing it through a small orifice into a region of lower pressure, then, as has been shown, it will be superheated in its final state. If the lower pressure $p_2$ is varied, the temperature $t_2$ will also vary, and the successive values of $p_2$ and $t_2$ will be represented by a series of points lying on a curve. By taking various initial pressures a series of such curves may be obtained. Sets of throttling curves for water vapor have been obtained by Grindley, Griessmann, Peake,
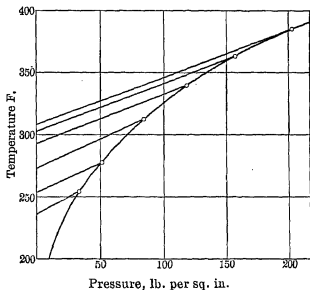


Fig. 96.

and Dodge. The curves deduced from Peake's experiments are shown in Fig. 96. Abscissas represent pressures, ordinates, temperatures. The curve from which the throttling curves start is the curve $t = f(p)$ that represents the relation between the pressure and temperature of saturated steam.

It was the original purpose of Grindley, Griessmann, and Peake to make use of the throttling curves in finding the specific heat of superheated steam. The theory upon which this determination rests is simple. From Eq. (4), Art. 161, we readily obtain

$$c - \frac{i_1' + x_1 r_1 - i_2''}{\quad} \quad (1)$$

The temperature difference $t_2' - t_2$ for any lower pressure $p_2$ is the vertical segment between the throttling curve and the saturation curve and is given directly by the experiment. Hence if the initial quality $x$ is known, and if $i_1''$ and $i_2''$ are accurately given by the steam tables, the mean value of $c_p$ is readily calculated. The results obtained were, however, discordant and of no value. The form of Eq. (1) is such that a slight error in any of the terms of the numerator of the fraction produces a large error in the calculated value of $c_p$.

The impossibility of deriving consistent values of $c_p$ by the method just described led to the belief that Regnault's formula for the total heat of saturated steam, hitherto regarded as authoritative, must be incorrect. The experiments of Knoblauch and Jakob on the specific heat having appeared, Dr. H. N. Davis of Harvard University discerned the possibility of reversing the method and deriving by it a new formula for total heat.

**164. The Davis Formula for Heat Content.** — The method employed by Dr. Davis in deriving from the throttling curves
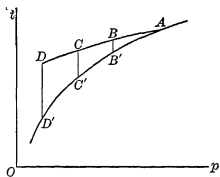


FIG. 97.

a formula for the heat content of steam may be described as follows: Let $AD$, Fig. 97, be one of the series of throttling curves, and $AD'$ the saturation curve. The heat content is constant along the throttling curve, that is

$$i_A = i_B = i_C = \text{etc.}$$

Let $p_2$ be the lower pressure corresponding to the points $B$, $B'$, and let $\Delta t$ denote the temperature difference indicated by the segment $B'B$. If the steam were made to pass from the saturation state $B'$ to the superheated state $B$ at the constant pressure $p_2$, the heat absorbed during the process would be $c_p \Delta t$, $c_p$ denoting the mean specific heat between $B'$ and $B$. It follows that

$$i_B - i_{B'} = c_p \Delta t,$$

that is,

$$i_A - i_{B'} = c_p \Delta t.$$

In a similar manner the differences $i_A - i_C$, $i_A - i_D$, etc. are obtained. The result is a relation between the heat content of saturated steam at the original pressure $p_1$ (state $A$) and the values of the saturation heat content for various lower pressures.

The temperatures corresponding to these pressures are now laid off on an arbitrarily chosen line $MN$, Fig. 98, and from the points $A$, $B'$, $C'$, etc., the segments $B'B'' = i_A - i_B$, $C''C'' = i_A - i_C$, etc. are laid off. A curve through the points $A$, $B''$, $C''$, $D''$, etc. is an isolated segment of
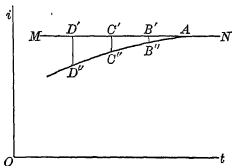


FIG. 98.

the curve giving the relation between the heat content $i$ and the temperature $t$. Necessarily only *relative* values are thus obtained.

From the individual throttling curves Dr. Davis thus obtained twenty-four overlapping segments of the $it$-curve, and by properly coördinating these segments he obtained finally a smooth curve covering the range 212° to 400° F. The curve was found to be represented by the second degree equation

$$i = a + 0.3745(t - 212) - 0.00055 \ (t - 212)^2;$$

and from the experiments of Henning and Joly on the latent heat of steam at 212° F., the value of the constant $a$ was found to be 1150.4.

**165. The Joule-Thomson Effect.** — The classical porous plug experiments of Joule and Lord Kelvin were undertaken for the purpose of estimating the deviation of certain actual gases from the ideal perfect gas. The gases tested were forced through a porous plug and the temperatures on the two sides of the plug were accurately determined. In the case of hydrogen the temperature after passing through the plug was slightly higher than on the high pressure side ; air, nitrogen, oxygen, and carbon dioxide showed a drop of temperature.

For an ideal perfect gas,

$$u_1 = Jc_v T + u_0, \text{ and } pv = BT;$$

hence,

$$(Jc_v + B)T_1 = (Jc_v + B)T_2$$

or

$$T_1 = T_2.$$

It follows that a perfect gas would show no change of temperature in passing through the plug, and that the change of temperature observed in the actual gas is, in a way, a measure of the degree of imperfection of the gas. The results of the experiments have been used to reduce the temperature scale of the air thermometer to the Kelvin absolute scale.

The ratio of the observed drop in temperature to the drop in pressure, that is, the ratio $\dfrac{\Delta T}{\Delta p}$, is called the **Joule-Thomson coefficient** and is denoted by $\mu$. According to the experiments of Joule and Kelvin $\mu$ varies inversely as the square of the absolute temperature. That is,

$$\mu = \frac{\alpha}{T^2}. \tag{1}$$

It may be assumed that this relation holds good for air, nitrogen, and other so-called permanent gases within the region of ordinary observation and experiment. At very low temperatures it seems probable that $\mu$ varies with the pressure as well as with the temperature.

An expression for $\mu$ in the case of superheated steam can readily be derived from the formula for the heat content, namely:

$$i = aT + \tfrac{1}{2}\beta T^2 - A\frac{m(n+1)}{T^n}p\left(1 + \frac{a}{2}p\right) - Acp + i_0.$$

Since $i$ is constant in a throttling process, we may define the Joule-Thomson coefficient more accurately as the derivative $\left(\dfrac{\partial T}{\partial p}\right)$. From calculus, we have

and from the definition of the heat content $i$,

$$\frac{\partial i}{\partial T} = c_p.$$

Hence

$$\mu = \left(\frac{\partial T}{\partial p}\right)_i = -\frac{1}{c_p}\frac{\partial i}{\partial p},$$

or

$$\mu = \frac{A}{c_p}\left[\frac{m(n+1)}{T^n}(1+ap)+c\right]. \qquad (2)$$

The following table contains values of $\mu$ calculated from Eq. (2).

| PRESSURE LB. PER SQ. IN. | 250° F. | 300° | 350° | 400° | 450° | 500° | 550° | 600° |
|---|---|---|---|---|---|---|---|---|
| 15 | 0.668 | 0.492 | 0.369 | 0.282 | 0.220 | 0.176 | 0.143 | 0.119 |
| 100 | | | 0.327 | 0.261 | 0.208 | 0.169 | 0.140 | 0.118 |
| 300 | | | | | 0.191 | 0.162 | 0.138 | 0.118 |

It will be observed that the value of $\mu$ varies with the pressure; however, as the temperature rises, the influence of pressure decreases; hence for gases far removed from the saturation limit, such as were used in the porous plug experiments, it seems probable that $\mu$ is a function of the temperature only, as found by Joule and Kelvin.

Dr. Davis has deduced from the throttling experiments of Grindley, Griessmann, Peake, and Dodge values of $\mu$ for superheated steam.* These were found by direct measurement of the mean slopes of the throttling curves. The values thus obtained agree very closely with those calculated from (2) and shown in the preceding table.

**166. Characteristic Equation of the Permanent Gases.** — From the cooling effect shown in the Joule-Thomson's experiments for all gases except hydrogen, it appears that those gases do not follow precisely the law expressed by the equation $pv = BT$. By making use of the relation $\mu = \dfrac{\alpha}{T^2}$ it is possible to derive a characteristic equation that represents more nearly the behavior of

Since the heat content $i$ is constant during a throttling process, the general equation

$$di = c_p\, dT - A\left(T\frac{\partial v}{\partial T} - v\right)dp$$

takes the form

$$c_p\frac{dT}{dp} = A\left(T\frac{\partial v}{\partial T} - v\right). \qquad (1)$$

Differentiating both members of (1) with respect to $T$, we obtain

$$\frac{\partial}{\partial T}\left(c_p\frac{dT}{dp}\right) = A\left(\frac{\partial v}{\partial T} + T\frac{\partial^2 v}{\partial T^2} - \frac{\partial v}{\partial T}\right)$$

$$= AT\frac{\partial^2 v}{\partial T^2}. \qquad (2)$$

But we have

$$\frac{dT}{dp} = \mu = \frac{\alpha}{T^2},$$

and from the general thermodynamic relations,

$$AT\frac{\partial^2 v}{\partial T^2} = -\left(\frac{\partial c_p}{\partial p}\right)_T.$$

Substituting these expressions in (2), we obtain

$$\frac{\partial}{\partial T}\left(c_p\frac{\alpha}{T^2}\right) + \left(\frac{\partial c_p}{\partial p}\right)_T = 0,$$

whence

$$\left(\frac{\partial c_p}{\partial p}\right)_T + \frac{\alpha}{T^2}\left(\frac{\partial c_p}{\partial T}\right)_p - \frac{2\,\alpha c_p}{T^3} = 0. \qquad (3)$$

This is a partial differential equation, the general solution of which is the equation

$$c_p = T^2\phi(T^3 - 3\,\alpha p). \qquad (4)$$

Here $\phi$ denotes an arbitrary function which must be determined from physical considerations. Since at high temperatures $c_p$ for permanent gases is given by the linear relation $c_p = a + b\,T$, we have from (4),

$$a + b\,T = T^2\phi(T^3),$$

whence

$$\phi(T^3) = \frac{a}{T^2} + \frac{b}{T},$$

and

$$\phi(T^3 - 3\,\alpha p) = \frac{a}{(T^3 - 3\alpha p)^{\frac{2}{3}}} + \frac{b}{(T^3 - 3\alpha p)^{\frac{1}{3}}}. \qquad (5)$$

Since the term $3\,\alpha p$ is small in comparison with the term $T^3$, we have approximately

$$(T^3 - 3\,\alpha p)^{-\frac{2}{3}} = T^{-2}\left(1 + \frac{2\,\alpha p}{T^3}\right)$$

$$(T^3 - 3\,\alpha p)^{-\frac{1}{3}} = T^{-1}\left(1 + \frac{\alpha p}{T^3}\right).$$

Introducing these expressions in (5) and substituting the resulting expression for $\phi(T^3 - 3\alpha p)$ in (4), we obtain finally

$$c_p = a\left(1 + \frac{2}{T^3}\frac{\alpha p}{}\right) + bT\left(1 + \frac{\alpha p}{T^3}\right)$$

$$= a + bT + \frac{\alpha p}{T^2}\left(\frac{2\,a}{T} + b\right). \tag{6}$$

It appears from (6) that the specific heat of the permanent gases varies with the pressure and temperature. At very high temperatures the term containing $p$ is small and the specific heat is given simply by $a + bT$; at low temperatures, however, this term becomes appreciable and the specific heat increases with the pressure. The specific heat curves have, therefore, somewhat the form shown in Fig. 71.

From (6), we have by differentiation

$$- AT\frac{\partial^2 v}{\partial T^2} = \left(\frac{\partial c_p}{\partial p}\right)_T = \frac{\alpha}{T^2}\left(\frac{2\,a}{T} + b\right),$$

$$\frac{\partial^2 v}{\partial T^2} = -\frac{\alpha}{AT^3}\left(\frac{2\,a}{T} + b\right).$$

Integrating, we obtain

$$\frac{\partial v}{\partial T} = \frac{\alpha}{A}\left(\frac{2}{3}\frac{a}{T^3} + \frac{1}{2}\frac{b}{T^2}\right) + f(p). \tag{7}$$

Introducing in (1) the expression for $\frac{\partial v}{\partial T}$ given by (7), we obtain after reduction

$$\frac{v}{T} = f(p) - \frac{\alpha}{AT}\left[\frac{1}{3}\frac{a}{T} + \frac{1}{2}b + \frac{\alpha p}{T^3}\left(\frac{2\,a}{T} + b\right)\right]. \tag{8}$$

To determine the function $f(p)$, we assume that the perfect gas equation $pv = BT$ holds when $T$ is very large. Hence $f(p) = \frac{B}{p}$, and (8) becomes

$$pv = BT - \frac{\alpha p}{AT}\left[\frac{1}{3}\frac{a}{T} + \frac{1}{2}b + \frac{\alpha p}{T^3}\left(\frac{2\,a}{T} + b\right)\right]. \tag{9}$$

Since the last term in the bracket is very small, it may be neglected, and (9) may be written

$$pv = BT - \frac{\alpha p}{AT}\left(\frac{1}{3}\frac{a}{T} + \frac{1}{2}b\right). \tag{10}$$

The equation given by Joule and Thomson, namely,

$$pv = BT - \frac{K\alpha p}{3\,T^2}. \tag{11}$$

Joule-Thomson effect has been employed by Linde in a very ingenious machine for the liquefaction of gases. A diagrammatic sketch of the machine is shown in Fig. 99. Air (or any other gas that is to be liquefied) is compressed to a pressure of about 65 atmospheres and is discharged into a pipe leading to the chamber $c$. A current of cold water in the vessel $b$ cools the air during its passage from the compressor to the receiving chamber. From $c$ the air passes through a valve $v$ into a vessel $d$, in which a pressure of about 22 atmospheres is maintained. As a result of the throttling the temperature of the air is lowered. Thus, if $p_1$ is the pressure in the chamber $c$ and $p_2$ the pressure in the vessel $d$, the drop in temperature is

$$t_2 - t_3 = \frac{\alpha}{T_2^2} (p_1 - p_2). \tag{1}$$



FIG. 99.

