

MOLECULAR ATTRACTION. VI. ON THE MUTUAL NEUTRALIZATION OF THE ATTRACTION BY THE ATTRACTED PARTICLES AND ON THE NATURE OF ATTRACTIVE FORCES

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Introduction

We have in several previous papers¹ discussed an equation of the form, $\frac{L - E_1}{\sqrt[3]{d} - \sqrt[3]{D}} = \text{constant}$, (L is heat of vaporization of a liquid, E_1 is the energy spent in overcoming external pressure, d and D are the densities of liquid and vapor respectively). This equation was derived theoretically on the assumption that the attraction between the molecules of a liquid varied inversely as the square of their distance apart and did not vary with the temperature. The equation has now been tested for thirty-three substances over wide ranges of temperature (usually from near the freezing-point of the liquid to the critical temperature), and the evidence in favor of the truth of the equation is exceedingly strong. This evidence will be briefly reviewed later. But admitting the truth of the equation, does it necessarily follow that the assumed law of attraction was the true one? Could it be possible that some other law of attraction, operating either by itself, or in connection with other energy changes, would give a similar equation? It is with this phase of the question that the present paper is concerned and we will endeavor to show that the assumptions upon which the equation is based are correct and that the equation is correctly deduced. Having given the evidence upon this point, we show further that the conclusion may be drawn with considerable certainty that the molecular attraction is mutually neutralized by the attracted particles. Finally, our knowledge of the laws of molecular

¹ Jour. Phys. Chem., 6, 209 (1902); 8, 383, 593 (1904); 9, 402 (1905); 10, 1 (1906).

attraction enables us to institute a comparison with other attractive forces and obtain some very suggestive results.

The conclusions to be drawn so closely concern our fundamental ideas of matter that we may be pardoned for briefly calling attention to laws and ideas, more or less generally admitted, upon which the present work is based.

The Fundamental Ideas Serving as a Basis for the Present Work

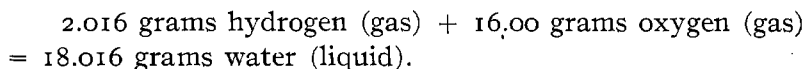
Our Idea of Matter.—Since scientists are somewhat divided in their belief as to the ultimate nature of matter, we would, even though it involves repetition from a previous paper, make clear our own position in this regard, for the question with which we are dealing leads back to a consideration of the nature of mass as we measure it, if not to a consideration of the nature of matter. Because we use the terms “molecule,” “molecular attraction,” and “distance between the molecules,” we do not wish to be understood as possessing the idea that a molecule is *necessarily* a little hard sphere or some other particular shape of a piece of “something” extended in space. In the latter part of this paper we have something to say (by way of speculation suggested by the facts to be considered), regarding the possible ultimate nature of mass. But in the present part of this paper we do not care to consider the nature of matter. We do not care whether it consists wholly of a “something” that possesses the property of extension, or wholly of energy, or is a mixture of the two. The law of gravitation has been shown to hold between certain large masses of a thing commonly called “matter.” If later it happens to be proved that matter (in the sense of an “extended something”) is not reality and that only energy exists, we do not suppose the proof will greatly affect the calculations of the astronomers, or the position of the heavenly bodies, or their movement in accordance with the law of gravitation. The object of this series of papers is to throw light upon the law of attraction which exists between smaller masses of the same material of which

these larger bodies are more conspicuous representatives. Following considerable precedent, we have called these "smaller masses" molecules, a term which conveys to every scientist a group of properties sufficiently clearly defined for the purpose in view. By the expression "distance between the molecules," we mean the distance between their centers of mass—an expression exactly analogous to the distance between two heavenly bodies. The "center of mass" is therefore a mathematical point, determined by the same principles that would be used for large masses. The term "molecular attraction" indicates a force which can be regarded as having its origin at the mathematical point thus determined. We are accordingly entirely free from any assumption as to the size of the particles (molecules), their nature or the ultimate cause of the force. What we really assume is, that in nature certain forces *act as though they proceeded from mathematical points*, and we clothe these mathematical points with the name "molecule."

The Kinetic Theory of Gases.—It is by no means necessary for us to point out how the laws of gases discovered by Boyle and Gay-Lussac, and the simple relations connecting the densities of gases, discovered by Gay-Lussac, but stated most clearly in terms of Avogadro's hypothesis, that equal volumes of all gases contain the same number of molecules, are explained by the kinetic theory of gases. Nor how this theory similarly explains Dalton's law for the pressure of mixed gases and Henry's law governing the solution of a gas in a liquid. Nor how the theory led Clerk Maxwell to the discovery of the law governing the viscosity of gases, and Waterston to the simple relation existing between the two specific heats of a gas. The Van der Waals theory also is a fruit of the kinetic theory and indeed the kinetic theory has been the stimulus and the guide to much of the work upon both liquids and gases. We do not believe that there are many chemists who will object to the acceptance of the kinetic theory of gases as a basis for further work.

According to the kinetic theory of gases we may regard the total energy of a gaseous molecule as being the sum of certain amounts of energy which may be quite clearly differentiated from each other. We would distinguish these energies as follows:

(1) *The Chemical Energy, or Energy of Combination of the Atoms Constituting the Molecule.*—It can be shown, independently of theory, that the molecule must possess this energy at the absolute zero of temperature, -273°C . (We do not suppose that all motion ceases at this temperature. Just what part of the motion ceases is perhaps even yet a matter of doubt.) To prove this proposition we will consider the reaction:



The amount of heat evolved by this reaction, when taking place at 18°C , has been measured by Thomsen and found to be 68420 calories. Now the total amount of heat necessary to raise the hydrogen and oxygen from the absolute zero to 18°C can be ascertained from the following data.

	Hydrogen	Observer	Oxygen	Observer
Melting-point	14.1°	Travers	Below 50°	Travers
Boiling-point.....	20.41	Travers	90.20	Travers
Specific heat of solid.	2.3 cal.	Kopp	0.25 cal.	Kopp
Specific heat of liquid	6.00 "	{ Estimated	0.347 "	Alt
Specific heat of gas..	3.410 "	{ Dewar	0.2175 "	Regnault
Heat of fusion.....	16.0 "	{ Wiedemann	4.9 "	Regnault
Heat of vaporization.	125.0 "	{ Estimated	50.92 "	Estimated
		{ Dewar		Alt

The specific heat of ice is given as 0.4627 by Regnault and the heat of fusion of ice as 79.90 calories by Smith.

If to the energy added to the substance as specific heat of the solid, liquid and gas respectively, there be added the heat of fusion and the heat of vaporization, we will obtain the total heat required to raise the body from the absolute zero

of temperature to the chosen temperature, in this case to 18°C . We have therefore for the total energy necessary to raise the temperature from 0° absolute to 18°C for,

2.016 grams of hydrogen	= 2286 calories
16.00 grams of oxygen	= 2015 "
18.016 grams of water	= 3865 "

The values given are probably maximum values and not very far from the truth except in the case of water, where we think the value would probably be considerably too large, due to the use of the specific heat for ice as found by Regnault between -78° and 0°C as representative of the average specific heat of ice, -273° to 0° . The value of the specific heat, judging from analogy, probably decreases as the temperature is decreased.

It appears therefore that in raising the 2.016 grams of hydrogen and the 16.00 grams of oxygen from the absolute zero to 18°C only 4301 calories of energy were required, while at this temperature 68420 calories were given out when they combined. Since the water formed possesses about 3865 calories of energy, it follows that the hydrogen and oxygen possessed at least 67,984 calories of chemical energy at the absolute zero. Further, since only the difference between the chemical energy of the H_2 and O_2 on the one hand and of the H_2O on the other, is ascertained, we cannot make any statement as to the actual amount of chemical energy possessed by the H_2 and O_2 at the absolute zero. We can only say that it is certainly *not less than* 67,984 calories. It may be many times more.

It follows from the above that the chemical energy has been either entirely unaffected by the change in temperature of 291° , or has been affected only in a very minor degree. For a stable chemical body, where the change in temperature is not large, we have little hesitation in saying that the chemical energy, E_c , of the body is a constant.

$$(1) \quad E_c = \text{constant.}$$

We will return later to a further discussion of the chemical energy.

(2) *The Translational or Kinetic Energy of the Molecule.*—This energy for any particular molecule is equal to one-half the mass of the molecule multiplied by the square of its velocity. It follows from the well-known investigation of Clerk Maxwell that the velocities of the different molecules of a gas vary somewhat, but the variation is confined within rather narrow limits and only very few of the molecules have a velocity greatly above or greatly below the average molecular velocity. This theorem of Maxwell regarding the distribution of velocity among the molecules of a gas has been proved with strictness for the supposition that the molecules act on each other only at the moment of collision. For such a condition, using the constants adopted in former papers, the sum of the translational energy, E_K , of all of the molecules can be represented by

$$(2) \quad E_K = \frac{3}{2} RT = 2.9817 \frac{T}{m} \text{ calories,}$$

where T is the absolute temperature, and m is the molecular weight referred to oxygen = 16.00 as standard.

It has never been shown that the translational energy of a molecule, when the molecule is subject to attractive force, can be calculated by this formula and the formula is therefore proven (with assumption of the kinetic theory) only for so-called "perfect" gases.