The air now passes from vessel $d$ at temperature $t_3$ into the space enclosing the chamber $c$ and thence back to the compressor. In passing back, the air absorbs heat from the air in $c$, and the temperature rises from $t_3$ to the final temperature $t_4$, which is nearly the same as the initial temperature $t_1$. Due to this cooling, the air in $c$ arrives at the valve $v$ with a temperature $t_2$, which becomes lower and lower as the process continues. As the temperature $t_2$ sinks the temperature $t_3$ also sinks, but as shown by (1), $t_3$ sinks more rapidly than $t_2$. Ultimately, the value of $t_3$ drops below the critical temperature of the gas,

# PRINCIPLES

## OF

# THERMODYNAMICS

BY

G. A. GOODENOUGH, M.E.

PROFESSOR OF THERMODYNAMICS IN THE UNIVERSITY
OF ILLINOIS

SECOND EDITION, REVISED

Griessmann: Zeit. des Verein. deutsch. Ing. **47**, 1852, 1880. 1903.
Grindley: Phil. Trans. **194 A**, 1. 1900.
Peake: Proc. Royal Society **76 A**, 185. 1905.

## THE JOULE-THOMSON EFFECT

Thomson and Joule: Phil. Trans. **143**, 357 (1853); **144**, 321 (1854); **152**,
    579 (1862).
Natanson : Wied. Annallen **31**, 502. 1887.
Preston: Theory of Heat, 699.
Bryan: Thermodynamics, 128.
Lorenz: Technische Wärmelehre, 273.
Davis: Proc. Amer. Acad. **45**, 243.

## CHARACTERISTIC EQUATION OF GASES

Zeuner: Technical Thermodynamics **2**, 313.
Lorenz: Technische Wärmelehre, 296.
Plank: Physikalische Zeit. **11**, 633.
Bryan: Thermodynamics, 138.

# CHAPTER XV

## TECHNICAL APPLICATIONS, VAPOR MEDIA

### THE STEAM ENGINE

**168. The Carnot Cycle for Saturated Vapors.** — Since the constant pressure line of a saturated vapor is also an isothermal, three of the processes of the Carnot cycle are approximately attainable in a vapor motor, namely: isothermal expansion, adiabatic expansion, and isothermal compression. The adiabatic compression might also be accomplished by a proper arrangement of the organs of the motor, though in practice this is never attempted. Hence, the Carnot cycle is
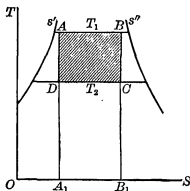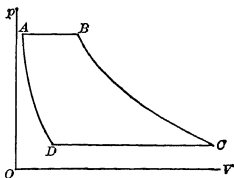


FIG. 100.                    FIG. 101.

discussed in connection with vapor motors merely for the purpose of furnishing an ideal standard by which to compare the cycles actually used.

The Carnot cycle on the $TS$-plane and $pV$-planes, respectively, is shown in Fig. 100 and 101. The isothermal expansion $AB$ occurs in the boiler, the adiabatic expansion $BC$ in the engine cylinder, the isothermal compression $CD$ in the condenser. To effect the adiabatic compression $DA$, the mixture of liquid and vapor in the state $D$ would have to be compressed

adiabatically in a separate cylinder and delivered to the boiler in the state represented by point $A$.

The heat received from the boiler per unit weight of fluid is

$$q_1 = r_1(x_b - x_a); \qquad \text{(area } A_1ABB_1) \qquad (1)$$

that rejected to the condenser is

$$q_2 = r_2(x_c - x_d); \qquad \text{(area } B_1CDA_1) \qquad (2)$$

and the heat transformed into work, represented by the cycle area, is

$$A\,W = q_1 - q_2 = \frac{T_1 - T_2}{T_1} r_1(x_b - x_a). \qquad (3)$$

The efficiency is

$$\eta = \frac{T_1 - T_2}{T_1}, \qquad (4)$$

and the weight of fluid used per horsepower-hour is

$$N = \frac{2546}{q_1 - q_2} = \frac{2546}{r_1(x_b - x_a)} \frac{T_1}{T_1 - T_2}. \qquad (5)$$

If point $A$ lies on the liquid line $s'$ and point $B$ on the saturation curve $s''$, then $x_a = 0$, $x_b = 1$, and (3) and (5) become, respectively,

$$A\,W = q_1 - q_2 = r_1 \frac{T_1 - T_2}{T_1}, \qquad (3')$$

$$N = \frac{2546}{r_1} \frac{T_1}{T_1 - T_2}. \qquad (5')$$

EXAMPLE. Let the upper and lower pressures be respectively 125 lb. per square inch absolute, and 4 in. of mercury. Then from the steam table $T_1 = 804$, $T_2 = 585.1$, $r_1 = 875.8$ B.t.u. From (4), the efficiency is

$$\frac{804 - 585.1}{804} = 0.272.$$

The heat transformed into work is $875.8 \times 0.272 = 238.2$ B.t.u., and the steam consumption is $\frac{2546}{238.2} = 10.7$ lb. per h. p.-hour.

**169. The Rankine Cycle.** — In the actual engine the isothermal compression is continued until the vapor is entirely condensed, thus locating the point $D$ on the liquid curve $s'$, Fig. 102. The liquid is then forced into the boiler by a pump and is there heated to the boiling temperature $t_s$. This heat-

It be assumed that the cylinder has no clearance, the $pv$-diagram necessarily takes the form shown in Fig. 103.
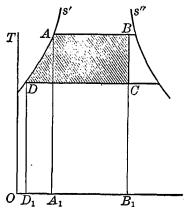


FIG. 102.
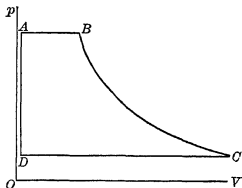
FIG. 103.

The heat supplied from the boiler per pound of steam is in this case

$$q_1 = q_{da} + q_{ab} = q_1' - q_2' + r_1 x_b ; \tag{1}$$

and the heat rejected to the condenser is

$$q_2 = r_2 x_c. \tag{2}$$

Hence, the heat transformed into work is

$$q_1 - q_2 = q_1' - q_2' + r_1 x_b - r_2 x_c, \tag{3}$$

and the efficiency of the cycle is

$$\eta = \frac{q_1 - q_2}{q_1} = 1 - \frac{r_2 x_c}{q_1' - q_2' + r_1 x_b}. \tag{4}$$

It is evident that this efficiency is less than that of the Carnot cycle.

The steam consumption per h. p.-hour is

$$N = \frac{2546}{q_1 - q_2} = \frac{2546}{q_1' - q_2' + r_1 x_b - r_2 x_c}. \tag{5}$$

The quality at point $C$ is determined from the relation

$$s_1' + \frac{x_b r_1}{T_1} = s_2' + \frac{x_c r_2}{T_2}. \tag{6}$$

EXAMPLE. — Using the data of the example of the last article, determine the efficiency and steam consumption of an engine running in a Rankine cycle with dry steam.

end of adiabatic expansion is

$$x_e = \frac{0.4957 - 0.1739 + 1.0893}{1.7497} = 0.806.$$

The available heat is

$$315.2 - 93.4 + 875.8 - 0.806 \times 1023.7 = 272.4 \text{ B. t. u.};$$

while the heat supplied in the boiler is

$$315.2 - 93.4 + 875.8 = 1097.6 \text{ B. t. u.}$$

Hence the efficiency is

$$\eta = \frac{272.4}{1097.6} = 0.248,$$

which may be compared with the efficiency 0.272 of the Carnot cycle under similar conditions.

The steam consumption is

$$N = \frac{2546}{272.4} = 9.35 \text{ lb. per h. p.-hour.}$$

## 170. Rankine's Cycle with Superheated Steam. — If superheated steam is used, the Rankine cycle has the form shown in Fig. 104. The heat $q_1$ supplied from the source is increased by the heat represented by the area $B_1BEE_1$, which comes from the superheater; and the heat available for transformation into work is increased by the amount represented by the area $FBEC$. Evidently the efficiency of the ideal cycle is increased by the use of superheated steam, but the increase is small. The advantage of superheated steam lies in another direction.
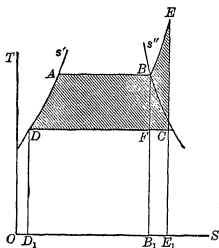


Fig. 104.

If $T_e$ denote the temperature of the superheated steam (*i.e.* at point $E$), the heat required for the superheating process $BE$ is $\int_{T_1}^{T_e} c_p dT$ where $c_p$ is the specific heat of superheated steam.

for $c_p$ given by Eq. (9), Art. 133. Then the heat represented by the area $D_1 DABEE_1$ is given by the expression

$$q_1 = q_1' - q_2' + r_1 + \int_{T_1}^{T_e} c_p dT. \tag{1}$$

However, as has been shown, the sum $q_1' + r_1 + \int_{T_1}^{T_e} c_p dT$ is practically equal to the heat content of the steam in the state $E$. Hence we may write

$$q_1 = i_e - q_2' \tag{2}$$

and calculate $i_e$ from the general formula (5) Art. 135.

If the point $C$ at the end of adiabatic expansion lies in the saturated region, as is usually the case, we have, as in the first case,

$$q_2 = r_2 x_c.$$

The heat transformed into work is, therefore,

$$q_1 - q_2 = i_e - q_2' - r_2 x_c, \tag{3}$$

and the efficiency is

$$\eta = 1 - \frac{r_2 x_c}{i_e - q_2}. \tag{4}$$

The value of $x_e$ is determined from the relation

$$s_e = s_2' + \frac{x_c r_2}{T_2}, \tag{5}$$

where $s$ is the entropy for the state $E$, and is calculated from the general equation (3), Art. 137.

EXAMPLE. — Find the efficiency of the Rankine cycle, using the data of the previous examples, but assuming the steam to be superheated to 1000° absolute.

From (6), Art. 135, the heat content of the superheated steam is

$$i = 1000(0.367 + 0.00005 \times 1000) - 125(1 + 0.0003 \times 125)\frac{C}{1000^6} - 0.0163 \times 125$$
$$+ 886.7 = 1294.8 \text{ B. t. u.};$$

and from (4), Art. 137, the entropy is

$$s = 0.8451 \log 1000 + 0.0001 \times 1000 - 0.2542 \log 125$$
$$- 125(1 + 0.0003 \times 125)\frac{C}{1000^6} - 0.3964 = 1.7002.$$

Hence
$$x_c = \frac{1.7002 - 0.1739}{1.7497} = 0.872.$$

Heat supplied $= i - q_{2'} = 1294.8 - 93.4 = 1201.4$ B. t. u.

Heat rejected $= r_2 x_c = 1023.7 \times 0.872 = 892.7$ B. t. u.

Available heat $= 1201.4 - 892.7 = 308.7$ B. t. u.

Efficiency $= \dfrac{308.7}{1201.4} = 0.257.$

Steam consumption $= \dfrac{2546}{308.7} = 8.25$ lb. per h. p.-hour.

**171. Incomplete Expansion.** — Because of the very large specific volume of saturated steam at low pressures, it is usually impracticable to continue the adiabatic expansion down to the lower pressure $p_2$. The exhaust valve opens and releases the steam at a pressure somewhat higher than $p_2$. The passage of the steam from the cylinder is an irreversible process in the nature of a free expansion and is indicated on the $pV$-diagram by the drop in pressure $EF$ (Fig. 106). The
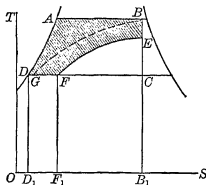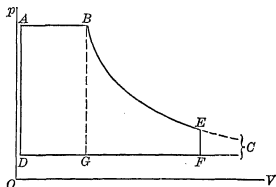


FIG. 105.          FIG. 106.

actual process may be replaced by an assumed reversible process, cooling at constant volume. On the $TS$-diagram the cooling is represented by a constant volume line $EF$ (Fig. 105) drawn as described in Art. 125.

Evidently this "cutting off the toe" of the diagram results in a decrease in the ideal efficiency, but it is justified by the smaller cylinder volume required ($DF$ instead of $DC$) and by other considerations.