(3) *The Internal Energy of a Molecule.*—Experiments have shown that the specific heat of a gas at constant pressure is nearly a constant over considerable ranges of temperature. The variation from absolute constancy appears to be due to variations from the gas laws, when the gases examined are far removed from the condition designated as "perfect" gases, and also to certain progressive changes taking place within the molecule as the temperature is raised—the progressive changes finally ending in the decomposition of the molecule. The measurements therefore make it very prob-

able that for a perfect gas, and one that is chemically stable (that is, one in which the chemical energy does not change with the temperature), the specific heat at constant pressure would be a constant.

But for such gases the law, $PV = RT$, holds true, and consequently, $PdV = RdT$, which for a change of one degree gives, $PdV = R$. If σ_p and σ_v denote the specific heat at constant pressure and constant volume respectively, we have,

$$(3) \quad \sigma_p - \sigma_v = PdV = R.$$

If the increase in the translational energy of the molecules of any gas be subtracted from the specific heat at constant volume of the gas, a certain residue remains (equal to zero for monatomic gases), which we shall consider as being due to a change in the internal energy, E_I , of a molecule. We will have, therefore,

$$(4) \quad \sigma_v = \frac{dE_K}{dT} + \frac{dE_I}{dT} = \text{constant}.$$

True strictly only for a "perfect" gas.

Now from the theory by Waterston,

$$(5) \quad \gamma = \frac{\sigma_p}{\sigma_v} = \frac{dE_K + dE_I + R}{dE_K + dE_I}, \text{ } dT \text{ being equal to } 1^\circ \text{ C.}$$

Wherefore, substituting for R its value, $2/3dE_K$, and solving,

$$(6) \quad E_I = \frac{\frac{5}{3} - \gamma}{\gamma - 1} E_K = 2.9817 \left(\frac{\frac{5}{3} - \gamma}{\gamma - 1} \right) \frac{T}{m} \text{ calories.}$$

The internal energy in a perfect gas is therefore proportional to the translational energy.

The exact function of the internal energy required by a molecule has never been satisfactorily explained, but the fact that it is proportional to the translational energy leads to the belief that the internal energy is a direct consequence of the translational energy. It should be understood, however, that equation 6 embodies no assumption whatever regarding the internal energy. That it is proportional to the translational

energy follows necessarily, if the specific heat at constant volume is a constant, and if the gas law, $PV = RT$, holds. Nor will the possibility that this internal energy is merely the rate of change of (the differential of) the chemical energy with the temperature, in any way affect our conclusion.

The data upon the specific heat of gases cannot be discussed briefly. Much of the data is given and discussed in Meyer's *Kinetic Theory of Gases* and in Nernst's *Theoretische Chemie*. Reference must be made to these or similar works for the actual data showing the constancy of the specific heat under the conditions set forth above.

(4) *The Energy of Position Due to the Attraction between the Molecules.*—It is the purpose of this series of papers to show that this potential energy is due to an attractive force emanating from each molecule—that this force varies inversely as the square of the distance apart of the molecules—is mutually neutralized by the attracting particles—and is unaffected by temperature changes. We will later deduce the law governing this energy.

(5) *The Energy of Volume Due to the External Pressure.*—This energy, it is evident, is measured simply by the pressure times the volume. Denoting the energy by E_E we have,

$$(7) \quad E_E = 0.0431833 PV \text{ calories,}$$

where P is expressed in millimeters of mercury. The constants used have been given in previous papers.

We can regard a perfect gas as a gas in which there is no energy due to attraction and therefore the energy of such a gas could be represented thus:

$$(8) \quad \Sigma E = E_{\text{Chemical}} + E_{\text{Kinetic}} + E_{\text{Internal}} + E_{\text{External}}.$$

We can also regard a perfect gas as one in which the molecules are so far removed from each other that their mutual attraction has no appreciable effect in modifying the motions of the particles. Such a gas would still possess potential energy due to the attraction and we would therefore have,

$$(9) \quad \Sigma E = E_{\text{Chemical}} + E_{\text{Kinetic}} + E_{\text{Internal}} + E_{\text{Attraction}} + E_{\text{External}}.$$

We could differentiate between the chemical energy as being a function of the atoms, the kinetic, internal, and attractive energies, as being a function of the molecule, and the external energy as being a function of the mass. The internal energy may be only the differential of the chemical energy with respect to the temperature, and consequently, be more directly a function of the atoms.

Equations 8 and 9 represent the condition of things in a perfect gas. If we now consider a saturated vapor, or a liquid, where the molecules are so close together that the gas laws are not obeyed, it is evident from what has been already stated that E_C , is, if the body be chemically stable, the same as for that substance when existing as a perfect gas. The value for the external energy, E_E , can be readily calculated independently of assumptions save the first law of thermodynamics. The internal energy, E_I , is, we have seen, proportional to the translational energy, E_K , and it is highly improbable that this proportionality would be destroyed by the nearness of the molecules and their increased mutual attraction. The kinetic energy of the molecules might itself be altered, equation 2 having been proved to hold only for a perfect gas. But where mathematical proof is lacking, experimental evidence has taken its place. Since van't Hoff showed that for undissociated dissolved substances the osmotic pressure given by a dissolved substance was equal to the pressure that the dissolved substance would exert were it a gas at that volume and temperature, it has been very probable that the osmotic pressure was due to the same cause as the gas pressure, *viz.*, the motion of the dissolved particles, and therefore, the kinetic energy of the dissolved substance is the same that it would be for a gas under the same conditions of temperature and volume.

The molecules of the dissolved substance could not have an average kinetic energy different from the average kinetic energy of the molecules of the solvent, a fact long ago pointed out by Ostwald.¹ Therefore it seems probable that equation 2 holds also for liquids.

¹ Solutions, pp. 147, 148.

(The work of Morse and Frazer¹ shows that the theory of van't Hoff needs some modification, and the work of Kahlenberg² is in evidence against the theory. We would, as regards the work of Kahlenberg, point out that his experiments, Nos. 53 and 59 and 60, show that the dissolved substance was obeying Boyle's law for gases (as concerns concentrations), and experiment No. 53 was *performed without stirring*. Also the manometer tube attached to Kahlenberg's osmotic cell, as given by him, was only of 0.5 mm bore, and consequently, to produce a rise of 50 cm in his manometer tube only 1/10 of a cubic centimeter of liquid needed to enter the cell. The amount of LiCl leaving the cell was 0.0130 and 0.0267 and of cane sugar 0.1149 and 0.2205 of a gram and *the osmotic pressure is determined by the relative rate of inflow and outflow*. It seems to us possible, also, that thermometer effects of the cell were not wholly eliminated from influencing the results. We would not therefore, as yet, abandon van't Hoff's theory and its results as a reason for believing that Equation 2 holds also for liquids and that the average kinetic energy of the molecules of a liquid is equal to the average kinetic energy of the molecules of its vapor at the same temperature.)

Further, Traube finds that his "co-volume" for liquids varies as the absolute temperature.³

We will give additional evidence on this subject in a subsequent paper.

If it be granted, then, that equation 2 holds also for liquids and for saturated vapors the energy of a molecule of a vapor differs from the energy of a molecule of a liquid only because of changes in E_A and E_E . The latter change is easily calculated and we can therefore obtain a measure of the former—the energy change due to the attraction.

¹ Am. Chem. Jour., 34, 1 (1905).

² Jour. Phys. Chem., 10, 3, 141 (1906).

³ Numerous papers. Among others, J. Traube: Grundriss d. phys. Chemie. Boltzmann: Festschrift (1904); Zeit. anorg. Chem., 40, 380 (1904). Sammlung: Chemischer und chemisch-technischer Vorträge, 4, 255.

Expressing the above belief in a different form, we may say that the energy necessary to change a liquid into a gas must, then, be spent solely in overcoming the external pressure and in altering the distance apart of the molecules. (Unless the molecule breaks apart also or nears the point of disruption.)

Denoting the heat of vaporization by L , and the energy necessary to overcome the external pressure during the change from liquid to gas by E_E , $L - E_E$ must equal the energy spent in overcoming the molecular attraction.

Derivation of the Equation.—The derivation of this equation as given in the first paper of this series was not carried out with strictness and we therefore give below a proof which we believe to be mathematically rigorous.

Let v and V represent the volume of the liquid and vapor before and after expansion, and d and D represent the corresponding densities. Let n equal the number of molecules and m the mass of each molecule. Suppose the molecules evenly distributed throughout the space occupied by them. Then $\sqrt[3]{v/n}$ and the $\sqrt[3]{V/n}$ represent the relative distance apart of the molecules of liquid and vapor respectively.

It is highly improbable that the molecules of a liquid are evenly distributed throughout the space occupied by them. But if they are shifted from their ideal position by reason of the attractive force, the particles would gain in kinetic energy exactly so much as they would lose in potential energy. We may therefore, without error, consider them to be shifted back into this ideal position of even distribution, and the fundamental supposition upon which the mathematical work given below is based, is, that the molecules of a liquid and the molecules of its vapor have *per se* (exclusive of E_A and E_E), the same energy *when they are in this ideal position of even distribution throughout the space occupied by them.*

If this supposition represents truly the condition of the molecular energy, then it is possible to find the law governing the forces which act between the molecules. For we have only to assume the law and deduce the corresponding equation. If the deduced equation fails to agree with the ex-

perimental facts then another law could be assumed and the process repeated until the correct supposition had been made.