Denoting by $p_3$ the pressure at $E$, the end of adiabatic expansion, we have:

$$q_1 - q_1 = q_2' + x_b'r_1. \tag{1}$$

Heat rejected by medium

$$
\begin{aligned}
q_2 &= q_{ef} + q_{fd} \\
&= u_e - u_f + x_f r_2 \\
&= (q_3' + x_e \rho_3) - (q_2' + x_f \rho_2) + x_f r_2. \tag{2}
\end{aligned}
$$

Heat transformed into work

$$q_1 - q_2 = q_1' + x_b r_1 - (q_3' + x_e \rho_3) - x_f (r_2 - \rho_2). \tag{3}$$

The qualities $x_e$ and $x_f$ are found from the equations

$$q_1' + \frac{x_b r_1}{T_1} = q_3' + \frac{x_e r_3}{T_3}, \tag{4}$$

and

$$x_e(v_3'' - v_3') = x_f(v_2'' - v_2'). \tag{5}$$

If the steam is admitted throughout the stroke without cut-off, the adiabatic expansion is lacking, and the diagram takes the form $ABGD$ (Figs. 105 and 106). The equations for this case are readily derived from the preceding equations by making

$$p_3 = p_1, \quad x_e = x_b.$$

**172. Effect of changing the Limiting Pressures.** — If the upper pressure $p_1$ be raised to $p_1'$ while the lower pressure $p_2$ is kept the same, the effect is to increase both $q_1$, the heat absorbed, and $q_1 - q_2$, the available heat, by an amount represented by the area $AA'B'B$ (Fig. 107). Evidently the ideal efficiency is thus increased. If $p_2$ be lowered to $p_2'$, keeping $p_1$ the same, $q_2$ is decreased and $q_1 - q_2$ increased without any change in $q_1$. For the ideal Rankine cycle the increase of available heat would be that represented by the area $D'DCC'$. For the modified cycle with incomplete expansion, however, the increase is represented by the relatively small area $D'DFF'$.
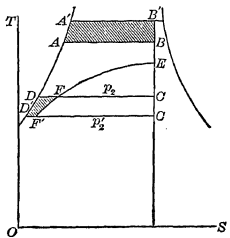


FIG. 107.

We may draw the conclusion that in the actual steam engine the limitation imposed by the cylinder volume prevents us from realizing much improvement in efficiency by lowering the back pressure $p_2$. Herein lies one important difference between the steam engine and steam turbine. With the turbine, as will be shown, a lowering of the condenser pressure results in a marked increase of efficiency.

**173. Imperfections of the Actual Cycle.** — In the discussion of the ideal Rankine cycle the following conditions are assumed:

1. That the wall of the cylinder and piston are non-conducting, so that the expansion after cut-off is truly adiabatic.

2. Instantaneous action of valves and ample port area so that free expansion or wiredrawing of the steam may not occur.

3. No clearance.

In the actual engine none of these conditions is fulfilled. The metal of the cylinder and piston conducts heat and there is, consequently, a more or less active interchange of heat, between metal and working fluid, thus making adiabatic expansion impossible. The cylinder must have clearance, and the effect of the cushion steam has to be considered. The valves do not act instantly and a certain amount of wiredrawing is inevitable. It follows that the cycle of the actual engine deviates in many ways from the ideal Rankine cycle, and that the actual efficiency must be considerably less than the ideal efficiency. We must regard the Rankine cycle as an ideal standard unattainable in practice but approximated to more and more closely as the imperfections here noted are gradually eliminated or reduced in magnitude.

The effects of some of these imperfections may be shown quite clearly by diagrams on the $TS$-plane.

In Fig. 108 is shown the cycle of a non-condensing steam engine. The feed water enters the boiler in the state represented by point $G$ and is changed into dry saturated steam at boiler pressure, represented by point $B$. When this dry steam is transferred to the engine cylinder, which has been cooled to the temperature of the exhaust steam, it is partly condensed, and the state of the mixture in the cylinder at cut-off is repre-

sented by point $C$. The heat thus absorbed by the cylinder walls is represented by the area $B_1BCC_1$. $CD$ represents the adiabatic expansion, $DE$ the assumed constant-volume cooling of the steam, and $EF$ the condensation of the steam at the temperature corresponding to the back pressure, which is slightly above atmospheric pressure. To close the cycle, the water at the temperature represented by $F$ (somewhat above 212°) must be cooled to the original temperature of the feed water; this process is represented by $FG$.

The heat supplied is represented by the area $G_1GABB_1$, the heat transformed into work by the area $FACDE$. It will be observed that two segments of the cycle, namely, $GF$ and $CB$, are traversed twice, and the



FIG. 108.

effect is a serious loss of efficiency. The loss due to starting the cycle at point $G$ instead of at point $F$ may be obviated to a large extent by the use of a feed water heater. The heat rejected in the exhaust is used to heat the feed water to a temperature represented by point $H$, which is only a little lower than the temperature of the exhaust. The area $G_1GHH_1$ represents the saving in the heat that must be supplied. The loss due to cylinder condensation, which is shown by the segment $BC$, cannot be wholly obviated; it may be reduced, however, by superheating and jacketing.

Losses due to wiredrawing and clearance are not shown on the diagram. The drop of pressure in the steam main and in the ports may be taken into account roughly by drawing a line $A'C'$ somewhat below the line $AB$, which represents full boiler pressure.

**174. Efficiency Standards.** The ratio of the heat transformed into useful work to the total heat supplied is usually termed the **thermal efficiency** of the engine. The thermal efficiency, however, does not give a useful criterion of the good or bad qualities

of an engine for the reason that it does not take account of the conditions under which the engine works. It has become customary, therefore, in estimating engine performance to make use of certain other ratios.

Let $q$ = heat supplied to the engine per pound of steam,

$\quad q_R$ = heat transformed into work by an engine working in an ideal Rankine cycle (Art. 169),

$\quad q_a$ = heat transformed into work by actual engine under the same conditions,

$\quad W_a$ = work equivalent of heat $q_a$, the *indicated* work,

$\quad W_b$ = the work obtained at the brake.

We have then

$$\eta_R = \frac{q_R}{q} = \text{thermal efficiency of ideal Rankine engine,}$$

$$\eta_a = \frac{q_a}{q} = \text{thermal efficiency of actual engine,}$$

$$\eta_i = \frac{\eta_a}{\eta_R} = \frac{q_a}{q_R} = \textbf{efficiency ratio (based on indicated work),}$$

$$\eta_b = \frac{A W_b}{q_R} = \text{brake efficiency ratio (based on work at brake),}$$

$$\eta_m = \frac{W_B}{W_A} = \text{mechanical efficiency.}$$

The ratios $\eta_i$ and $\eta_b$ are sometimes called the **potential efficiencies** of the engine, the first the indicated potential efficiency, the second the brake potential efficiency. When the term *efficiency* is used without qualification it usually means the efficiency ratio or potential efficiency rather than the thermal efficiency.

It is clear that the useful criterion of the performance of an engine is the ratio $\eta_b$. We have

$$\eta_b = \eta_i \times \eta_m.$$

Of the heat $q$ supplied, only the heat $q_R$ could be transformed into work by the ideal engine using the Rankine cycle; hence the heat $q_R$ rather than the total heat $q$ should be charged to the engine. The ratio $\eta_i = \frac{q_a}{q_R}$ is a measure of the extent to

which the engine transforms into work the heat $q_R$ that may possibly be thus transformed; it may be called the **cylinder efficiency**. The ratio $\eta_m$ measures the mechanical perfection of the engine. Hence, the product $\eta_i \times \eta_m$ measures the performance of the engine both from the thermodynamic and the mechanical standpoints.

The efficiencies $\eta_i$ and $\eta_b$ may be given other equivalent definitions that are frequently useful.

Let $N_R$ = steam consumption of ideal Rankine engine per h. p.-hour.

$N_a$ = steam consumption per h. p.-hour of actual engine.

$N_b$ = steam consumption per b. h. p.-hour of actual engine.

Then
$$\eta_i = \frac{N_R}{N_a}, \quad \eta_b = \frac{N_R}{N_b}.$$

EXAMPLE. An actual engine operating under the conditions defined in the example of Art. 169 shows a steam consumption of 14.1 lb. per i. h. p.-hour and 18 lb. per b. h. p.-hour. Since for the ideal engine the steam consumption is 9.35 lb. per h. p.-hour, we have

$$\eta_i = \frac{9.35}{14.1} = 0.663, \text{ and } \eta_b = \frac{9.35}{18} = 0.52.$$

### EXERCISES

In Ex. 1 to 5 find the heat transformed into work, efficiency, and steam consumption per h. p.-hour.

**1.** Carnot cycle, $p_1 = 110$ lb., $p_2 = 15$ lb. absolute, $x_b = 0.85$.

**2.** Rankine cycle, same data as in Ex. 1.

**3.** Rankine cycle, $p_1 = 110$ lb., $p_2 = 5$ in. of mercury, steam superheated to 450° F.

**4.** Rankine cycle $p_1 = 110$ lb., $p_2 = 15$ lb., $x_b = 0.85$ and adiabatic expansion carried to 27 lb. per square inch.

**5.** Data the same as Ex. 4 except that steam is not cut off.

**6.** Let $p_2$ be fixed at 5 in. of mercury. Take $x_b = 1$ and draw a curve showing the relation between $\eta$ and $p_1$. Rankine's cycle.

**7.** Taking the data of Ex. 2, find the increase of available heat and efficiency when a condenser is attached and $p_2$ is lowered to 5 in. of mercury.

**8.** Make the same calculation for the cycle with incomplete expansion,
Ex. 4, and compare the results.

**9.** The efficiency $\eta_i$ of an engine is 0.55 and the mechanical efficiency is 0.85. If the heat transformed into work by the ideal Rankine engine is 190 B. t. u. per pound, what is the steam consumption of the actual engine per b. h. p.-hour?

**10.** The steam consumption of a Rankine engine is 9.2 lb. per h. p.-hour, and the efficiency ratio $\eta_i$ is 0.70. Find the heat transformed into work by the actual engine per pound of steam.


## THE STEAM TURBINE

**175. Comparison of the Steam Turbine and Reciprocating Engine.** — The essential distinction between the two types of vapor motors — turbines and reciprocating engines — lies in the method of utilizing the available energy of the working fluid. In the reciprocating engine this energy is at once utilized in doing work on a moving piston; in the turbine there is an intermediate transformation, the available energy being first transformed into the energy of a moving jet or stream, which is then utilized in producing motion in the rotating element of the motor.

While the turbine suffers from the disadvantage of an added energy transformation with its accompanying loss of efficiency, it has a compensating advantage mechanically. With any motor the work must finally appear in the rotation of a shaft. Hence, intermediate mechanism must be employed to transform the reciprocating motion of the piston to the rotation required. Evidently this is not the case with the turbine, which is thus from the point of view of kinematics a much more simple machine than the reciprocating engine. Many attempts have been made to construct a motor (the so-called rotary engine) in which both the intermediate mechanism of the reciprocating engine and the intermediate energy transformation of the turbine should be obviated. These attempts have uniformly resulted in failure.

With ideal conditions it is easily shown that the two methods of working produce the same available work and, therefore, give the same efficiency with the same initial and final conditions. Thus the Rankine ideal cycle, Fig. 102, gives the maximum available work per pound of steam of a reciprocating

engine with the pressures $p_1$ and $p_2$. It likewise gives (Art. 152) the kinetic energy per pound of steam of a jet flowing without friction from a region in which the pressure is $p_1$ into a region in which it is $p_2$. Hence if this kinetic energy $\dfrac{w^2}{2\,g}$ is wholly transformed into work, the work of the turbine per unit weight of fluid is precisely equal to that of the reciprocating engine. Under ideal conditions, therefore, neither type of motor has an advantage over the other in point of efficiency.

Under actual conditions, however, there may be a considerable difference between the efficiencies of the two types. Each type has imperfections and losses peculiar to itself. The reciprocating engine has large losses from cylinder condensation; the turbine, from friction between the moving fluid and the passages through which it flows. It is a question which set of losses may be most reduced by careful design.

Aside from the question of economy, the turbine has certain advantages over the reciprocating engine in the matters of weight, cost, and durability (associated with certain disadvantages) and these have been sufficient to cause the use of turbines rather than reciprocating engines in many new power plants and also in some of the recently built steamships.

**176. Classification of Steam Turbines.** — Steam turbines may be divided broadly into two classes in some degree analogous to the impulse water wheel and the water turbine, respectively. In the first class, of which the de Laval turbine may be taken as typical, steam expands in a nozzle until the pressure reaches the pressure of the region in which the turbine wheel rotates. The jet issuing from the nozzle is then directed against the buckets of the turbine wheel, Fig. 109, and the impulse of the jet produces rotation. It will be noted that with this type of turbine only a part of the buckets are filled with steam at any instant, even if several
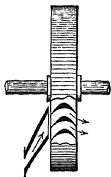


FIG. 109.
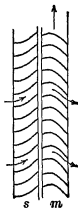
The pressure of the steam is reduced during the passage through the blades both in the guide and turbine wheels. In the turbine of the first type all the available internal energy of the steam is transformed into kinetic energy of motion before the steam enters the turbine wheel, while in the turbine of the second type part of the internal energy is transformed into work during the passage of the fluid through the wheel.

Fig. 110.

The terms *impulse* and *reaction* have been used to designate turbines of the first and second class, respectively. Since, however, impulse and reaction are both present in each type, these terms are somewhat misleading, and the more suitable terms *velocity* and *pressure* have been proposed. Thus a de Laval turbine is a velocity turbine; a Parsons turbine is a pressure turbine.

**177. Compounding.** — The high velocity of a steam jet resulting from a considerable drop of pressure renders necessary some method of compounding in order that the peripheral speed of the turbine wheels may be kept within reasonable limits without reducing the efficiency of the turbine. With velocity turbines three methods of compounding are employed.

1. *Pressure Compounding.* The total drop of pressure $p_1 - p_2$ may be divided among several wheels, thus reducing the jet velocity at each wheel. If, for example, the change of heat content is $i_1 - i_2$ and the expansion takes place in a single nozzle, the ideal velocity of the jet is $w = \sqrt{2\,gJ(i_1 - i_2)}$; if, however, $i_1 - i_2$ is divided equally among $n$ wheels, the jet velocity is reduced to $w = \sqrt{\dfrac{2\,gJ}{n}(i_1 - i_2)}$. The general arrangement of a turbine with several pressure stages is shown in Fig. 111. Steam passes successively through orifices $m_1$, $m_2$, etc. in partitions $b_1$, $b_2$, etc., which divide the interior of the

passing through the orifice $m_2$ the pressure drops from $p_2$ to $p_3$; as a result the velocity is again increased and the jet passes through the second wheel. The pressure and velocity changes are shown roughly in the diagram at the bottom of the figure.