We will assume that the molecular attraction varies inversely as the square of the distance apart of the molecules and is a mutual property of each pair of molecules. Hence the force $= \frac{\mu^2 m^2}{r^2}$, where μ is the attraction at unit distance on unit mass and r is the distance apart of the molecules whose mass is represented by m .

If, now, we consider two molecules whose distance apart is $x\sqrt[3]{v/n}$ before expansion (vaporization), after expansion their distance apart will be $x\sqrt[3]{V/n}$ and the work done in pulling them apart will be

$$(10) \quad \int_{x\sqrt[3]{V/n}}^{x\sqrt[3]{v/n}} m^2 \mu^2 \frac{dr}{r^2} = \frac{m^2 \mu^2}{x} \left(\frac{1}{\sqrt[3]{v/n}} - \frac{1}{\sqrt[3]{V/n}} \right),$$

where x is an unknown constant. If we in turn consider the work, W_1 , done in pulling all of the molecules away from one molecule, and sum up, we will have, similarly,

$$(11) \quad W_1 = m^2 \mu^2 \left(\frac{1}{\sqrt[3]{v/n}} - \frac{1}{\sqrt[3]{V/n}} \right) \left(\frac{1}{x} + \frac{1}{x_1} + \frac{1}{x_2} + \dots + \frac{1}{x_{n-2}} \right).$$

If now we take any other molecule and similarly sum up the energy, W_2 , required to pull all of the molecules away from it, we have for the work so done,

$$(12) \quad W_2 = m^2 \mu^2 \left(\frac{1}{\sqrt[3]{v/n}} - \frac{1}{\sqrt[3]{V/n}} \right) \left(\frac{1}{x'} + \frac{1}{x'_1} + \frac{1}{x'_2} + \dots + \frac{1}{x'_{n-2}} \right).$$

By similarly extending the process to other molecules, each considered in turn as a center, we will obtain a series of similar expressions, n in number. The last factor of each member of the series depends only upon the number of the molecules n , and is entirely independent of the nature of the molecules or of the forces. We may, therefore, denote this last factor in the different series by $c_1, c_2, c_3, \dots, c_n$.

Summing up the entire n series of equations we will have

$$(13) \quad W_1 + W_2 + W_3 + \dots + W_n = m^2 \mu^2 \left(\frac{1}{\sqrt[3]{v/n}} - \frac{1}{\sqrt[3]{V/n}} \right) (c_1 + c_2 + c_3 + \dots + c_n).$$

The last factor of this equation is a constant if the number of molecules remains the same. Let C represent this constant. We have then for the total work of expansion, W ,

$$(14) \quad W = m^2 \mu^2 \left(\frac{1}{\sqrt[3]{v/n}} - \frac{1}{\sqrt[3]{V/n}} \right) C.$$

Equation 14 gives the entire energy required to pull all of the molecules from each other as vaporization proceeds. It must therefore equal the internal heat of vaporization and we have for mass M ,

$$(15) \quad M(L - E_E) = m^2 \mu^2 C \left(\frac{1}{\sqrt[3]{v/n}} - \frac{1}{\sqrt[3]{V/n}} \right).$$

Letting $d = \frac{nm}{v}$, $D = \frac{nm}{V}$, $M = nm$, we have

$$(16) \quad \frac{M(L - E_E)}{\sqrt[3]{d} - \sqrt[3]{D}} = \frac{M^2 \mu^2 C}{n^2 \sqrt[3]{m}},$$

or for a constant mass,

$$(17) \quad \frac{L - E_E}{\sqrt[3]{d} - \sqrt[3]{D}} = \text{constant}.$$

The constant of equation 17, we shall call μ' .

(In the previous derivation of this equation, 17, we assumed, $c_1 = c_2 = c_3 = \dots = c_n$, a fact which is experimentally true, but which is contradictory to the law of attraction assumed, if the latter is unmodified. Also we regarded the entire attraction in each case as proceeding from one molecule and being measured by $\frac{\mu m}{r^2}$, instead of being a mutual property of the two molecules and being measured by $\frac{\mu^2 m^2}{r^2}$. See further below.)

Evidence Proving the Equation.—The evidence proving that $\frac{L - E_E}{\sqrt[3]{d} - \sqrt[3]{D}}$ is equal to a constant, has been given in the second, third and fifth papers of this series. We would only summarize here by saying that thirty-five substances have now been examined, at intervals of 10° C, over wide ranges of temperature, extending usually from near the boiling-point of the substance to the critical temperature. Within 10° of the critical temperature there is an apparent divergence due to causes shown. Omitting these observations out of 435 remaining observations on 26 different substances only thirty differed from the mean value of the constant for that substance by more than 2 percent and only four of these thirty by more than 5 percent. The reason for most of these divergences is suspected and investigation will be made of them later. Of the remaining substances, CO_2 , N_2O , and SO_2 gave probably as good agreement as the data permitted. Five other substances were associated and showed, as was to be expected, a divergence from a constant value for the constant, and SnCl_4 likewise showed a divergence. The evidence in favor of the truth of the equation is therefore most convincing. That the equation itself is true can hardly be doubted when the evidence is examined. But does it follow that the assumed law of attraction is the true one?

The Neutralization of the Attraction by the Attracted Particles

The answer to this question is of great interest. For if the attraction between the molecules varies inversely as the square of their distance apart, then the resultant attraction caused by the large number of molecules must apparently increase as we proceed outward from an interior centrally chosen particle. This follows because the number of molecules increases as the cube of the distance from the centrally chosen molecule, whereas the attraction varies only inversely as the square of that distance. Hence the resultant attraction of any mass upon a particle exterior to the mass, when

regarded as proceeding from the center of that mass, must vary as the mass.

The molecular sphere of action could not, therefore, be small but would embrace the entire mass taken. Now we regard the evidence that the molecular sphere of action is small, as being beyond dispute, and will not attempt here to give the evidence for this idea. But we will point out that the derived equation 16, itself bears evidence that we have in previous papers been considering only one phase of the question. The equation was given in the form, $\frac{M(L - E_E)}{\sqrt[3]{d} - \sqrt[3]{D}} = \frac{M^2 \mu^2 C}{n^2 \sqrt[3]{m}}$, where M represents the mass of liquid taken for the vaporization. Now in the test of the equation, the number of molecules was assumed constant, and this was justifiable, since it would be experimentally possible to have them constant. But should they vary, we know experimentally that the left-hand side of the equation varies simply with the mass taken. While the right-hand side of the equation varies, not alone because of the variation thus caused in M , but also because of the variation caused at the same time in C and in n . Since C is a function of n it might be supposed, as one occurs in the numerator and the other in the denominator, that the variation would cancel. We have not succeeded in summing up the $n(n - 1)$ terms represented by the C of equation 16, but the relation of C to n can be obtained by attacking the problem somewhat differently.

Helmholtz in 1854 investigated the amount of energy that would be given out by the contraction of the sun in order to determine if the energy continually radiated from that body could be thus obtained. In this investigation he assumed that the particles of which the sun was composed were at the same temperature before as after the contraction, the excess of energy having been radiated off into space. He also assumed that the force acting between the particles of the sun's mass obeyed the Newtonian law of gravitation. Hence the investigation was essentially the same as the one above carried out. But Helmholtz made possible a better mathe-

matical treatment by the assumption that the sun was homogeneous in density. We take the liberty of giving below the investigation as given by Helmholtz.¹

Consider a homogeneous gaseous sphere whose radius is R_0 and density σ . Let M_0 represent its mass. Let dM represent an element of mass taken anywhere in the interior or at the surface of the sphere. Let R be the distance of dM from the center of the sphere, and let M represent the mass of the sphere whose radius is R . The element of mass in polar coordinates is

$$(18) \quad dM = \sigma R^2 \cos \phi \, d\phi \, d\theta \, dR.$$

The element is subject to the attraction of the whole sphere within it. As can be shown, the attraction of the spherical shell outside of it balances in opposite directions so that it need not be considered in discussing the forces acting upon dM . Every element in the infinitesimal shell whose radius is R is attracted towards the center by a force equal to that acting on dM ; therefore, the whole shell may be treated at once. Let dM_s represent the mass of the elementary shell whose radius is R . It is found by integrating 18 with respect to θ and ϕ . Thus,

$$(19) \quad dM_s = \sigma R^2 dR \int_0^{2\pi} \left\{ \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} \cos \phi \, d\phi \right\} d\theta = 4\pi \sigma R^2 dR.$$

The force to which dM_s is subject is $-\frac{K^2 M dM_s}{R^2}$. The element of work done in moving dM_s through the element of distance dR is

$$dW_s = -dM_s \frac{K^2 M}{R^2} dR.$$

The work done in moving the shell from the distance CR to

¹ Celestial Mechanics. Moulton, p. 58.

R is the integral of this expression between the limits CR and R , or

$$W_s = -dM_s K^2 M \int_{CR}^R \frac{dR}{R^2} = \frac{dM_s K^2 M}{R} \left(\frac{C-1}{C} \right).$$

But $M = \frac{4}{3}\pi\sigma R^3$; hence, substituting the value of dM_s from equation 19 and representing the work done on the elementary shell by $W_s = dW$, it follows that

$$dW = \frac{16}{3}\pi^2\sigma^2 K^2 \left(\frac{C-1}{C} \right) R^4 dR.$$

The integral of this expression from 0 to R_0 gives the total amount of work done in the contraction of the homogeneous sphere from radius CR_0 to R_0 . That is,

$$(20) \quad W = \frac{16}{3}\pi^2\sigma^2 K^2 \left(\frac{C-1}{C} \right) \int_0^{R_0} R^4 dR = \frac{16}{15}\pi^2\sigma^2 K^2 \left(\frac{C-1}{C} \right) R_0^5,$$

which may be written

$$(21) \quad W = \frac{3}{5}K^2 \left(\frac{1}{R_0} - \frac{1}{CR_0} \right) M_0^2.$$

Now if the contraction takes place between the limits $\sqrt[3]{\frac{3V}{4\pi}}$ and $\sqrt[3]{\frac{3\bar{V}}{4\pi}}$ we have for the work done,

$$(22) \quad W = \frac{3}{5}K^2 M_0^2 \left(\frac{1}{\sqrt[3]{\frac{3V}{4\pi}}} - \frac{1}{\sqrt[3]{\frac{3\bar{V}}{4\pi}}} \right) = 0.9682 K^2 M^{5/3} (\sqrt[3]{\bar{d}} - \sqrt[3]{\bar{D}}).$$

Comparing this expression with equation 14 we have only to replace the attraction at unit distance between the elements of mass, K , by the molecular attraction at unit distance μ , and observe that $C = 0.9682n^{5/3}$, if the mass were of uniform density throughout. We cannot see how the transformation from a sphere of uniform density to one of uniformly distributed particles could effect any change in the energy relations involved. We would therefore write:

$$(23) \quad \frac{M(L - E_E)}{\sqrt[3]{\bar{d}} - \sqrt[3]{\bar{D}}} = 0.9682\mu^2 M^{5/3}.$$

So long as a constant mass is taken, the equation will reduce to the form, $\frac{L - E_E}{\sqrt[3]{d} - \sqrt[3]{D}} = \text{constant}$. If, however, the mass be varied, the equation informs us that the work done should vary as the five-thirds power of the mass. It should require three and two-tenths times as much heat to vaporize 2 grams of a liquid as to vaporize 1 gram. As a matter of fact, we know that it only requires twice as much heat to vaporize 2 grams as to vaporize 1 gram. How is this discrepancy to be explained?

In attacking this problem we would call attention to the fact that the equation, $\frac{L - E_E}{\sqrt[3]{d} - \sqrt[3]{D}} = \text{constant}$, does correctly represent the variation of the energy change caused by the attraction with the distance, as is shown by the evidence accumulated in previous papers and as indicated in the brief summary above. It seems reasonable therefore to suspect the cause of the variation to be due to the numerator of the function representing the law of the force, $f = \frac{\mu^2 m^2}{d^2}$, and not to the denominator.

If now, we study the action of other attractive forces, such as magnetic forces, we find an explanation of the apparent contradiction at once suggested. The magnetic force varies directly as the product of the strengths of the poles and inversely as the square of their distance apart. But the interposition of a piece of sheet iron into the magnetic field between the magnet and the attracted particles serves to cut off the attraction, more or less completely, from the formerly attracted particles. Whether we look upon the interposed sheet of iron as actually absorbing the force, or as merely changing the direction of the lines of force, is not essential, the result at least is clear—particles beyond the interposed sheet of iron are subject to less attraction because of the interposition. So if we were to imagine a magnetized particle of iron surrounded by other particles of iron, evenly distributed, and similarly magnetized, the attraction would

vary inversely as the square of the distance apart of the particles and yet the sphere of action of any particular particle would be small, due to the shielding action of the particles. And it seems to us that we may have here an exact representation of molecular attraction.

There is much indirect evidence to support such a conclusion. The attraction designated as chemical affinity is mutually absorbed by the combining bodies. At least the force is canceled by the combination so far as its effect on other particles is concerned. The combination of one sodium atom with one chlorine atom certainly serves to shield other bodies from the attractions of both the sodium and the chlorine, rendering them in large measure chemically inert. And this action is commonly represented by saying that the "bond" of the sodium is neutralized or saturated by the "bond" of the chlorine. As we have just mentioned, a similar effect happens with magnetic forces. If electrical forces be considered we find again the same to be true. And if we undertake to consider yet more closely the nature of attractions in general, is it not apparent, that, whatever the ultimate nature of the attractive force may be, yet it cannot be infinitely multiplied? That just so much force must emanate from each particle, and if this force is exerted on one particle there will be somewhat less of the force remaining for the remaining particles? *Is it not unreasonable to suppose that a particle could exert its attractive pull upon one thousand, or one million, or one hundred million, particles and yet always have just as much of its force remaining to exert on other particles brought within the same distance?* We are not confusing force and energy. Can a man by means of a rope exert the same pull on each of twenty other men that he could exert on one man? Does not each stress exerted lessen by just so much the power of the man to exert a similar pull upon other things? Can we multiply, *ad infinitum*, any force about whose real nature we know anything at all, merely by the introduction of further objects upon which the force can be exerted? Is there any

form of wave motion, vibration, or emanation, known, whose effect can be thus infinitely increased?

Look at the question from the other side. Is it reasonable, that the introduction of particles of matter into the space surrounding a molecule should be absolutely without influence on the emanation which proceeds from the molecule and gives rise to the phenomena of attraction? And that this filling in of the space surrounding a molecule with other particles of matter (or centers of energy, if you choose), should be able to continue, *ad infinitum*, without disturbing the attractive radiation proceeding from the body?

Moreover, the mere fact that all of the attractive forces, whose law of variation with the distance we know, do vary inversely as the square of the distance from the attracting body, *is evidence that the attractive force is in each case some sort of wave motion or emanation whose intensity decreases directly in proportion to the increase in the surface of the wave or emanation front*, since and because this surface varies as the square of its distance from the origin. Can we, on the one hand, believe that the intensity of these forces thus decreases, and on the other, consider them unmodified by the presence of matter and capable of infinite multiplication by the introduction of additional matter into an infinite range of action?

In place of such a conception we would introduce the idea *that the attractive forces, whatever their nature, whether chemical, molecular, magnetic, electrical, or gravitational, which proceed from a particle, are definite in amount. If this attraction is exerted upon another particle the amount of the attraction remaining to be exerted upon other particles is diminished by an exactly equivalent amount.*

We are of course aware that no such diminution of the attraction is supposed, or is supposed possible, for gravitational forces. That certain facts have led to the belief, difficult of conception as it may be, that this force attracts every particle of matter in the universe exactly as if no other particle of matter were present. And that these facts would at once be urged as contradicting the above statement as to

the attractive forces. We would answer by calling attention in detail to the evidence in favor of the above idea.

Further Evidence Regarding the Molecular Attraction

As regards the molecular attraction the conclusions cited above have been based on evidence which, for purposes of examination, may conveniently be divided into five steps as follows:

1. The equality of the energy *per se* of the molecules of a liquid and of the molecules of its vapor at the same temperature. That is, $E_C + E_K + E_I$ for a molecule of a liquid equals $E_C + E_K + E_I$ for a molecule of its vapor, the difference in their energy consisting of a difference in E_A and E_E .

2. The assumption that the attraction was a mutual property of each pair of molecules, varying directly as the mass of the molecules (so long as the same chemical body is considered), and inversely as the square of the distance apart of the molecules. Later modified by 5 below.

3. The derivation of an equation expressing the energy relations necessitated by the above two conditions.

4. The experimental evidence deduced in favor of the equation.

5. The facts leading to the supposition that the molecular attraction is mutually absorbed by the attracting particles.

Examining these steps separately let us see which are open to doubt. Considering first the fourth—the experimental evidence in favor of the equation—we would here add nothing new. But we would put one portion of the evidence in a more striking form. We will use the equation derived by Helmholtz in 1854 as expressing the energy given out by the contraction of the sun, to calculate the energy given out by the contraction of isopentane from a gas to a liquid. The equation of Helmholtz has been given, equation 22, and is, for a change of volume corresponding to a change of density from D to d ,

$$(24) \quad W = 0.9682 K^2 M^{5/3}.$$

To apply this equation to 1 gram of isopentane we have only to substitute for the constant in the above equation, the value for this constant that we have already found, 105.4. The equation then becomes,

$$(25) \quad W = 105.4 (\sqrt[3]{\bar{a}} - \sqrt[3]{\bar{b}}).$$

We give below in Table I the data and the results. The values given by equation 25 are in the column headed W. Under the heading $L - E_E$ we give the values of the internal heat of vaporization as actually determined from Young's measurements. It is inconceivable to us that the agreement between W and $L - E_E$ could be accidental.