The method of compounding here described is called **pressure compounding**. Each drop in pressure constitutes a **pressure stage**.

2. *Velocity Compounding.* The steam may be expanded in a single stage to the back pressure $p_2$, thus giving a relatively high velocity; and the jet may then be made to pass through a succession of moving wheels alternating with fixed guides. This system is shown diagrammatically in Fig. 112. The jet passes into the first moving wheel, where it loses part of its absolute velocity, as indicated by the velocity curve $w$. It then passes through the fixed guide $g_1$ with practically constant velocity and has its direction changed so as to be effective on entering the second moving wheel. Here the velocity is again reduced and the decrease of kinetic energy appears as work done on the wheel. This process may be again repeated, if desired, by adding a second guide and a third wheel. However, the work obtainable from a wheel is small after the second moving wheel is passed, and a third wheel is not usually employed.
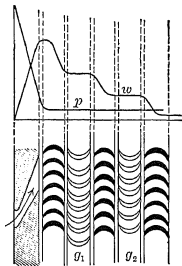


FIG. 111.
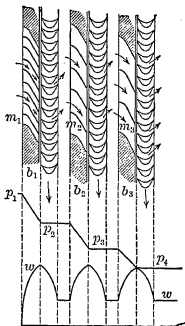


FIG. 112.

3. *Combination of Pressure and Velocity Compounding.* Evidently the two methods of compounding may be combined in a

five sets of nozzles delivering steam to a corresponding number of wheels running in separate chambers, and each wheel has two sets of blades separated by guide vanes.

Pressure turbines are always of the multiple pressure-stage type, and the number of stages is large. The arrangement is that shown in Fig. 113. The steam flows through alternate guides and moving blades, its pressure falling gradually as indicated by the curve $pp$. The absolute velocity of flow increases through the fixed blades and decreases in the moving blades as indicated by the velocity curve $ww$. This curve, it will be observed, rises as the pressure falls much as if the turbine were a large diverging nozzle. The steam velocity with this type of turbine is, however, relatively low even in the last stages.
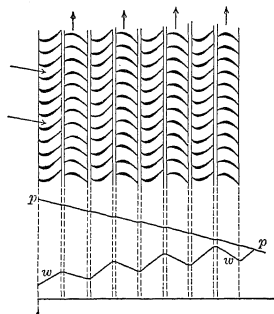


FIG. 113.

**178. Work of a Jet.** — While the problems relating to the impulse and reaction of fluid jets belong to hydraulics, it is desirable to introduce here a brief discussion of the general case of the impulse of a jet on a moving vane.

Let the curved blade have the velocity $c$ in the direction indicated, Fig. 114, and let $w_1$ denote the velocity of a jet directed against the blade. The velocity $w_1$ is resolved into two components, one equal to $c$, the velocity of the blade, the other, therefore, the velocity $a_1$ of the jet relative to the blade. The angle of the blade and the velocity $c$ should be so adjusted that the direction of $a_1$ is tangent to the edge of the blade at entrance.

The jet leaves the blade with a relative velocity $a_2$ equal in magnitude to $a_1$, neglecting friction, but of less magnitude if friction is taken into account. This velocity $a_2$ combined with the velocity $c$ of the blade gives the absolute exit velocity $w_2$. It is convenient to draw all the velocities from one point $O$ as shown in the velocity diagram.

The absolute entrance and exit velocities $w_1$ and $w_2$ may be resolved into components $w_1'$ and $w_2'$ in the direction of the motion of the vane and $w_1''$ and $w_2''$ at right angles to this direction, that is, parallel to the axis of the wheel that carries the vane. These latter may be termed the *axial* components, the former the *peripheral* components. The driving impulse of the jet depends



FIG. 114.

upon the change in the peripheral component only. To deduce an expression for the impulse we proceed as follows :

Let $\Delta m$ denote the mass of fluid flowing past a given cross section in the time $\Delta t$; then the stream of fluid in contact with the blade may be considered as made up of a number of mass elements $\Delta m$, and in the time element $\Delta t$ one mass element enters the vane with a peripheral velocity $w_1'$ and another leaves it with a peripheral velocity $w_2'$. The effect is the same as if a single element $\Delta m$ by contact with the blade had its velocity decreased from $w_1'$ to $w_2'$ in the time $\Delta t$. From the fundamental principle of mechanics, the force required to produce the acceleration $\dfrac{w_2' - w_1'}{\Delta t}$ is

$$p = \Delta m \frac{w_2' - w_1'}{\Delta t}. \tag{1}$$
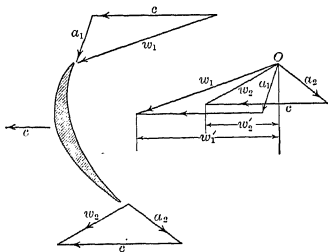
$\Delta m$; an equal and opposite force is, therefore, the impulse of $\Delta m$ on the vane.

If $M$ denotes the weight of steam flowing per second, then $\Delta m = \dfrac{M}{g}\Delta t$, and we have for the force exerted by the jet on the vane in the direction of the velocity $c$,

$$p = \frac{M}{g}(w_1' - w_2'). \tag{2}$$

Evidently this equation holds equally well when the weight $M$ flowing from the nozzle is divided among several moving vanes.

The product $pc$ of the peripheral force and peripheral velocity of vane gives the work per second; therefore,

$$\text{work per second} = \frac{Mc}{g}(w_1' - w_2'), \tag{3}$$

and

$$\text{work per pound of fluid} = \frac{c}{g}(w_1' - w_2'). \tag{4}$$

When, as is usually the case, the direction of $w_2'$ is opposite to that of $w_1'$, the sign of $w_2'$ must be considered negative and the algebraic difference $w_1' - w_2'$ in (2), (3), and (4) becomes the arithmetic sum $w_1' + w_2'$.

**179. Single-stage Velocity Turbine.** — In analyzing the action of the single-stage velocity turbine, it is convenient to start with an ideal frictionless turbine and then take up the case of the actual turbine.



Fig. 115.

Let the jet emerge from the nozzle with the velocity $w_1$, Fig. 115, at an angle $\alpha$ with the plane of the wheel. Combining $w_1$ with $c$, the peripheral velocity of the blade, the velocity $a_1$ of the jet relative to the blade is obtained. The angle $\beta$ between the direction of $a_1$ and the plane of the wheel determines the angle of the blade at entrance. If the blade is symmetrical, the exit relative velocity $a_2$ makes the same angle $\beta$ with the plane of the wheel, and since the frictionless case is assumed, $a_2 = a_1$. Combining $a_2$ and $c$, the result is the absolute exit velocity $w_2$.
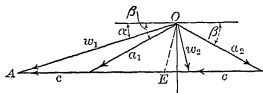
The energy of the jet with the velocity $w_1$ is $\dfrac{w_1{}^2}{2\,g}$ per pound of medium flowing; and the jet at exit has the energy $\dfrac{w_2{}^2}{2\,g}$.

The work absorbed by the wheel per unit weight of steam in this ideal frictionless case is, therefore,

$$W = \frac{w_1{}^2 - w_2{}^2}{2\,g}, \tag{1}$$

and the ideal efficiency is

$$\eta = \frac{w_1{}^2 - w_2{}^2}{w_1{}^2}. \tag{2}$$

From the triangle $OAE$, Fig. 115, we have

$$w_2{}^2 = w_1{}^2 + (2\,c)^2 - 2\,w_1(2\,c)\cos\alpha; \tag{3}$$

whence

$$w_1{}^2 - w_2{}^2 = 4(w_1\,c\cos\alpha - c^2). \tag{4}$$

Combining (2) and (4), we get,

$$\eta = 4\,\frac{c}{w_1}\Big(\cos\alpha - \frac{c}{w_1}\Big). \tag{5}$$

Equation (5) shows that the efficiency is greater the smaller the angle $\alpha$; and that with a given constant angle $\alpha$, the efficiency depends upon the ratio $\dfrac{c}{w_1}$. It is readily found that $\eta$ takes its maximum value $\eta_{\max} = \cos^2\alpha$ when the ratio $\dfrac{c}{w_1}$ takes the value $\frac{1}{2}\cos\alpha$.

As an example, let $\alpha = 20°$, whence $\cos\alpha = 0.9397$ and $\cos^2\alpha = 0.883$. If $w = 3600$ ft. per second, then to get the maximum efficiency 0.883, the ratio $\dfrac{c}{w_1}$ must be $\frac{1}{2}\cos\alpha = 0.47$, whence $c = 0.47 \times 3600 = 1692$ ft. per second, a value too high for safety. If $c$ be given the permissible value 1200 ft. per second, we have $\dfrac{c}{w_1} = \frac{1}{3}$, and $\eta = 4 \times \frac{1}{3}(0.9397 - 0.3333) = 0.809$.

In the actual turbine, friction in the nozzle and blades reduces the efficiency considerably below the value given by (5). The velocity diagram with friction is shown in Fig. 116. The ideal jet velocity $w$ is reduced by friction in the nozzle to $w_1$. This

actual jet velocity $w_1$ combined with velocity $c$ gives the relative velocity $a_1$, as before. The exit relative velocity $a_2$ is smaller than $a_1$ because of friction in the blades, and as a result the absolute exit velocity $w_2$ is smaller than in the ideal case.
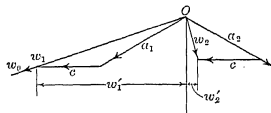


FIG. 116.

The work per pound of steam may be found from the velocity diagram either by calculation or by direct measurement. Having the components $w_1'$ and $w_2'$, the work per pound of steam is given by the expression

$$W = \frac{c}{g}(w_1' - w_2').$$ (6)

This work may be compared with the work obtained from the ideal frictionless turbine given by (1) or with the energy of the jet per pound of steam, namely, $\frac{w_0^2}{2\,g}$.

**180. Multiple-stage Velocity Turbine.** — In the Rateau turbine and in others of similar construction, the principle of pressure compounding is employed. The turbine consists essentially of several de Laval turbines in series, running in separate chambers. See Fig. 111. The action of this type of turbine is conveniently studied in connection with a Mollier diagram, Fig. 117.

Let the initial state of the steam entering the turbine at the pressure $p_1$ be that indicated by the point $A$. If $p_2$ is the pressure in the first chamber, a frictionless adiabatic expansion from $p_1$ to $p_2$ is represented by $AB$, and the decrease in the heat content $i_1 - i_2$ is represented by the length of the segment $AB$. Under ideal conditions, this drop in the heat content would all be transformed into kinetic energy of the jet of steam flowing into the chamber, and this in turn would be given up to the wheel. Actually, however, friction losses are encountered and the jet has an exit velocity $w_2$, thereby carrying away the kinetic energy $\frac{w_2^2}{2\,g}$. The velocity diagram for the single wheel under

consideration is similar to that shown in Fig. 116. The work lost in overcoming friction in the nozzles and blades and the exit energy $\frac{w_2^2}{2\,g}$ are transformed into heat, and this heat, except a small fraction that is radiated, is expended in further super-heating (or raising the quality of) the steam. Hence, instead of the final state $B$, we have a final state $C$ on the same con-stant-pressure curve. Referring to Fig. 117, $AC'$ represents
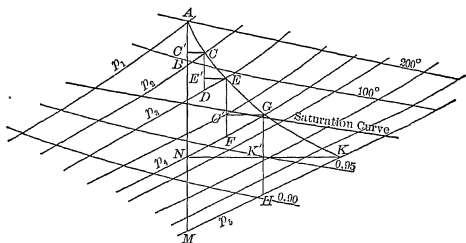


FIG. 117.

the part of the heat drop that is utilized by the wheel, while $C'B$ represents the part that is rendered unavailable by internal losses of various kinds.

The steam in the state $C$ flows into the second chamber where the pressure is $p_3$. Frictionless adiabatic expansion would give the second state $D$, but the actual state is represented by the point $E$. Again $CE'$ represents the effective drop of heat con-tent in this stage, while $E'D$ represents the part of the drop going back into the steam.

The same process is repeated in succeeding stages until finally the steam drops to condenser pressure in the last stage. The final state is represented by the point $K$, and the curve $AEK$ represents the change of state of the steam during its passage through the turbine. The final state under ideal fric-tionless conditions is represented by point $M$. The segment $AM$ represents the ideal heat drop, which, as has been shown, is equal to the available heat of the Rankine cycle. The segment

$AN$ represents the heat drop utilized. The ratio $\dfrac{AN}{AM}$ depends upon the magnitude of the internal losses, such as friction in nozzles and blades, leakage from stage to stage, windage, exit velocity, etc. Roughly, this ratio may lie between 0.50 and 0.80.

**181. Turbine with both Pressure and Velocity Stages.** — In certain turbines, notably the Curtis turbine, velocity compounding is employed. There are relatively few (three to seven) pressure stages, but in each chamber there are two or three rows of moving blades attached to the wheel rim and these are separated by alternate rows of guide blades, as shown in Fig. 112.
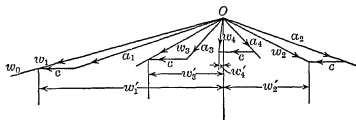


FIG. 118.