TABLE I.—ISOPENTANE

Temperature	Density of liquid	Density of vapor	$\sqrt[3]{\bar{a}} - \sqrt[3]{\bar{b}}$	W	$L - E_E$
0° C	0.6392	0.001090	0.7385	79.9	81.3
20	0.6196	0.002358	0.7194	75.8	75.2
40	0.5988	0.004480	0.6781	71.5	70.7
60	0.5769	0.007819	0.6340	66.8	66.4
80	0.5540	0.01284	0.5871	61.9	61.8
100	0.5278	0.02022	0.5357	56.4	56.7
120	0.4991	0.03106	0.4788	50.5	50.9
140	0.4642	0.04728	0.4127	43.5	44.0
160	0.4206	0.07289	0.3316	34.9	35.4
180	0.3498	0.1258	0.2035	21.4	21.0
185	0.3142	0.1574	0.1399	14.7	14.0
187	0.2857	0.1833	0.0905	9.5	8.9
187.4	0.2761	0.1951	0.0712	7.5	6.9
187.8	0.2343	0.2343	0.0	0.0	0.0

The formula used by Helmholtz to represent the contraction of the sun does represent the contraction of isopentane from the gaseous to the liquid condition. And not only isopentane but essentially as well all of the non-associated substances examined by us. For we have already published¹ similar comparisons for all of these substances, the only difference being that we added to the energy given out by the contraction, the value of the energy due to the action of the external

¹ See third paper of this series, Tables 1 to 21, and fifth paper, Tables 15 to 24.

pressure, and thus obtained the heat of vaporization. We have here republished the results for isopentane as coming from Helmholtz's formula only to emphasize the statement that we have not gone beyond the facts when we declare that, *as regards variation with the distance, the law of molecular attraction is identically the same as the law of gravitation, and precisely the same formula is applicable to both.*

The formula is,

$$(26) \quad E_A = \mu' (\sqrt[3]{d} - \sqrt[3]{D}),$$

where μ' has the meaning assigned previously in this and earlier papers.

As regards the third step mentioned above—the derivation of the equation—we can detect no flaw in the proof given by the author, or the proof given by Helmholtz, the basis of the mathematics as expressed in steps 1 and 2 being granted.

As regards the second step—the assumption of the law of the attraction—the fact that a true equation was deduced, entirely theoretically, from the assumption, is the surest evidence that the assumed law was the true one. One point remains to be examined here. Could any other law of attraction have produced the same equation, or one equally in accord with the facts?

To satisfy ourselves upon this point we have in a similar manner deduced the corresponding equations on the assumption that the attraction varied as the third, the fourth, the fifth, and the sixth powers of the distance between the molecules. These equations would take the form:

For the inverse third power of the distance,

$$(27) \quad \frac{M(L - E_E)}{d^{2/3} - D^{2/3}} = 0.4841\mu^2 M^{1/3} = \text{constant for a constant mass.}$$

For the inverse fourth power of the distance,

$$(28) \quad \frac{M(L - E_E)}{d - D} = 0.3227\mu^2 M = \text{constant for a constant mass.}$$

For the inverse fifth power of the distance,

$$(29) \quad \frac{M(L - E_E)}{d^{4/3} - D^{4/3}} = 0.2420\mu^2 M^{2/3} = \text{constant for a constant mass.}$$

For the inverse sixth power of the distance,

$$(30) \quad \frac{M(L - E_E)}{d^{6/3} - D^{6/3}} = 0.1936\mu^2 M^{1/3} = \text{constant for a constant mass.}$$

Applying these equations to isopentane, the constant given by equation 27 is shown in the column headed $\frac{1}{r^3}$, the constant given by equation 28 in the column headed $\frac{1}{r^4}$, etc. The values at the critical temperature, 187.8° C, were obtained by substituting for $L - E_E$ its value, 0.0431833 ($V - v$) $\left(T \frac{dP}{dT} - P\right)$, and getting the limit of the resulting equation where V was equal to v . The resulting equations are:

For the limit of equation 27,

$$(31) \quad \text{Constant} = 0.0477 V^{5/3} \left(\frac{dP}{dT} T - P\right).$$

For the limit of equation 28,

$$(32) \quad \text{Constant} = 0.0431833 V^{6/3} \left(\frac{dP}{dT} T - P\right).$$

For the limit of equation 29,

$$(33) \quad \text{Constant} = 0.04239 V^{7/3} \left(\frac{dP}{dT} T - P\right).$$

For the limit of equation 30,

$$(34) \quad \text{Constant} = 0.04191 V^{8/3} \left(\frac{dP}{dT} T - P\right).$$

The critical temperature is 187.8° C, the critical pressure is 25,020 millimeters of mercury, the critical volume is 4.268, and the $\frac{dP}{dT}$ at the critical temperature is 406, from the measurements by Dr. Sydney Young.

It will be seen that when the equation is deduced on the assumption that the attraction varies inversely as the square of the distance apart of the molecules a constant is obtained, and on no other supposition does the corresponding equation give a constant. It is evident therefore that no simple change in the assumption as to the variation of the attraction with the distance will serve to explain the fact that the heat of vaporization does vary proportionately to the mass taken.

TABLE II—ISOPENTANE.

Temperature	L—EE	<i>d</i>	D	$\frac{1}{r^2}$	$\frac{1}{r^3}$	$\frac{1}{r^4}$	$\frac{1}{r^5}$	$\frac{1}{r^6}$
0°C.	81.35	0.6392	0.001090	107.2	111.2	127.5	147.8	171.5
50	68.62	0.5881	0.005967	104.5	102.6	117.9	139.6	166.3
100	56.67	0.5278	0.02022	105.8	97.9	111.6	134.6	165.1
150	40.13	0.4445	0.05834	106.9	92.9	104.0	126.7	160.5
180	21.04	0.3498	0.1258	103.4	85.7	93.9	114.7	148.1
187.8	0.0	0.2344	0.2344	107.2	86.9	94.0	114.4	148.3

The law of the attraction assumed, seems, therefore, to be the only assumption that will give an equation in accord with the facts.

As regards now the first step—the equality of the energy *per se* of a molecule of a liquid and of a molecule of its vapor—we have already stated in outline the facts which lead us to that belief. This first step is the most fundamental and important step in our work and is the most open to doubt. The fact that using this belief as a basis we derived an equation that appears to be true, is perhaps, again the best evidence that the belief expresses, at least partly, the truth. But only in part, for in attempting to derive a direct method for testing this belief we find that it will require some modification. An account of this work could not be introduced within the limits of this paper and we hope shortly to publish this investigation in a separate article. Recognizing the doubt, we would state that any errors introduced by our statement have undoubtedly canceled, since one is certainly able to calculate the energy given out by the contraction of a vapor

into a liquid from the same formula used to calculate the energy given out by the contraction of the sun.

As regards now the fifth step—the conclusion that the molecular attraction is mutually absorbed or canceled by the attracting particles—we have only to say here that the conclusion is necessitated by the four previous steps and the further well-known facts, that the molecular sphere of action is small, and that the heat of vaporization of a liquid is proportional to the mass of the liquid taken for evaporation.

The Nature of the Attractive Forces

We would now return to a consideration of the idea proposed on page 151 of this paper, *that the attractive forces, whatever their nature, whether chemical, molecular, magnetic, electrical, or gravitational, which proceed from a particle are definite in amount. If this attraction is exerted upon another particle the amount of the attraction remaining to be exerted upon other particles is diminished by an exactly equivalent amount.*

We would call attention to what is actually known as to the action of attractive forces by the table on p. 158.

The general resemblance between these forces is so striking, we think, as to warrant a very serious consideration of any idea which leads to the belief that all of the forces do not follow the same law. Are they not perhaps all, in fact, one and the same force?

Considering the chemical force of attraction, the fact that this force does vary as some function of the distance apart of the atoms concerned has, we think, been already shown by the work of Richards¹ and Traube.² The latter says, "*Wie von mir zuerst festgestellt wurde, ist der Raum eines Atoms keine Konstante, sondern ändert sich von Stoff zu Stoff und ist um so kleiner, je grösser die Affinität des betreffenden Atomes zu den Atomen ist, mit welchen es in unmittelbarer Verbindung steht. Die Kontraktion der Atome ist daher*

¹ Proc. Am. Acad., 37, 1 (1901); 15 (1902); 38, 7 (1902); 39, 23 (1904).

² Zeit. anorg. Chem., 40, 380 (1904).

Force	Medium of propagation	Effect of temperature	Is the attraction neutralized?	Is the attraction directive?	Law of distance, d	Numerator factor of force
Chemical	Ether	No effect	Neutralized	Yes	?	Nature of atom \times Nature of atom
Molecular	Ether	No effect	Neutralized	?	$\frac{1}{d^2}$	Nature of molecule \times Nature of molecule
Magnetic	Ether	?	Neutralized	Yes	$\frac{1}{d^2}$	Strength of pole \times Strength of pole
Electrical	Ether	?	Neutralized	Yes	$\frac{1}{d^2}$	Charge \times Charge
Gravitational	Ether	No effect	Not neutralized	No	$\frac{1}{d^2}$	Mass \times Mass

ein unmittelbares Maass der Affinität.” Concerning Traube’s claim to priority in this discovery see remark by Richards.¹ While we prefer not to accept the conclusion of these investigators that the atoms themselves suffer a contraction, we cannot doubt from the evidence that they have brought

¹ Proc. Am. Acad., 39, 23, 583 (1904).

forward that the chemical attraction between atoms is one of the deciding factors as to the distance apart of these atoms when combined into a molecule. That is to say, the distance apart of the atoms is some function of the chemical affinity. The problem is as yet too complicated to permit of finding the law of the attraction, and at present we must limit ourselves to the statement that the inverse square law of the distance is possible also with this force. When Newton discovered the law of gravitation others at once seized upon that law as a possible explanation of chemical affinity. Newton himself showed that the chemical attraction decreased more rapidly with the distance than was required by the inverse square law. But if the chemical attraction is mutually absorbed or canceled by the attracting particles, then it again becomes possible that the force itself varies inversely as the square of the distance from any particular atom, itself alone considered. Moreover, we know that this mutual absorption of the chemical attraction does take place.

We have made the statement that temperature has no effect upon chemical affinity. We have shown as a reason for this statement that 2.016 grams of H_2 and 16.00 grams of O_2 at the absolute zero possess at least 67,984 calories of chemical energy, while the total energy necessary to raise the H_2 and the O_2 from the absolute zero to $18^\circ C$ is only 4301 calories. Now of this 4301 calories we can account for all but about 165 calories as necessitated by the changes in E_K , E_I , E_A and E_E . The details of this calculation will be given in the subsequent paper referred to above. At present we give the result only, as indicating the very minute influence that temperature has upon chemical affinity. It is possible that E_I is really the differential of the chemical energy. But even if this be true, it may more reasonably be referred to a slight alteration in the distance apart of the atoms composing the molecule, than to a real alteration of the chemical affinity.

In what form can the enormous amount of energy possessed by the hydrogen and oxygen at the absolute zero

exist? Clausius has shown¹ that no system of particles could exist in stable equilibrium if all of the energy possessed by those particles was present as kinetic energy. Nor could all of the energy exist as potential energy. The energy must be partly kinetic and partly potential. Now it can be shown that when two particles exist under a mutual attraction varying inversely as the square of the distance apart of the particles, that the system composed of these two particles assumes the most stable equilibrium when one-half of the total energy is kinetic and one-half is potential. We cannot but believe it probable, that in a system of particles a similar distribution of energy would take place. The enormous amount of chemical energy that is existent at the absolute zero of temperature must, it seems to us, be present, one-half as potential and one-half as kinetic energy. That is to say, the hydrogen atoms and oxygen atoms at the absolute zero would revolve in pairs around a common center of gravity with enormous velocity, held in their orbits by the chemical attraction. This conception seems to us quite sufficient to explain the repulsive tendency referred to by Richards in his fourth paper above cited. We shall deal with this subject more fully later. We would only remark that the above conception of the mechanism of chemical affinity introduces no new assumption, save that the attraction obeys the inverse square law. This being true the other results follow if the principles underlying mechanics be true.

Our statement concerning the magnetic and electrical forces, not being the subject of dispute, may be passed over without comment.

As regards the gravitational force we meet the first and only exceptions to a complete similarity between the forces. The gravitational attraction is supposed not to be absorbed or neutralized by the attracting particles.

The questions involving the nature and laws of the attractive forces cannot, we are well aware, be settled by any appeal to our minds as to the relative difficulty or ease of the

¹ See Meyer: *Kinetic Theory of Gases*, p. 344.

conception. But on the other hand such an appeal is *not without value*. If in the last analysis the testimony of consciousness cannot be trusted we had just as well give up the search for truth. We cannot hope to obtain to any absolute knowledge or full conception of any of the more elementary ideas such as time, space, matter, or motion. But we may attain to a partial knowledge of these ideas and this partial knowledge, we trust, may represent the reality truly, so far as it represents it at all. And in attempting to attain this partial knowledge, if one goes directly contrary to the testimony of one's mind as to the possibility or impossibility of a conception, one should not forget that the process of denying the truth of the testimony of consciousness once begun, can be as legitimately extended to an absolute agnosticism. Must be so extended, if one is consistent. One can refuse to examine the foundations for a house but one cannot undermine the foundations and yet continue to build the house. We do not believe, therefore, that the difficulties in the conception of the action of gravitational forces can longer be passed over as constituting no objection to the present statement of that law. Since Newton in 1682 deduced the law, all of the attempts—and they have been numerous—to formulate a sufficient cause for the law, have completely failed. The attempts have ended not alone in failure to formulate a cause for the law, but in emphasizing, most distinctly, the difficulty of forming such a conception at all.

May not the real cause of the trouble lie in the fact that scientists have been trying to explain how a force can be infinitely multiplied and absolutely unaffected by intervening matter, when force with such properties has really no existence? The line of apsides of Mercury's orbit has a slight motion unaccounted for by the law of gravitation. Dr. Asaph Hall pointed out that the observations could be satisfied by changing the law of gravitation by very slightly increasing the exponent of the distance factor. May not this slight divergence, explained as an *increase* in the exponent of the denominator, be explained rather by a *decrease* in the numerator,

due to a neutralization of the attraction by the attracted particles. The planets are but dots in space, and the distortion of the field of force by the attraction which they would neutralize would be extremely small.

It will be further urged that we have no evidence of any shielding action in the case of gravitational forces and that, besides, gravitation is proportional to mass and not to surface in any way. In reply we would point out that we are dealing with a very fundamental question, and that we have, as yet, no explanation of mass. Mass is best represented perhaps, by the term "inertia," but the question is, What is "inertia?" Why has a molecule of lead more inertia than a molecule of aluminum? We have not, so far as the author knows, one iota of evidence, save in the suggestiveness of the periodic table of the chemical elements, that there is really more of the "ultimate material" in the molecule of lead than in the molecule of aluminum. For anything *we know* to the contrary, mass might be created at the same time as the attraction, a sort of action and reaction due to the same cause. And why this suggestion?

Because if one attempts to consider what changes must be made in the numerator factor of the forces in order to derive a common expression for all of the attractive forces, one starts with the broad idea that the force is measured by the effect which it produces. In producing this effect an opposite and equal effect must be produced on the force itself. This is according to Newton's third law of motion. Any other supposition would mean that the forces could be increased indefinitely. Force is transference of energy. We have no law as to the conservation of force but we have a law as to the conservation of energy. The amount of energy in the universe is constant. In a given time a constant amount of energy could not produce an infinite amount of force. But this production of an infinite, inexhaustible force is exactly what the law of gravitation necessitates, if it expresses the entire truth. We repeat *that one cannot believe that one particle of matter in the universe can attract every other particle*

of matter in the universe and itself suffer no diminution in its power to attract yet other particles of matter and hold also that the law of the conservation of energy is true. For these two beliefs necessitate that a constant energy, in a given time should be able to produce an infinite force, and this is impossible.

We reach therefore the conclusion that the attractive force given out by a particle in a given time is definite in amount. If therefore a portion of this attraction is expended upon one particle there remains exactly an equivalent amount less to be expended on the remaining particles. *Consequently, the attraction can be measured by the amount of the neutralized force.* This deduction we claim to be founded on the first law of thermodynamics, the conservation of energy. Now the amount of attractive force which can be neutralized will vary inversely as the square of the distance apart of the particles, because the surface front of the attractive wave of force increases as the square of the distance apart of the particles, and its intensity must correspondingly diminish, since the force cannot be infinitely multiplied. We can therefore write, attractive forces are measured by:

$$\frac{\text{amount of attraction neutralized at unit distance} \times \text{amount of attraction neutralized at unit distance}}{d^2}$$

Examining the numerator of the above fraction, there appears nothing improbable as regards its application as a general expression to take the place of the first four forces given in the table—chemical, molecular, magnetic and electrical. As regards gravitational force it makes mass proportional to the amount of attraction absorbed at unit distance. Is this idea necessarily wrong?

We doubt if the idea is necessarily opposed to established astronomical data. We might suggest that one reason why no shielding action had been detected among the heavenly bodies was because the mass really did vary with the amount of the shielding and exactly canceled the effect produced. Whether the idea is supported by molecular phenomena is more a subject of doubt. It might possibly explain the in-

creased specific heat of a solid and liquid as compared with the corresponding vapor. We will return to this point in a later paper.

Chemical, magnetic, and electrical forces show decided evidence of directive action. We distinguish, moreover, positive and negative electricity, positive and negative poles of a magnet, and positive and negative elements, as indicating some difference in the kind of attractive force which they exert. As evidence of variation in the intensity of the molecular forces with their spatial relation around the molecule, might be cited the phenomena of crystalline form, of water of crystallization and molecular combinations in general, and also those cases where a liquid appears to show a definite and symmetrical structure. The evidence is not convincing, nor is there evidence indicating positive and negative molecular attraction. With gravitational forces similarly, there is no evidence showing directive, or positive and negative tendencies, unless the earth's magnetic field should be such an evidence.

The exceedingly close relationship between the electrical and chemical forces have often suggested their identity. The close relationship between electrical and magnetic forces is also recognized. There is also some evidence that molecular attraction is closely connected with electrical phenomena. Thus it has been pointed out by Abegg that liquids which cause dissociation are themselves most associated. We would note further a correspondence between the amount of dissociation produced by a liquid on a dissolved substance and the size of the molecular attraction, μ' , as obtained by us. Perhaps it is also not without significance that the metals are the best conductors of electricity, are monatomic, and have a very great cohesion.

The amount of the molecular attraction, and the greater or less interpenetration of the molecular attraction among other molecules before it is neutralized, may, it seems to us, be the determining factor in the elasticity, ductility, malle-

ability, brittleness, and hardness of substances in general, and of metals more particularly.