The velocity diagram for a single pressure stage with two velocity stages is shown in Fig. 118. The velocities in relation to the successive sets of blades are shown in Fig. 119. The jet emerges from the nozzle with an absolute velocity $w_1$, which is smaller than the ideal $w_0$ because of friction in the nozzle. Combining $w_1$ with the peripheral velocity $c$ of the first moving blade $m_1$, the result is the velocity $a_1$ of jet relative to blade $m_1$. The angle $\alpha$ between $a_1$ and the plane of rotation is the proper entrance angle of the blade $m_1$. The exit relative velocity $a_2$, which is smaller than $a_1$, due to friction in the blade, is combined with the velocity $c$, giving the absolute exit velocity $w_2$ which makes the angle $\beta$ with the plane of rotation. The jet enters the stationary guide blade $s$ with the velocity $w_2$ and emerges with a smaller
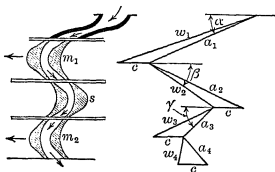


FIG. 119.

blade $m_2$. Combination of $w_3$ with $c$ gives the relative velocity $a_2$ and the entrance angle $\gamma$ for the blade $m_2$. The exit velocity $a_4$ is determined from $a_3$ and the friction in the blade, and by combining $a_4$ and $c$, the absolute exit velocity $w_4$ is obtained.

In the diagram, Fig. 119, the blades have been taken as symmetrical. Sometimes, however, the exit angles of the last sets of blades are made smaller than the entrance angles. The diagram can easily be modified to suit this condition.

The work per pound of steam for this wheel is readily determined from the velocity diagram. From the first set of blades $m_1$ the work $\frac{c}{g}(w_1' - w_2')$ and from the second set of blades $m_2$ the work $\frac{c}{g}(w_3' - w_4')$ is obtained. Hence the total work per pound of steam is

$$W = \frac{c}{g}(w_1' - w_2' + w_3' - w_4'). \qquad (1)$$

Care must be taken that $w_2'$ and $w_4'$ be given their proper algebraic signs.

The state of the fluid as it passes through the turbine may be shown by the Mollier diagram precisely similar to that shown in Fig. 117. Starting with an initial state indicated by point $A$, the available drop from the initial pressure $p_1$ to the pressure $p_2$ in the first chamber is represented by $AB$. The heat utilized in useful work $W$ as given by (1) is represented by $AC'$. Hence projecting $C'$ horizontally to $C$ on the line of constant pressure $p_2$, we get the state of the steam as it enters the second stage nozzles.

**182. Pressure Turbine.** — In the pressure type of turbine there is always a large number of stages, the guide blades and moving blades alternating in close succession. The fact that the pressure falls continuously, both through the guide blades and the moving blades, makes the velocity diagram essentially different from that of the velocity turbine. Referring to Fig. 120, let $w_1$ denote the absolute velocity of the steam entering the

stationary blade $s_1$, and $w_2$ the absolute exit velocity. If there were no change of pressure, $w_2$ would be smaller than $w_1$ because of friction; but the drop in pressure $\Delta p$ causes a decrease in heat content $\Delta i$, and as a result, there is an increase of velocity given by the relation

$$\frac{w_2^2 - w_1^2}{2\,g} = J(1-y)\Delta i$$

Thus the exit velocity $w_2$ is greater than the entrance velocity $w_1$. Combining $w_2$ with $c$, the velocity of the moving blade, we obtain $a_2$, the velocity of entrance relative to the moving blade. Now the pressure drops through the moving blades also; hence as a result the velocity of exit $a_2$ is greater than $a_1$, just as $w_2$, is greater than $w_1$. Combining $a_2$ with $c$, the result is $w_1$, the absolute velocity of entrance into the next row of fixed blades.

The work done in any single stage, consisting of one set of stationary blades and one set of moving blades, is obtained from the velocity diagram for that stage in the usual way. Thus, if we have the diagram shown in Fig. 120 for a particular stage, the work per pound of steam for that stage is given by the product

$$\frac{c}{g}\,(w'_2 - w'_1).$$

If the fixed and moving blades have the same entrance angles and exit angles, it may be assumed that the velocity diagram has the symmetrical form shown in Fig. 121; that is, $w_1 = a_1$ and $w_2 = a_2$. In this case, the work may be obtained by a simple graphical construction. Using point $B$ as a center and with a radius $BA$ let a circular arc $ADC$ be described and from $E$ let a perpendicular be dropped cutting this arc in $D$. Denoting the length $ED$ by $h$, we have
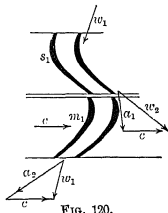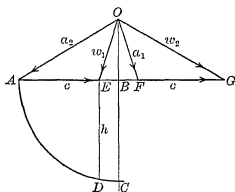
$$h^2 = A E \times E G = c \left( w_2' - w_1' \right).$$

It follows that the work per pound of steam is given by the expression $\dfrac{h^2}{g}$ provided $h$ is measured to the same scale as the velocity vectors $w_1$, $w_2$.

**183. Influence of High Vacuum.** — In Art. 172 it was pointed out that the reciprocating engine is unable to take advantage of a very low back pressure for the reason that the cylinder volume cannot be made sufficiently large to permit the expansion of the steam to the condenser pressure. No such restriction applies to the steam turbine. The blades in the final stages may be made long enough to pass the required volume of steam at the lowest pressures obtainable. The advantage of the turbine in this respect is shown graphically in Fig. 107. Since the cylinder volume of the reciprocating engine is limited to the volume indicated by the point $E$, the effect of lowering the back pressure from $p_2$ to $p_2'$ is the addition of the area $D'DFF'$ to the area of the original cycle. The turbine, however, can accomodate volumes indicated by points $C$ and $C''$; hence if the pressure is lowered from $p_2$ to $p_2'$, the area of the ideal cycle is increased by the area $D'DCC''$. It is evident, therefore, that high vacuum is much more effective in the case of the steam turbine than in the case of the reciprocating engine.

The superior efficiency of the steam turbine at low pressures and the ability of the turbine to make effective use of high vacuum has led to the introduction of the low-pressure turbine in combination with the reciprocating engine. The engine takes steam at boiler pressure and exhausts into the turbine at about atmospheric pressure. In general, the combination is more efficient than either the engine alone or the turbine alone using the entire range of pressure.

### EXERCISES

**1.** In a single-stage velocity turbine the jet emerges from the nozzle with a velocity of 3150 ft. per second and the direction of the jet makes an angle of 22½° with the plane of rotation. (a) Find the circumferential velocity

that will give maximum efficiency. (b) Find the efficiency if the circumferential velocity is 1100 ft. per second.

**2.** Find the work per pound of steam in case (b) of Ex. 1.

**3.** Using the data of Ex. 1 and 2 assume that the exit relative velocity is reduced 10 per cent by friction in the blades. Draw a velocity diagram and by measurement or calculation find the work done per pound of steam. Compare this result with that found for the ideal frictionless case.

**4.** A reciprocating engine receives steam at a pressure of 160 lb. per square inch, superheated 120°. The steam expands adiabatically to a pressure of 16 in. of mercury and is then discharged into a low pressure turbine where it expands adiabatically to a pressure of 2 in. of mercury. Find the percentage by which the efficiency is increased by the addition of the turbine. Assume ideal conditions.

**5.** A turbine of the Curtis type has three pressure stages. The initial pressure is 140 lb. with the steam superheated 120° F., and the condenser pressure is 3 in. of mercury. The loss of energy due to friction, etc., is 30 per cent of the total available energy. (a) Find the condition of the steam entering the condenser. (b) Find the consumption per h. p.-hour. (c) Determine the intermediate pressures in the cells on the assumption that the work developed in each stage shall be approximately the same.

## REFRIGERATION WITH VAPOR MEDIA

**184. Compression Refrigerating Machines.** — The essential organs of a compression machine using vapor as a medium are shown in Fig. 122. The action of the machine may be studied to advantage in connection with the $TS$-diagram, Fig. 123. The medium is drawn into the compressor cylinder through the suction pipe from the coils in the brine tank.
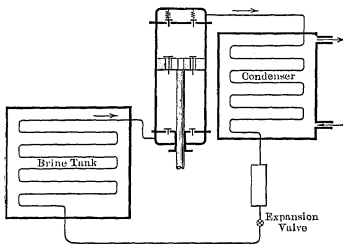


FIG. 122.

It may be assumed that the medium entering is in the saturated state at the temperature $T_1$, which may be taken equal to the temperature of the brine. This state is represented by point $B$.

Fig. 123. The vapor is compressed adiabatically to a final pressure $p_2$, which is determined by the upper temperature $T_2$ that may be obtained with the cooling water available. The adiabatic compression is represented by $BC$. The superheated vapor in the state $C$ is discharged into the coils of the cooler or condenser, where heat is abstracted from it. The coils are surrounded by cold water which flows continuously. First the gas is cooled to the state of saturation; this process is represented by the curve $CD$, and the heat abstracted by the area $C_1CDD_1$. Then heat is further removed at the constant temperature $T_2$ (and pressure $p_2$) and the vapor condenses. At the end of the process, the medium is liquid and its state is represented by the point $E$ on the liquid curve.
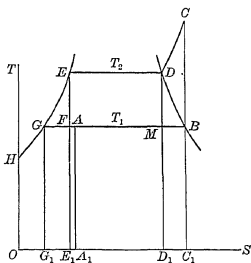


FIG. 123.

It should be noted that there are two parts of the fluid circuit: one including the discharge pipe and coils at the higher pressure $p_2$, and one including the brine coils and the suction pipe at the lower pressure $p_1$. These are separated by a valve called the **expansion valve**. The liquid in the state represented by point $E$ is allowed to trickle through the valve into the region of lower pressure. The result of this irreversible free expansion is to bring the medium to a new state represented by point $A$. In this state the medium, which is chiefly liquid with a small percentage of vapor, passes into the coils in the brine tank or in the room to be cooled. The temperature of the brine being higher than that of the medium, heat is absorbed by the medium, and the liquid vaporizes at constant pressure. This process is represented by the line $AB$ and the heat absorbed from the surrounding brine by the area $A_1ABC_1$.

The position of the point $A$ is determined as follows: The passage of the liquid through the expansion valve is a case of throttling or wiredrawing of the character discussed in Art. 162.

Hence, the heat content at $A$ must be equal to the heat content at $E$, that is,

$$q'_2 = q'_1 + x_a r_1$$

Graphically, the area $OHGAA_1$ is equal to the area $OHEE_1$; or taking away the common area $OHGFE_1$, the rectangle $E_1FAA_1$ is equal to the triangle $GEF$. (See Art. 162).

Since the throttling process represented by $EA$ is assumed to be adiabatic, the work that must be done on the medium is the difference between $Q_1$, the heat absorbed, and $Q_2$, the heat rejected to the condenser. We have then

$$Q_2 = \text{area } C_1CDEE_1,$$
$$Q_1 = \text{area } A_1ABC_1,$$
$$W = \text{area } C_1CDEE_1 - \text{area } A_1ABC_1$$
$$= \text{area } BCDEE_1A_1AB$$
$$= \text{area } BCDEGB.$$

If the expansion valve be replaced by an expansion cylinder, permitting a reversible adiabatic expansion from $p_2$ to $p_1$, as indicated by the line $EF$, we have

$$Q_2 = \text{area } C_1CDEE_1,$$
$$Q_1 = \text{area } E_1FBC_1,$$
$$W = \text{area } BCDEFB.$$

The effect of using the expansion valve rather than the expansion cylinder is thus to decrease the heat removed by the area $E_1FAA_1$ and to increase the work done by an equivalent amount.

**185. Vapors used in Refrigeration.** — The three vapors that are used to any extent as refrigerating media are ammonia, sulphur dioxide, and carbon dioxide. Of these, ammonia is used almost exclusively in America and largely in Europe. The other two are used to a small extent chiefly in Europe.

The choice of vapor to be used depends chiefly upon two things: (1) The suction and discharge pressures that must be employed to give proper lower and upper temperatures $T_1$ and $T_2$. The lower temperature must be such as to keep the proper temperature in the brine or the space to be kept cool, while the upper temperature is fixed by the temperature of the cooling water

ailable. (2) The volume of the medium required for a given
mount of refrigeration. This determines the bulk of the
achine.

If the upper temperature be taken as 68° F. ($T_2 = 528$) and
e lower temperature as 14° F., the pressures and the volume
tios for the three vapors mentioned are about as follows:

|  | NH$_3$ | SO$_2$ | CO$_2$ |
|---|---|---|---|
| ction pressure, lb. per sq. in. | 41.5 | 14.75 | 385 |
| scharge pressure, lb. per sq. in. | 124 | 47.61 | 826 |
| olume, taking that of CO$_2$ as 1 | 4.4 | 12 | 1 |

It appears that carbon dioxide requires for proper working
ry high pressures, so high, in fact, as to be practically prohib-
ve except in machines of small size. With sulphur dioxide
e pressures are low, but the necessary volume of medium is
gh, being nearly three times that required by ammonia and
velve times that required by carbon dioxide. With ammonia,
e pressures are reasonable and the volume of medium is not
:cessive; hence from these considerations, ammonia is seen to
e most advantageous.

From the point of view of economy, ammonia and sulphur
oxide are about equal. Carbon dioxide shows a somewhat
aller efficiency than the others under similar conditions be-
use, on account of the small latent heat of carbon dioxide, the
sses due to superheating and the passage through the expan-
on valve are a larger per cent of the total effect.