Our knowledge at present, is hardly sufficient to warrant speculation regarding the ultimate cause and nature of the attractive forces. They may be one and the same force—the molecular attraction being the unneutralized portion of the chemical attraction, magnetic attraction being a manifestation of the latter, and electricity closely connected with the former. Gravitation would be the unneutralized portion of the molecular attraction. We consider it possible that the attractive forces are one and the same force manifested under different conditions. We consider it likely that all of the forces are produced by some interaction between matter and ether. We consider it highly probable that the forces obey the same law whether their ultimate cause and identity be the same or not. We hope to develop the subject further in later papers.

Summary

1. The evidence that the molecular attraction varies inversely as the square of the distance apart of the molecules, and does not vary with the temperature, is reviewed and strengthened.

2. It is pointed out that the molecular attraction must be neutralized by the attracting molecules.

3. It is shown that the equation deduced by Helmholtz in 1854 to represent the energy given out by the contraction of the sun will, by changing the constant, represent accurately the energy given out by isopentane and other substances in changing from a saturated vapor to a liquid.

4. It is shown that a large amount of chemical energy is possessed by hydrogen and oxygen at the absolute zero, and that this energy is probably existent half as potential, half as kinetic energy.

5. It is shown that chemical attraction is probably unaffected by temperature.

6. The idea is introduced that the attractive forces, whatever their nature, whether chemical, molecular, magnetic, electrical, or gravitational, which proceed from a particle are definite in amount. If this attraction is exerted upon another particle the amount of the attraction remaining to be exerted upon other particles is diminished by an exactly equivalent amount.

7. The laws governing attractive forces are compared and it is suggested that all of the forces really obey the same law, *viz.*, the attractive forces are measured by the amount of the attraction neutralized, which is:

$$\frac{\text{amount of attraction neutralized at unit distance}}{d^2} \times \frac{\text{amount of attraction neutralized at unit distance}}{d^2}$$

8. The idea that the gravitational attraction of a particle could remain undiminished regardless of the amount of the attraction exerted upon other particles is shown to be contrary to the law of the conservation of energy.

*Chemical Laboratory,
University of North Carolina,
December 10, 1906.*

NEW BOOKS

Ice Formation ; with Special Reference to Anchor-ice and Frazil. *By Howard T. Barnes. First Edition. 15 × 23 cm; pp. x + 260. New York: John Wiley and Sons, 1906.*—"Nowhere can man witness a more wonderful sight of the delicate poising of the forces of Nature than in the spectacle of one of our northern rivers in winter. The full magnitude of the struggle which goes on between ice and water is only realized in its entirety where an engineering problem has to be met and the ice conditions studied. The steadiness of the temperature of the water throughout the winter is a matter of great interest. It never varies more than a few thousandths of a degree from the freezing-point, even though the temperature of the air may be 30° or 40° lower. As a constant temperature thermostat we have nothing to equal it even with all the appliances of one of our modern laboratories.

"Evidence shows that the greater bulk of our water-power lies in the northern portion of the American continent, from the great lakes and along the St. Lawrence valley through the snow belt. Hence, as water-power development advances, the circumstances under which ice formation takes place become more and more important. To the hydraulic engineer the question of ice formation is of vital importance, and too much attention cannot be given to this matter for a more thorough understanding of the problems involved. What presents itself during the summer months for consideration is nothing to what must be met during the winter months, when ice is forming rapidly, and ice bridges, dams, and shoves may change the whole character of the levels and channels in a single night. Rivers are thus known to have been turned entirely out of their course into new channels during a winter of unusual severity, and in some instances the reversal of a rapid is of yearly occurrence."

The intense cold of the Canadian winter gives rise to some types of ice formation which are either non-existent or of minor importance in regions where the cold weather is intermittent. The author distinguishes sheet ice, frazil, and anchor ice. Sheet ice is the solid ice which forms on the surface of the water. It is the only ice with which most people are familiar.

"Frazil is a French-Canadian term for fine spicular ice, from the French for forge-cinders, which it is supposed to resemble. It is always formed in an open channel, where the current is flowing too swiftly for the border-ice to meet over the service, and it is often called 'slush-ice'. It is a surface-formed ice, which cannot remain attached and freeze into a surface sheet. It occurs in varying degrees of fineness, depending on the degree of agitation of the water. On a smooth gliding surface flat plates of ice may be formed, and give rise to the term 'plate-ice'. In rapids or at the foot of waterfalls, only fine particles of ice are formed in minute needle crystals, which grow in bulk when carried far in open water.

"Artificial frazil-ice may be formed by subjecting water to rapid agitation in a cold atmosphere. A tub of water placed out-of-doors in winter and rapidly stirred, soon turns to slush by the copious growth of these fine crystals. It is

safe to say that a long stretch of open water becomes loaded to the bottom with slush-ice during a period of intense cold and great wind agitation, frequently occurring in our northern rivers in winter. During such a time the water appears dull in color, presenting an appearance of being mixed with fine sand. At any time during cold weather, the water may be seen to be harboring numerous fine crystals by withdrawing a sample in a clear day for inspection. The amount it may contain will depend entirely on the weather conditions. A dull stormy day, with a wind that blows against the current, is productive of the greatest amount. This is the result of the surface agitation, together with the rapid extraction of heat. A bright, sunny day, although very cold, does not show much formation, on account of the absorption of the sun's rays near the surface, offsetting the cooling effect of the air. At night, under a clear sky with wind agitation, a large amount will be formed, depending on the temperature of the air. In this case both conduction to the air and radiation from the bottom and volume of the water are operating. Very little radiant heat is stopped by the atmosphere, on account of the minute amount of water-vapor present in the air under these circumstances. A stretch of open water makes a very much greater quantity of ice in the form of frazil crystals than could be produced as a surface-sheet, if the water were sufficiently quiet to allow such to grow. It is this which causes an open channel to be of so much trouble to engineering operations whenever frost occurs; for although a surface-sheet may form lower down, the fine ice is carried far under the surface-ice by the currents. Serious changes of level often occur in a river, by the damming up, or complete stoppage of a channel by frazil carried under the surface-ice, and building down on both sides of the channel. Great masses of frazil accumulate in the quiet bays by the drifting in of the fine crystals, and their subsequent settling upwards to the under side of the surface-sheet. The crystals soon become attached to the surface-ice, and attain depths reaching to the bottom of the river; in some cases we have observed a depth of 80 feet.

"In taking soundings through the ice, the lead may usually be sunk through the masses of frazil, but often these become frozen together so hard as to resist all efforts at penetration. The distance to which frazil-ice will be carried depends on the swiftness of the currents, and the amount of open channel above. In the St. Lawrence River, at Montreal, the frazil, generated for the most part in the Lachine Rapids, is found attached as far down as Verrans, some twelve miles below. In this case the river is open above the rapids, as far as Lake St. Louis, seven miles above."

Frazil is formed in the laboratory every time we make a freezing-point determination. Those who are not fortunate enough to be chemists become familiar with it as orange sherbet, which is frazil sweetened and flavored.

Anchor-ice is ice attached to the bottom of the river irrespective of the nature of formation. It is formed in two ways. Immense quantities of frazil become attached to the bottom by freezing to the layers of ice already formed there. The interesting problem is as to the formation of these original layers of ice or, in other words, as to the formation of anchor-ice *in situ*. Ice can form on the river bed only when the ground is colder than the water above it. Since conduction of heat away from the water to the ground is apparently not a factor to be considered seriously, the only other possible way in which heat can

be lost is by radiation to the air through the water. From this point of view the formation of ice on the river-bed is analogous to the formation of hoar frost on the surface of the earth. Since we know that the shorter heat waves are absorbed by water, we must assume that water is transparent for some of the longer heat-waves. While this is not definitely proved, there is evidence which makes it seem plausible and it certainly explains the formation of anchor-ice.

"If we sum up the various facts of common observation in connection with anchor-ice, we see that everything points to radiation as the prime cause. Thus we find that a bridge or cover prevents the ice forming underneath. Such a cover would act as a check to radiation, and reflect the heat-waves back again to the bottom. Anchor-ice rarely forms under a layer of surface-ice. It forms on dark rocks more readily than on light ones, which is in accord with what we know in regard to the more copious radiation of heat from dark surfaces. Anchor-ice never forms under a cloudy sky either by day or night, no matter how severe the weather, but it forms very rapidly under a clear sky at night. Anchor-ice is readily melted off under a bright sun. It seems highly probable, then, that radiation of heat supplies the necessary cooling to the bottom of a river to form the first layers of ice, after which the growth or building-up of the ice is aided by the entangling and freezing of frazil-crystals which are always present in the water.

"The growth of anchor-ice is exceedingly beautiful, taking place in arborescent forms and resembling bushy weeds. So hard and thick does it become that it is often very difficult to thrust a sounding-rod through it. It is very granular in structure, as is shown by an examination of the masses which rise to the surface. Through clear water the ice looks weed-like, with long tentacles rising up out of the mass. It often has immense power in lifting rocks and boulders up bodily, and many of these are carried far down-stream attached to irregular masses of ice."

These copious quotations are sufficient to show the interesting nature of the book. To the reviewer the chapter on sheet, frazil and anchor-ice is the most interesting in the book but there is much profitable reading in the other chapters, as may be seen from their headings: physical laws governing the transfer of heat; physical constants of ice; formation and structure of ice; precise temperature measurements; river temperatures; theories to account for frazil and anchor-ice; methods of overcoming the ice problem in engineering work.