**186. Calculation of a Vapor Machine.**—The following analysis
pplies to the ideal cycle shown in Fig. 123. Denoting by $T_c$
e temperature at the end of compression indicated by the
int $C$, the heat that must be removed per minute from the
perheated vapor to bring it to the saturation state (the heat
presented by the area $C_1CDD_1$) is

$$Mc_p(T_c - T_2),$$

which $c_p$ denotes the specific heat of superheated vapor, and
$T$, the weight of the medium required per minute. The heat
jected by the vapor during condensation (area $D_1DEE_1$) is
$Ir_2$. Hence the heat rejected by the medium per minute is

$$ \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad (1) $$

Denoting by $x_1$ the quality of the mixture of liquid and vapor in the state represented by point $A$, we have for the heat absorbed by the medium from the brine or cold room (represented by the area $A_1ABC_1$)

$$Q_1 = Mr_1(1 - x_1). \qquad (2)$$

But area $OHGAA_1 =$ area $OHEE_1$, that is,

$$q_1' + r_1x_1 = q_2'; \qquad (3)$$

whence combining (3) and (2),

$$Q_1 = M(r_1 - q_2' + q_1') = M(q_1'' - q_2'). \qquad (4)$$

The work required per minute is, therefore,

$$W = J(Q_2 - Q_1) = JM[q_2'' - q_1'' + c_p(T_c - T_2)], \qquad (5)$$

and the net horsepower required to drive the machine is,

$$H = \frac{778\,M}{33000}[q_2'' - q_1'' + c_p(T_c - T_2)]. \qquad (6)$$

Combining (6) and (4), we have

$$H = \frac{778\,Q_1[q_2'' - q_1'' + c_p(T_c - T_2)]}{33000(q_1'' - q_2')}. \qquad (7)$$

To the horsepower thus calculated should be added perhaps 10 to 20 per cent to allow for imperfections of the cycle, and to the gross horsepower must be added 10 to 20 per cent to allow for the friction of the mechanism.

Assuming the vapor entering the compressor to be dry and saturated, as indicated by point $B$, Fig. 123, the volume of vapor entering the compressor per stroke is

$$V_c = \frac{Mv_1''}{N} \qquad (8)$$

where $v_1''$ is the specific volume of vapor at the pressure $p_1$ and $N$ the number of working strokes per minute. If the medium enters the compressor as a mixture of quality $x_m$ as indicated by point $M$, then approximately

$$V_c = \frac{Mx_mv_1''}{N}. \qquad (9)$$

The net cylinder volume as determined by (8) or (9) must

The weight of cooling water required per minute is readily found from (1) when the initial and final temperatures of the water are fixed. Denoting this weight by $G$ and the initial and final temperatures by $t''$ and $t'$, respectively, we have

$$G(t'' - t') = M[r_2 + c_p(T_c - T_2)]. \qquad (10)$$

To determine the value of $Q_2$ from (1) the temperature $T_c$ at the end of compression must be obtained. For adiabatic compression $T_c$ may be found by the following method. Referring to Fig. 123, the decrease of entropy in passing from $C$ to $D$ is the same as passing from $B$ to $D$. If $c_p$, the specific heat along curve $CD$, is assumed to be constant, we have

$$s_c - s_d = c_p \log_e \frac{T_c}{T_2}.$$

But

$$s_b - s_d = s_1' + \frac{r_1}{T_1} - \left(s_2' + \frac{r_2}{T_2}\right),$$

hence

$$c_p \log_e \frac{T_c}{T_2} = s_1' + \frac{r_1}{T_1} - \left(s'_2 + \frac{r_2}{T_2}\right). \qquad (11)$$

Since $c_p$, $T_1$, $T_2$, $s_1'$, $s_2$, $r_1$, and $r_2$ are known quantities, $T_c$ is easily calculated.

EXAMPLE. Required the dimensions and the horsepower of an ammonia refrigerating machine that is to abstract 15,000 B. t. u. per minute from a cold chamber which is to be kept at a temperature of 30° F. The temperature of the ammonia in the condenser may be taken as 85° F. and that of the ammonia in the brine coils 20° F. Assume one double-acting compressor making 75 r. p. m.

From the table of the properties of saturated ammonia, we have the following values corresponding to $t_1 = 20°$ and $t_2 = 85°$:

$p_1 = 47.46$ lb. per square inch, $r_1 = 560$ B. t. u., $q_1' = -13$ B. t. u.,

$q_1'' = 547$ B. t. u., $s_1' = -0.027$, $\frac{r_1}{T_1} = 1.168$, $v_1'' = 6.01$ cu. ft.,

$p_2 = 166.8$ lb. per square inch, $r_2 = 496$ B. t. u., $q_2' = 61$ B. t. u.,

$q_2'' = 557$ B.t.u., $s_2' = 0.118$, $\frac{r_2}{T_2} = 0.910$, $v_2'' = 1.78$.

end of compression, we have, from (11),

$$0.51 \log_e \frac{T_c}{544.6} = -0.027 + 1.168 - (0.118 + 0.910) = 0.113,$$

whence

$$\log T_c = \log 544.6 + 0.4343 \times \frac{0.113}{0.51} = 2.83231,$$

$$T_c = 679.7,$$

and

$$t_c = 679.7 - 459.6 = 220.1° \text{ F.}$$

The weight of ammonia that must be circulated per minute is, from (4),

$$M = \frac{Q_1}{\eta_1'' - \eta_2'} = \frac{15000}{547 - 61} = 30.86 \text{ lb.}$$

The net horsepower is, from (6),

$$\frac{778 \times 30.86}{33000} [557 - 547 + 0.51(220.1 - 85)] = 57.4.$$

Adding 15 per cent for cycle imperfections, the compressor will require about 66 horsepower. The steam engine required to drive the compressor should develop, say, 80 horsepower.

The volume of the compressor cylinder is, from (8),

$$V_c = \frac{30.86 \times 6.01}{2 \times 75} = 1.24 \text{ cu. ft.}$$

Adding 15 per cent for clearance, etc., the required volume is 1.43 cu. ft. This is given by a stroke of 20 in. and a cylinder diameter of $12\frac{1}{2}$ in.

# TABLE I

## Properties of Saturated Steam

| Pressure Inches of Hg. | Temp. Fahr. | Heat Content | | Latent Heat | | Entropy | | | Volume of One Pound |
|---|---|---|---|---|---|---|---|---|---|
| | | of Liquid | of Vapor | Total | Internal | of Liquid | of Vaporization | of Vapor | |
| $p$ | $t$ | $i'$ | $i''$ | $r$ | $\rho$ | $s'$ | $\dfrac{r}{T}$ | $s''$ | $v$ |
| 0.5 | 58.81 | 26.9 | 1087.1 | 1060.2 | 1002.9 | .0532 | 2.0431 | 2.0963 | 1259.3 |
| 1.0 | 79.12 | 47.2 | 1096.7 | 1049.5 | 989.8 | .0916 | 1.9482 | 2.0398 | 656.7 |
| 1.5 | 91.90 | 59.9 | 1102.5 | 1042.6 | 982.2 | .1150 | 1.8905 | 2.0055 | 443.0 |
| 2.0 | 101.27 | 69.2 | 1106.6 | 1037.4 | 975.9 | .1317 | 1.8497 | 1.9814 | 338.3 |
| 2.5 | 108.81 | 76.7 | 1109.9 | 1033.2 | 970.8 | .1451 | 1.8178 | 1.9629 | 274.3 |
| 3.0 | 115.15 | 83.1 | 1112.7 | 1029.6 | 966.5 | .1561 | 1.7915 | 1.9476 | 231.2 |
| 3.5 | 120.63 | 88.5 | 1115.0 | 1026.5 | 962.8 | .1656 | 1.7692 | 1.9348 | 200.1 |
| 4.0 | 125.48 | 93.4 | 1117.1 | 1023.7 | 959.5 | .1739 | 1.7497 | 1.9236 | 176.6 |
| 4.5 | 129.85 | 97.7 | 1118.9 | 1021.2 | 956.5 | .1813 | 1.7325 | 1.9138 | 158.1 |
| 5.0 | 133.81 | 101.7 | 1120.6 | 1018.9 | 953.7 | .1880 | 1.7170 | 1.9050 | 143.2 |
| 6 | 140.83 | 108.7 | 1123.4 | 1014.7 | 948.8 | .1997 | 1.6901 | 1.8898 | 120.7 |
| 7 | 146.90 | 114.8 | 1125.9 | 1011.1 | 944.7 | .2097 | 1.6672 | 1.8769 | 104.4 |
| 8 | 152.28 | 120.2 | 1128.0 | 1007.9 | 940.9 | .2186 | 1.6473 | 1.8659 | 92.2 |
| 9 | 157.12 | 125.0 | 1130.0 | 1005.0 | 937.5 | .2265 | 1.6296 | 1.8561 | 82.6 |
| 10 | 161.52 | 129.4 | 1131.7 | 1002.3 | 934.3 | .2336 | 1.6138 | 1.8474 | 74.8 |
| 11 | 165.57 | 133.4 | 1133.3 | 999.9 | 931.5 | .2401 | 1.5994 | 1.8395 | 68.38 |
| 12 | 169.31 | 137.2 | 1134.7 | 997.6 | 928.8 | .2460 | 1.5862 | 1.8322 | 63.03 |
| 13 | 172.80 | 140.6 | 1136.0 | 995.4 | 926.3 | .2516 | 1.5739 | 1.8254 | 58.48 |
| 14 | 176.07 | 143.9 | 1137.3 | 993.4 | 924.0 | .2568 | 1.5627 | 1.8195 | 54.55 |
| 15 | 179.16 | 147.0 | 1138.5 | 991.5 | 921.8 | .2616 | 1.5522 | 1.8138 | 51.13 |
| 16 | 182.08 | 150.0 | 1139.6 | 989.6 | 919.6 | .2662 | 1.5423 | 1.8085 | 48.11 |
| 17 | 184.84 | 152.7 | 1140.6 | 987.9 | 917.6 | .2705 | 1.5330 | 1.8035 | 45.46 |
| 18 | 187.47 | 155.4 | 1141.6 | 986.2 | 915.7 | .2746 | 1.5242 | 1.7988 | 43.09 |
| 19 | 189.99 | 157.9 | 1142.5 | 984.6 | 913.8 | .2785 | 1.5158 | 1.7943 | 40.96 |
| 20 | 192.38 | 160.3 | 1143.4 | 983.1 | 912.1 | .2822 | 1.5079 | 1.7901 | 39.04 |
| 21 | 194.69 | 162.6 | 1144.2 | 981.6 | 910.4 | .2857 | 1.5003 | 1.7860 | 37.29 |
| 22 | 196.91 | 164.8 | 1145.0 | 980.2 | 908.8 | .2891 | 1.4931 | 1.7822 | 35.68 |
| 23 | 199.04 | 167.0 | 1145.8 | 978.8 | 907.2 | .2923 | 1.4862 | 1.7785 | 34.22 |
| 24 | 201.10 | 169.0 | 1146.5 | 977.5 | 905.7 | .2955 | 1.4796 | 1.7751 | 32.88 |
| 25 | 203.09 | 171.0 | 1147.2 | 976.2 | 904.2 | .2985 | 1.4732 | 1.7717 | 31.65 |
| 26 | 205.01 | 173.0 | 1147.9 | 974.9 | 902.7 | .3014 | 1.4670 | 1.7674 | 30.52 |
| 27 | 206.87 | 174.9 | 1148.6 | 973.7 | 901.4 | .3042 | 1.4611 | 1.7653 | 29.46 |
| 28 | 208.68 | 176.7 | 1149.2 | 972.5 | 900.0 | .3069 | 1.4554 | 1.7623 | 28.47 |
| 29 | 210.43 | 178.4 | 1149.8 | 971.4 | 898.8 | .3095 | 1.4499 | 1.7594 | 27.55 |

| PRESSURE LB. PER SQ. IN. | TEMP. FAHR. | HEAT CONTENT | | LATENT HEAT | | | | | VOLUME OF ONE POUND |
|---|---|---|---|---|---|---|---|---|---|
| | | of Liquid | of Vapor | Total | Internal | ol Liquid | Vaporization | ol Vapor | |
| $p$ | $t$ | $i'$ | $i''$ | $r$ | $\rho$ | $s'$ | $\dfrac{r}{T}$ | $s''$ | $v''$ |
| 14.7 | 212.0 | 180.0 | 1150.4 | 970.4 | 897.7 | .3121 | 1.4449 | 1.7570 | 26.73 |
| 15 | 213.0 | 181.1 | 1150.8 | 969.7 | 896.8 | .3137 | 1.4417 | 1.7554 | 26.23 |
| 16 | 216.3 | 184.4 | 1152.0 | 967.6 | 894.5 | .3186 | 1.4315 | 1.7501 | 24.08 |
| 17 | 219.4 | 187.5 | 1153.0 | 965.5 | 892.1 | .3234 | 1.4220 | 1.7451 | 23.20 |
| 18 | 222.4 | 190.5 | 1154.1 | 963.6 | 889.9 | .3275 | 1.4129 | 1.7404 | 22.10 |
| 19 | 225.2 | 193.4 | 1155.0 | 961.6 | 887.7 | .3317 | 1.4043 | 1.7360 | 21.00 |
| 20 | 227.9 | 196.1 | 1155.9 | 959.8 | 885.7 | .3357 | 1.3961 | 1.7318 | 20.01 |
| 21 | 230.5 | 198.7 | 1156.8 | 958.1 | 883.8 | .3395 | 1.3883 | 1.7278 | 19.12 |
| 22 | 233.0 | 201.2 | 1157.7 | 956.5 | 882.0 | .3431 | 1.3809 | 1.7240 | 18.31 |
| 23 | 235.4 | 203.6 | 1158.5 | 954.8 | 880.0 | .3467 | 1.3738 | 1.7205 | 17.57 |
| 24 | 237.8 | 206.0 | 1159.2 | 953.2 | 878.0 | .3501 | 1.3669 | 1.7170 | 16.89 |
| 25 | 240.0 | 208.3 | 1160.0 | 951.7 | 876.2 | .3533 | 1.3604 | 1.7137 | 16.27 |
| 26 | 242.2 | 210.5 | 1160.7 | 950.2 | 874.5 | .3565 | 1.3540 | 1.7105 | 15.70 |
| 27 | 244.3 | 212.7 | 1161.5 | 948.8 | 872.9 | .3595 | 1.3479 | 1.7074 | 15.17 |
| 28 | 246.4 | 214.8 | 1162.1 | 947.3 | 871.2 | .3625 | 1.3419 | 1.7044 | 14.70 |
| 29 | 248.4 | 216.8 | 1162.8 | 946.0 | 869.8 | .3653 | 1.3362 | 1.7015 | 14.21 |
| 30 | 250.3 | 218.8 | 1163.4 | 944.6 | 868.2 | .3681 | 1.3307 | 1.6988 | 13.76 |
| 31 | 252.2 | 220.7 | 1164.0 | 943.3 | 866.8 | .3708 | 1.3253 | 1.6961 | 13.34 |
| 32 | 254.0 | 222.5 | 1164.6 | 942.1 | 865.4 | .3734 | 1.3201 | 1.6935 | 12.94 |
| 33 | 255.8 | 224.3 | 1165.1 | 940.8 | 864.0 | .3760 | 1.3151 | 1.6911 | 12.57 |
| 34 | 257.6 | 226.1 | 1165.7 | 939.6 | 862.7 | .3784 | 1.3102 | 1.6886 | 12.22 |
| 35 | 259.3 | 227.8 | 1166.2 | 938.4 | 861.3 | .3808 | 1.3054 | 1.6863 | 11.89 |
| 36 | 261.0 | 229.5 | 1166.8 | 937.3 | 860.1 | .3832 | 1.3008 | 1.6840 | 11.58 |
| 37 | 262.6 | 231.2 | 1167.3 | 936.1 | 858.8 | .3855 | 1.2963 | 1.6818 | 11.29 |
| 38 | 264.2 | 232.8 | 1167.8 | 935.0 | 857.6 | .3878 | 1.2918 | 1.6796 | 11.02 |
| 39 | 265.7 | 234.4 | 1168.3 | 933.9 | 856.4 | .3900 | 1.2876 | 1.6776 | 10.76 |
| 40 | 267.3 | 236.0 | 1168.8 | 932.8 | 855.1 | .3921 | 1.2834 | 1.6755 | 10.50 |
| 41 | 268.8 | 237.5 | 1169.3 | 931.8 | 854.0 | .3942 | 1.2793 | 1.6735 | 10.26 |
| 42 | 270.2 | 239.0 | 1169.7 | 930.7 | 852.8 | .3962 | 1.2753 | 1.6715 | 10.03 |
| 43 | 271.7 | 240.5 | 1170.1 | 929.7 | 851.7 | .3982 | 1.2714 | 1.6696 | 9.81 |
| 44 | 273.1 | 241.9 | 1170.6 | 928.7 | 850.6 | .4002 | 1.2676 | 1.6678 | 9.60 |
| 45 | 274.5 | 243.3 | 1171.0 | 927.7 | 849.5 | .4021 | 1.2638 | 1.6659 | 9.40 |
| 46 | 275.8 | 244.6 | 1171.4 | 926.8 | 848.5 | .4040 | 1.2602 | 1.6642 | 9.21 |
| 47 | 277.2 | 246.0 | 1171.8 | 925.8 | 847.4 | .4059 | 1.2566 | 1.6625 | 9.02 |
| 48 | 278.5 | 247.3 | 1172.2 | 924.9 | 846.4 | .4077 | 1.2531 | 1.6608 | 8.85 |
| 49 | 279.8 | 248.7 | 1172.6 | 923.9 | 845.3 | .4095 | 1.2496 | 1.6591 | 8.68 |
| 50 | 281.1 | 250.0 | 1173.0 | 923.0 | 844.4 | .4112 | 1.2463 | 1.6575 | 8.51 |
| 51 | 282.3 | 251.3 | 1173.4 | 922.1 | 843.4 | .4130 | 1.2429 | 1.6559 | 8.36 |
| 52 | 283.5 | 252.6 | 1173.8 | 921.2 | 842.4 | .4147 | 1.2397 | 1.6544 | 8.20 |
| 53 | 284.8 | 253.8 | 1174.2 | 920.4 | 841.5 | .4164 | 1.2365 | 1.6529 | 8.06 |
| 54 | 286.0 | 255.0 | 1174.5 | 919.5 | 840.5 | .4180 | 1.2333 | 1.6513 | 7.92 |
| 55 | 287.1 | 256.2 | 1174.9 | 918.7 | 839.6 | .4196 | 1.2303 | 1.6499 | 7.78 |
| 56 | 288.3 | 257.4 | 1175.2 | 917.8 | 838.7 | .4212 | 1.2272 | 1.6484 | 7.65 |
| 57 | 289.4 | 258.6 | 1175.6 | 917.0 | 837.8 | .4228 | 1.2243 | 1.6471 | 7.52 |
| 58 | 290.6 | 259.7 | 1175.9 | 916.2 | 836.9 | .4243 | 1.2213 | 1.6456 | 7.40 |
| 59 | 291.7 | 260.8 | 1176.2 | 915.4 | 836.0 | .4258 | 1.2184 | 1.6442 | 7.28 |

| | TEMP. FAHR. | HEAT CONTENT | | LATENT HEAT | | ENTROPY | | | VOLUME OF ONE POUND |
|---|---|---|---|---|---|---|---|---|---|
| | | of Liquid | of Vapor | Total | Internal | of Liquid | Vaporization | of Vapor | |
| $t$ | $t'$ | $i'$ | $i''$ | $r$ | $\rho$ | $s'$ | $\dfrac{r}{T}$ | $s''$ | $v''$ |
| | 292.8 | 262.0 | 1176.6 | 914.6 | 835.2 | .4273 | 1.2156 | 1.6429 | 7.168 |
| | 293.9 | 263.1 | 1176.9 | 913.8 | 834.3 | .4288 | 1.2128 | 1.6416 | 7.057 |
| | 294.9 | 264.2 | 1177.2 | 913.0 | 833.4 | .4302 | 1.2101 | 1.6403 | 6.949 |
| | 296.0 | 265.3 | 1177.5 | 912.2 | 832.5 | .4316 | 1.2074 | 1.6390 | 6.845 |
| | 297.0 | 266.3 | 1177.8 | 911.5 | 831.8 | .4330 | 1.2047 | 1.6378 | 6.744 |
| | 298.0 | 267.4 | 1178.1 | 910.7 | 830.9 | .4344 | 1.2021 | 1.6365 | 6.646 |
| | 299.1 | 268.4 | 1178.4 | 910.0 | 830.2 | .4358 | 1.1995 | 1.6353 | 6.551 |
| | 300.1 | 269.5 | 1178.7 | 909.2 | 829.3 | .4372 | 1.1969 | 1.6341 | 6.459 |
| | 301.1 | 270.5 | 1179.0 | 908.5 | 828.5 | .4385 | 1.1944 | 1.6329 | 6.370 |
| | 302.0 | 271.5 | 1179.3 | 907.8 | 827.7 | .4398 | 1.1920 | 1.6318 | 6.283 |
| | 303.0 | 272.5 | 1179.5 | 907.1 | 827.0 | .4411 | 1.1895 | 1.6306 | 6.198 |
| | 303.9 | 273.4 | 1179.8 | 906.4 | 826.2 | .4424 | 1.1871 | 1.6295 | 6.115 |
| | 304.9 | 274.4 | 1180.1 | 905.7 | 825.5 | .4437 | 1.1847 | 1.6284 | 6.035 |
| | 305.8 | 275.4 | 1180.4 | 905.0 | 824.7 | .4450 | 1.1823 | 1.6273 | 5.957 |
| | 306.8 | 276.3 | 1180.6 | 904.3 | 823.9 | .4462 | 1.1800 | 1.6262 | 5.882 |
| | 307.7 | 277.3 | 1180.9 | 903.6 | 823.2 | .4474 | 1.1777 | 1.6251 | 5.809 |
| | 308.6 | 278.2 | 1181.1 | 902.9 | 822.4 | .4486 | 1.1755 | 1.6241 | 5.737 |
| | 309.5 | 279.1 | 1181.4 | 902.3 | 821.8 | .4498 | 1.1732 | 1.6230 | 5.666 |
| | 310.4 | 280.0 | 1181.6 | 901.6 | 821.0 | .4510 | 1.1710 | 1.6220 | 5.597 |
| | 311.2 | 280.9 | 1181.9 | 901.0 | 820.4 | .4522 | 1.1688 | 1.6210 | 5.530 |
| | 312.1 | 281.8 | 1182.1 | 900.3 | 819.6 | .4533 | 1.1667 | 1.6200 | 5.464 |
| | 313.8 | 283.6 | 1182.7 | 899.0 | 818.2 | .4556 | 1.1625 | 1.6181 | 5.338 |
| | 315.5 | 285.3 | 1183.1 | 897.8 | 816.9 | .4578 | 1.1584 | 1.6162 | 5.219 |
| | 317.2 | 287.0 | 1183.6 | 896.6 | 815.6 | .4600 | 1.1543 | 1.6143 | 5.104 |
| | 318.8 | 288.7 | 1184.0 | 895.4 | 814.3 | .4622 | 1.1503 | 1.6125 | 4.995 |
| | 320.4 | 290.3 | 1184.5 | 894.2 | 813.0 | .4642 | 1.1465 | 1.6107 | 4.890 |
| | 321.9 | 291.9 | 1184.9 | 893.0 | 811.7 | .4663 | 1.1427 | 1.6090 | 4.789 |
| | 323.4 | 293.5 | 1185.3 | 891.8 | 810.4 | .4683 | 1.1390 | 1.6073 | 4.692 |
| | 324.9 | 295.0 | 1185.7 | 890.7 | 809.3 | .4703 | 1.1353 | 1.6056 | 4.599 |
| | 326.5 | 296.6 | 1186.1 | 889.5 | 808.0 | .4723 | 1.1317 | 1.6040 | 4.511 |
| | 327.9 | 298.1 | 1186.5 | 888.4 | 806.8 | .4742 | 1.1282 | 1.6024 | 4.425 |
| | 329.3 | 299.6 | 1186.9 | 887.3 | 805.6 | .4761 | 1.1248 | 1.6009 | 4.343 |
| | 330.7 | 301.0 | 1187.3 | 886.3 | 804.6 | .4779 | 1.1214 | 1.5993 | 4.264 |
| | 332.1 | 302.5 | 1187.7 | 885.2 | 803.4 | .4797 | 1.1181 | 1.5978 | 4.188 |
| | 333.5 | 303.9 | 1188.1 | 884.2 | 802.3 | .4815 | 1.1149 | 1.5964 | 4.114 |
| | 334.8 | 305.3 | 1188.4 | 883.1 | 801.1 | .4833 | 1.1117 | 1.5950 | 4.043 |
| | 336.2 | 306.7 | 1188.8 | 882.1 | 800.0 | .4850 | 1.1085 | 1.5935 | 3.975 |
| | 337.5 | 308.0 | 1189.1 | 881.1 | 799.0 | .4867 | 1.1054 | 1.5921 | 3.909 |
| | 338.8 | 309.4 | 1189.5 | 880.1 | 797.9 | .4884 | 1.1024 | 1.5908 | 3.845 |
| | 340.1 | 310.7 | 1189.8 | 879.1 | 796.8 | .4901 | 1.0994 | 1.5895 | 3.784 |
| | 341.3 | 312.0 | 1190.1 | 878.2 | 795.8 | .4917 | 1.0965 | 1.5882 | 3.724 |
| | 342.6 | 313.3 | 1190.5 | 877.2 | 794.8 | .4933 | 1.0936 | 1.5869 | 3.666 |
| | 343.8 | 314.5 | 1190.8 | 876.3 | 793.8 | .4949 | 1.0907 | 1.5856 | 3.610 |
| | 345.0 | 315.8 | 1191.1 | 875.3 | 792.7 | .4965 | 1.0879 | 1.5844 | 3.555 |
| | 346.2 | 317.0 | 1191.4 | 874.4 | 791.8 | .4980 | 1.0851 | 1.5831 | 3.502 |