Look at it from whatever point of view you may, it is a delightful paradox that the worst floods at Montreal occur when there is not very much water in the river.

Wilder D. Bancroft.

A History of Chemical Theories and Laws. By *M. M. Pattison Muir*. First Edition. 15 × 23 cm; pp. xx + 555. New York: John Wiley and Sons, 1907. Price: \$4.00 net.—"The more I try to understand chemistry, the more I am convinced that the methods, achievements, and aims of the science can be realized only by him who has followed the gradual development of chemical ideas. A just judgment can be passed on the relative importance of the methods which are used, the results which are obtained, and the problems which are being attacked by the chemists of to-day, only when a careful study has been made of the methods employed, the results gained, and the points of attack selected by the chemists of the past."

"What is meant in chemistry by the expression, 'a homogeneous substance?' In other words, what is 'a chemically distinct substance?' What happens when chemically distinct substances interact? These are the two main questions of chemistry; and these have always been the two main questions of chemistry, although the forms wherein these questions have been stated have differed much at different times.

"To trace the forms which the two fundamental inquiries of chemistry have presented at different periods, to describe some of the methods which have been used to find answers to these inquiries, and to set forth the general results of the application of these methods, is the object of this book."

The question as to what constitutes a homogeneous substance is treated under the following general headings: the recognition of homogeneous substances, and the description of chemical changes as the interactions of these substances; the marks of elements and compounds; the laws of chemical combination; the atomic hypothesis, the molecular and atomic theory; the more searching examination of the compositions of homogeneous substances, allotropy; elements which do not react; chemical nomenclature and notation.

The question as to what happens when homogeneous substances interact is dealt with under the headings: the classification of homogeneous substances; acids, bases, salts; radicals, types, dualism, the unitary hypothesis; chemical equivalency, isomerism and constitutional formulas; application of the hypothesis of ionization to the classification of homogeneous substances; the periodic law; the conditions and general laws of chemical change; chemical affinity; chemical equilibrium; the elucidation of chemical reactions by measurements of physical properties.

The book is well written and the typography excellent. Good books of this kind are too scarce and it would be well if we could have more of them. The closing paragraph of the book is an effective one.

"The study of the connexions between composition and properties has entered a new phase. The old questions remain. The answers which have been given by the labors of countless generations of naturalists, through more than two milleniums, have not solved these problems. Physicists and chemists have joined in the quest of finding new answers to the old questions: What is a homogeneous substance? What happens when homogeneous substances interact?"

Wilder D. Bancroft

Lehrbuch der Elektrochemie. By Max Le Blanc. *Vierte vermehrte Auflage.* 14 × 22; pp. viii + 319. Leipzig: Oskar Leinder, 1906. Price: paper, 6 marks; bound, 7 marks.—The author has succeeded in condensing his material to such an extent that there is only about 10 percent increase in the number of pages. The author cites Kahlenberg's work on stannic chloride and copper oleate in benzene to prove that 'instantaneous' reactions do take place between undissociated substances. In the fifth edition we shall probably learn that the dielectric constant is not always a measure of the dissociating power of a solvent. Billitzer's work on single potentials is taken up more in detail this time, though the objections to it are not urged. Altogether, we may welcome this edition as a distinct improvement over the preceding ones.

Wilder D. Bancroft

Physikalische Chemie für Anfänger. By Ch. M. van Deventer. Mit einem Vorwort von J. H. van't Hoff. Dritte auflage, besorgt von Ernst Cohen. 15 × 21 cm; pp. xx + 161. Amsterdam: S. L. van Looy (Leipzig: Wilhelm Engelmann), 1905. Price: paper, \$.80.—This is rather an interesting little book because the method of presentation does not correspond at all to anything with which we are familiar in this country. After defining chemistry and substance, the author brings in the law of the conservation of weight (mass); the law of definite composition; the laws of constant and multiple proportions; the law of the equivalence of the elements and the laws of Gay-Lussac. Then comes a chapter on the behavior of gases followed by one on thermochemistry. One chapter is devoted to solutions and one to spectroscopy and photochemistry. The last chapter is on the periodic system.

Wilder D. Bancroft

Elektrolytische Alkalichloridzerlegung mit flüssigen Metallkathoden. By R. Lucion. (Monographien über angewandte Elektrochemie. XXIII Band.) 17 × 24 cm; pp. viii + 206. Halle: Wilhelm Knapp, 1906. Price: paper, 9 marks.—The book opens with a description of the general theory of electrolysis with a mercury cathode. Then comes a chapter on practical difficulties and a long one containing a description of the patented processes. The last section deals with the processes using a lead cathode, of which the Acker process is the only one in actual operation.

The reviewer would have liked to have seen a little more stress laid on the methods of purifying salt. The remarks on the life of carbon anodes, p. 13, seem a little inconsistent with the fact of the graphite anodes in the Castner process lasting about two years. These, however, are minor points. Taken as a whole, the book is an admirable one and contains a large amount of valuable information presented in a compact and convenient form.

Wilder D. Bancroft

Manuel de Manipulations d'Électrochimie. By C. Marie. Préface de H. Moissan; Données numériques réunies par G. Noel. 16 × 25 cm; pp. viii + 166. Paris: H. Dunod et E. Pinat, 1906. Price: paper, 8; bound, 9.50 francs.—This manual covers electrolytic work only and does not include electric furnace experiments. Seventy-four pages are devoted to a general introduction, twenty-two pages to inorganic preparations, and forty-one pages to organic preparations. This is followed by twenty-five pages of tables. The book does not differ essentially from the corresponding books in German. Making the compounds is the essential thing and the study of conditions is a very secondary matter.

Wilder D. Bancroft

Petrogenesis. (Die Wissenschaft, Heft 13). By C. Doelter. 14 × 22 cm; pp. xii + 261. Braunschweig: Friedrich Vieweg und Sohn, 1906. Price: paper, 7 marks; linen, 7.80.—The headings of the chapter are: vulcanism and the interior of the earth; the forms of volcanic rocks; the structure of volcanic rocks; relation between mineralogical and chemical composition of rocks; differentiation of the magmas; relative ages of plutonic rocks; occlusions in rocks; assimilation and corrosion; artificial rocks; solidification of fused magmas; contact metamorphosis; formation of crystalline slates; sediments.

This book brings out clearly the great need of proper experimental work such as the Geophysical Laboratory at Washington has undertaken. With only the facts that can be obtained from a study of geological formations, it is absolutely impossible to formulate any rational theory. There is nothing to show for instance whether the phenomenon of a basic lava followed by an acid one and still later by a basic one is purely a phenomenon due to fusibility or whether it must have been accompanied by a rise of temperature on the third eruption. This particular problem is really relatively simple but no one has yet gone at it the right way.

Wilder D. Bancroft

Cours de Chimie organique. By *Fréd. Swarts*. 16 × 24 cm. pp. 665. Paris: A. Hermann, 1906. Price: paper, 15 francs.—This work is intended for students of medicine, engineering, and pharmacy, and in one sense is a very complete text-book—nothing (except an analytical table of contents, and references to the literature) being left out altogether.

Laboratory manipulation, *énergie superficielle*, stereochemistry, density-curves for solutions, dynamics of etherification (with an integration), tautomerism, theory of fractional distillation, the Geneva nomenclature, etc., etc., are taken up as occasion offers; structural formulas of alkaloids and camphors, of members of the indigo group, and of derivatives of uric acid, are given in full; and many more compounds are classified and more or less described than is at all usual in works written for the constituency to which the author addresses himself.

The method of treatment is as different as can be from that of Remsen's classical little book. Isomerism, and its explanation by structural formulas is brought in on page 6 (really page 2, not counting the preface); an alcohol is defined as "a hydrocarbon in which some of the hydrocarbonated hydrogen has been replaced by hydroxyl;" "organic acids are characterized by the presence in their molecule of one or more COOH groups;" and so on throughout.

The book is neatly printed, and the author has endeavored "to treat his subject as a branch of general chemistry;" but *Multa, non multum* should be written on the title-page.

W. Lash Miller

Thermodynamique, Leçons professées à la Faculté des Sciences. By *G. Lippmann*. Rédigées par *A. Mathias* et *A. Renault*. Seconde édition, conforme à la première. 16 × 25 cm; pp. vii + 251. Paris: A. Hermann, 1905. Price: paper, 3 francs.—This second edition of Lippman's *Thermodynamique* is a reproduction of the Sorbonne lectures as originally edited by Mathias and Renault in 1889. The admirable qualities of the work as an introduction to the study of thermodynamics are well known. If the book is not to be rewritten, it is at least gratifying that it is not to be allowed to go out of print.

J. E. Trevor

Die elektrochemischen Deutschen Reichspatente. *Auszüge aus den Patentschriften.* By *P. Ferchland* and *P. Rehländer*. (Monographien über angewandte Elektrochemie. XXIV. Band.) 17 × 24 cm; pp. viii + 230. Halle: Wilhelm Knapp, 1906. Price: paper, 10 marks.—The authors give brief abstracts of the German electrochemical patents. It is obvious that the book is not one to read through from beginning to end. As a reference work, however, it is very valuable.

Wilder D. Bancroft