| PRESSURE LB. PER SQ. IN. | TEMP. FAHR. | HEAT CONTENT | | LATENT HEAT | | ENTROPY | | | VOLUME OF ONE POUND |
|---|---|---|---|---|---|---|---|---|---|
| | | of Liquid | of Vapor | Total | Internal | of Liquid | Vaporization | of Vapor | |
| $p$ | $t$ | $i'$ | $i''$ | $r$ | $\rho$ | $s'$ | $\dfrac{r}{T}$ | $s''$ | $v''$ |
| 130 | 347.4 | 318.2 | 1191.7 | 873.5 | 790.8 | .4995 | 1.0824 | 1.5819 | 3.452 |
| 132 | 348.6 | 319.4 | 1192.0 | 872.6 | 789.9 | .5010 | 1.0797 | 1.5807 | 3.402 |
| 134 | 349.7 | 320.6 | 1192.3 | 871.7 | 788.9 | .5025 | 1.0770 | 1.5795 | 3.354 |
| 136 | 350.8 | 321.8 | 1192.6 | 870.8 | 788.0 | .5039 | 1.0744 | 1.5783 | 3.307 |
| 138 | 352.0 | 323.0 | 1192.9 | 869.9 | 787.0 | .5054 | 1.0719 | 1.5773 | 3.262 |
| 140 | 353.1 | 324.2 | 1193.2 | 869.0 | 786.1 | .5068 | 1.0693 | 1.5761 | 3.218 |
| 142 | 354.2 | 325.3 | 1193.5 | 868.2 | 785.2 | .5082 | 1.0668 | 1.5750 | 3.175 |
| 144 | 355.3 | 326.5 | 1193.8 | 867.3 | 784.3 | .5096 | 1.0644 | 1.5740 | 3.133 |
| 146 | 356.4 | 327.6 | 1194.0 | 866.5 | 783.4 | .5110 | 1.0619 | 1.5729 | 3.092 |
| 148 | 357.4 | 328.7 | 1194.3 | 865.6 | 782.4 | .5123 | 1.0595 | 1.5718 | 3.052 |
| 150 | 358.5 | 329.8 | 1194.6 | 864.8 | 781.6 | .5137 | 1.0571 | 1.5708 | 3.014 |
| 160 | 363.6 | 335.0 | 1195.8 | 860.8 | 777.4 | .5202 | 1.0456 | 1.5658 | 2.834 |
| 170 | 368.5 | 340.2 | 1197.1 | 856.9 | 773.2 | .5263 | 1.0349 | 1.5612 | 2.676 |
| 180 | 373.1 | 345.0 | 1198.2 | 853.2 | 769.3 | .5321 | 1.0246 | 1.5567 | 2.534 |
| 190 | 377.6 | 349.6 | 1199.3 | 849.6 | 765.5 | .5377 | 1.0149 | 1.5526 | 2.407 |
| 200 | 381.8 | 354.1 | 1200.3 | 846.2 | 762.0 | .5430 | 1.0057 | 1.5487 | 2.292 |
| 210 | 385.9 | 358.4 | 1201.3 | 842.9 | 758.5 | .5481 | .9968 | 1.5449 | 2.188 |
| 220 | 389.9 | 362.5 | 1202.2 | 839.6 | 755.1 | .5530 | .9884 | 1.5414 | 2.093 |
| 230 | 393.7 | 366.5 | 1203.0 | 836.5 | 751.8 | .5577 | .9803 | 1.5380 | 2.006 |
| 240 | 397.4 | 370.4 | 1203.9 | 833.5 | 748.7 | .5622 | .9726 | 1.5348 | 1.926 |
| 250 | 401.0 | 374.1 | 1204.7 | 830.6 | 745.7 | .5666 | .9651 | 1.5317 | 1.852 |
| 260 | 404.5 | 377.8 | 1205.5 | 827.7 | 742.7 | .5708 | .9579 | 1.5287 | 1.784 |
| 270 | 407.8 | 381.3 | 1206.2 | 824.9 | 739.8 | .5749 | .9510 | 1.5259 | 1.722 |
| 280 | 411.1 | 384.7 | 1206.9 | 822.2 | 737.0 | .5788 | .9443 | 1.5231 | 1.663 |
| 290 | 414.3 | 388.1 | 1207.6 | 819.5 | 734.2 | .5826 | .9378 | 1.5204 | 1.608 |
| 300 | 417.4 | 391.3 | 1208.3 | 817.0 | 731.5 | .5863 | .9315 | 1.5178 | 1.558 |

# TABLE II

## Properties of Saturated Steam below 212° F.

| Pressure | | Volume of One Pound (Cu. Ft.) | Weight of One Cubic Foot | | Total Heat | Latent Heat | Temp. Fahr. |
|---|---|---|---|---|---|---|---|
| Lb. per Sq. In. | Inches of Hg. | | Pounds | Grains | | | |
| $p$ | — | $v''$ | $\gamma$ | — | $q''$ | $r$ | $t$ |
| 0.0885 | 0.1802 | 3288 | 0.000304 | 2.129 | 1073.7 | 1073.7 | 32 |
| 0.0960 | 0.1955 | 3047 | 0.000328 | 2.297 | 1074.7 | 1072.7 | 34 |
| 0.1039 | 0.2116 | 2826 | 0.000354 | 2.477 | 1075.8 | 1071.7 | 36 |
| 0.1125 | 0.2291 | 2623 | 0.000381 | 2.669 | 1076.8 | 1070.8 | 38 |
| 0.1217 | 0.2478 | 2437 | 0.000410 | 2.872 | 1077.8 | 1069.8 | 40 |
| 0.1315 | 0.2677 | 2265 | 0.000442 | 3.091 | 1078.8 | 1068.8 | 42 |
| 0.1420 | 0.2891 | 2107 | 0.000475 | 3.322 | 1079.8 | 1067.7 | 44 |
| 0.1532 | 0.3119 | 1961 | 0.000510 | 3.570 | 1080.8 | 1066.7 | 46 |
| 0.1653 | 0.3366 | 1827 | 0.000547 | 3.831 | 1081.8 | 1065.7 | 48 |
| 0.1781 | 0.3627 | 1703 | 0.000587 | 4.110 | 1082.8 | 1064.7 | 50 |
| 0.1918 | 0.3905 | 1587 | 0.000630 | 4.411 | 1083.8 | 1063.7 | 52 |
| 0.2064 | 0.4202 | 1483 | 0.000674 | 4.720 | 1084.7 | 1062.7 | 54 |
| 0.2219 | 0.4518 | 1385 | 0.000722 | 5.054 | 1085.7 | 1061.6 | 56 |
| 0.2385 | 0.4856 | 1294 | 0.000773 | 5.410 | 1086.7 | 1060.6 | 58 |
| 0.2562 | 0.5217 | 1210 | 0.000827 | 5.785 | 1087.6 | 1059.6 | 60 |
| 0.2749 | 0.5598 | 1132 | 0.000883 | 6.043 | 1088.6 | 1058.5 | 62 |
| 0.2949 | 0.6005 | 1060 | 0.000943 | 6.604 | 1089.6 | 1057.5 | 64 |
| 0.3161 | 0.644 | 993 | 0.001007 | 7.048 | 1090.5 | 1056.4 | 66 |
| 0.3386 | 0.689 | 931 | 0.001074 | 7.52 | 1091.5 | 1055.4 | 68 |
| 0.3625 | 0.738 | 873 | 0.001145 | 8.02 | 1092.4 | 1054.3 | 70 |
| 0.3879 | 0.789 | 820 | 0.001220 | 8.54 | 1093.3 | 1053.3 | 72 |
| 0.4148 | 0.844 | 770 | 0.001300 | 9.10 | 1094.3 | 1052.2 | 74 |
| 0.4433 | 0.903 | 723 | 0.001383 | 9.68 | 1095.2 | 1051.2 | 76 |
| 0.4735 | 0.964 | 680 | 0.001471 | 10.30 | 1096.1 | 1050.1 | 78 |
| 0.5054 | 1.029 | 639 | 0.001564 | 10.95 | 1097.1 | 1049.0 | 80 |
| 0.539 | 1.098 | 601.4 | 0.001663 | 11.64 | 1098.0 | 1048.0 | 82 |
| 0.575 | 1.171 | 565.7 | 0.001768 | 12.37 | 1098.9 | 1046.9 | 84 |
| 0.613 | 1.248 | 532.2 | 0.001879 | 13.15 | 1099.8 | 1045.8 | 86 |
| 0.653 | 1.329 | 500.8 | 0.001997 | 13.98 | 1100.7 | 1044.7 | 88 |
| 0.695 | 1.415 | 471.4 | 0.002121 | 14.85 | 1101.6 | 1043.6 | 90 |
| 0.739 | 1.506 | 443.9 | 0.002253 | 15.77 | 1102.5 | 1042.5 | 92 |
| 0.787 | 1.602 | 418.2 | 0.002391 | 16.74 | 1103.4 | 1041.4 | 94 |
| 0.837 | 1.704 | 394.2 | 0.002537 | 17.76 | 1104.3 | 1040.3 | 96 |
| 0.890 | 1.812 | 371.8 | 0.002690 | 18.79 | 1105.2 | 1039.2 | 98 |
| 0.946 | 1.925 | 350.9 | 0.002850 | 19.95 | 1106.1 | 1038.1 | 100 |

| TEMP. FAHR. | PRESSURE | | VOLUME OF ONE POUND (CU. FT.) | WEIGHT OF ONE CUBIC FOOT | | TOTAL HEAT | LATENT HEAT |
| | Lb. per Sq. In. | Inches of Hg. | | Pounds | Grains | | |
| $t$ | $p$ | — | $v''$ | $\gamma$ | — | $q''$ | $r$ |
| 102 | 1.004 | 2.044 | 331.4 | 0.003017 | 21.12 | 1107.0 | 1037.0 |
| 104 | 1.066 | 2.171 | 313.2 | 0.003193 | 22.35 | 1107.9 | 1035.9 |
| 106 | 1.131 | 2.303 | 296.2 | 0.003376 | 23.63 | 1108.7 | 1034.8 |
| 108 | 1.199 | 2.441 | 280.4 | 0.003566 | 24.96 | 1109.6 | 1033.7 |
| 110 | 1.271 | 2.588 | 265.6 | 0.003765 | 26.36 | 1110.5 | 1032.5 |
| 120 | 1.689 | 3.439 | 203.4 | 0.004916 | 34.42 | 1114.8 | 1026.9 |
| 130 | 2.219 | 4.518 | 157.5 | 0.00635 | 44.45 | 1119.0 | 1021.1 |
| 140 | 2.885 | 5.874 | 123.1 | 0.00812 | 56.86 | 1123.1 | 1015.2 |
| 150 | 3.714 | 7.56 | 97.2 | 0.01029 | 72.0 | 1127.1 | 1009.3 |
| 160 | 4.737 | 9.64 | 77.4 | 0.01293 | 90.5 | 1131.1 | 1003.2 |
| 170 | 5.988 | 12.19 | 62.09 | 0.01611 | 112.7 | 1135.0 | 997.1 |
| 180 | 7.506 | 15.28 | 50.23 | 0.01991 | 139.4 | 1138.8 | 990.9 |
| 190 | 9.335 | 19.01 | 40.94 | 0.02443 | 171.0 | 1142.5 | 984.6 |
| 200 | 11.523 | 23.46 | 33.60 | 0.02976 | 208.3 | 1146.2 | 978.2 |
| 210 | 14.122 | 28.75 | 27.77 | 0.03601 | 252.1 | 1149.7 | 971.7 |
| 212 | 14.697 | 29.92 | 26.75 | 0.03738 | 261.7 | 1150.4 | 970.4 |

# TABLE III

## PROPERTIES OF SATURATED VAPOR OF AMMONIA

| TEMPERA-TURE, F. $t$ | PRESSURE LB. PER SQ. IN. $p$ | HEAT CONTENT | | LATENT HEAT | | | ENTROPY | | VOLUME OF ONE POUND $v''$ | TEMPERA-TURE, F. $t$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | | of Liquid $i'$ | of Vapor $i''$ | of Vapori-zation $r$ | Internal $\rho$ | External $\psi$ | of Liquid $s'$ | Vaporization $\frac{r}{T}$ | | |
| -30 | 13.51 | -67 | 536 | 603 | 554 | 49 | -0.146 | 1.404 | 19.78 | -30 |
| -25 | 15.54 | -62 | 537 | 599 | 549 | 50 | -0.133 | 1.379 | 17.34 | -25 |
| -20 | 17.82 | -57 | 538 | 595 | 545 | 50 | -0.121 | 1.354 | 15.23 | -20 |
| -15 | 20.36 | -51 | 540 | 591 | 540 | 51 | -0.109 | 1.329 | 13.43 | -15 |
| -10 | 23.18 | -46 | 541 | 587 | 536 | 51 | -0.098 | 1.305 | 11.88 | -10 |
| -5 | 26.32 | -41 | 542 | 583 | 532 | 51 | -0.086 | 1.281 | 10.53 | -5 |
| 0 | 29.78 | -35 | 543 | 578 | 527 | 51 | -0.074 | 1.257 | 9.36 | 0 |
| 5 | 33.52 | -30 | 544 | 574 | 522 | 52 | -0.062 | 1.234 | 8.38 | 5 |
| 10 | 37.80 | -24 | 545 | 569 | 517 | 52 | -0.051 | 1.212 | 7.46 | 10 |
| 15 | 42.41 | -19 | 546 | 565 | 513 | 52 | -0.039 | 1.190 | 6.69 | 15 |
| 20 | 47.46 | -13 | 547 | 560 | 508 | 52 | -0.027 | 1.168 | 6.01 | 20 |
| 25 | 52.98 | -8 | 548 | 556 | 503 | 53 | -0.016 | 1.147 | 5.41 | 25 |
| 30 | 59.00 | -2 | 549 | 551 | 498 | 53 | -0.005 | 1.125 | 4.88 | 30 |
| 35 | 65.52 | 3 | 550 | 547 | 493 | 53 | 0.007 | 1.104 | 4.41 | 35 |
| 40 | 72.6 | 9 | 551 | 542 | 489 | 53 | 0.018 | 1.084 | 4.01 | 40 |
| 45 | 80.3 | 15 | 552 | 537 | 483 | 54 | 0.029 | 1.064 | 3.63 | 45 |
| 50 | 88.6 | 20 | 552 | 532 | 478 | 54 | 0.041 | 1.044 | 3.30 | 50 |
| 55 | 97.5 | 26 | 553 | 527 | 473 | 54 | 0.052 | 1.024 | 3.01 | 55 |
| 60 | 107.1 | 32 | 554 | 522 | 468 | 54 | 0.063 | 1.004 | 2.74 | 60 |
| 65 | 117.5 | 37 | 554 | 517 | 463 | 54 | 0.074 | 0.985 | 2.51 | 65 |
| 70 | 128.3 | 43 | 555 | 512 | 458 | 54 | 0.085 | 0.966 | 2.30 | 70 |
| 75 | 140.5 | 49 | 555 | 506 | 452 | 54 | 0.096 | 0.947 | 2.11 | 75 |
| 80 | 152.8 | 55 | 556 | 501 | 447 | 54 | 0.107 | 0.928 | 1.94 | 80 |
| 85 | 166.8 | 61 | 557 | 496 | 442 | 54 | 0.118 | 0.910 | 1.78 | 85 |
| 90 | | | | | | | | | 1.64 | 90 |

# INDEX