COLLOID DYNAMICS[1]

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> "Simplicity and symmetry should be among the chief aims of a scientific theory. It is probable that the same laws which regulate the movement of electrons within the atom also determine the paths of planets in their orbits; a complete understanding of the simplest phenomenon may enable us to explain the Universe."

ABSTRACT

Several phenomena, at present little known or neglected, are described and explained: spontaneous dispersion of liquids, change in surface tension of solutions with pH, transformation of chemical into surface energy, "thermo-osmosis," etc.

New experimental methods are given for the determination of (*a*) swelling pressure of gels, (*b*) concentration of soap in films, (*c*) velocity of adsorption at liquid surfaces.

The similarity between the following variables and phenomena is discussed:

P′	= Colloid pressure; Swelling pressure of gels; Surface pressure of adsorbed molecules.	P	= Osmotic pressure
V′	= Volume of gel; Volume of Surface Region.	V	= Volume of solution
T′	= Colloid potential; pH, in special cases.	T	= Temperature, or heat potential.
E′	= Colloid energy; Electro-chemical energy.	E	= Heat energy or molecular energy.
S′	= Colloid entropy: $\int \frac{dE'}{T'}$	S	= Heat entropy: $\int \frac{dE}{T}$

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[1] A résumé of a series of five lectures delivered at the School of Chemistry and Physics of The Pennsylvania State College in January, 1927.

M' = Mass of oriented molecules	M = Mass of solute molecules.
F' = Partial molal free energy, = $\frac{dE'}{dM'}$	F = Partial molal free energy = $\frac{dE}{dM}$
Adsorption at surfaces	Distribution of crystalloid between two phases.
Spontaneous dispersion	Boiling of liquids
Lyophobic and lyophyllic colloids	Vapors and permanent gases
Electro-osmosis	"Thermo-osmosis"
Stream Potential	"Stream Temperature"
Electro-phoresis	"Thermo-phoresis"; Crook's Radiometer
Colloid Engine; Muscular System	Heat Engine
Propagation of nerve stimuli	Propagation of disturbances in elastic media, e.g. sound waves.

The parallelism in most cases is complete, the relations between the colloid variables P', V', T', etc., being identical with those holding between the "crystalloid" or "gas" variables, P, V, T, etc. The fundamental relation for crystalloids or colloids is

$$\begin{aligned} dE &= TdS - PdV + F_n dM_n \\ &= T'dS' - P'dV' + F_n dM_n \end{aligned}$$

or, in general, introducing *t*, the time variable, and equating to zero:

$$F_n dM_n - P_n dV_n + T_n dS_n - X_n dt_n = 0$$

This is a symmetrical equation in which X stands for dE/dt, or "power" function, and n for any number of variables of the same type: M_n may represent the mass of gas, colloid, solute, electrons, etc., P_n may stand for gas pressure, colloid pressure, osmotic pressure, electromotive force, and so on. The relation between entropy and time is similar to that between mass and volume; in other words, *entropy extends in time* just as *mass extends in space.* Or, the events of which our world is composed may be separated into a space-component, mass, and a time-component, entropy.

This point of view leads to a simple thermodynamic distinction between animate and inanimate systems: in a non-living process entropy may be considered at rest or in simple motion; in a living system entropy is in complex motion; by comparing the two, a quantitative measure of the life factor may be obtained. Systems containing catalysts or enzymes are apparently of an intermediate type in which the displacement of entropy in time is of a predictable character.

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WHAT IS A COLLOID?

The original definition of colloids endows them with negative characteristics only; they *are not* crystalline, *do not* diffuse through membranes, *do not* exert osmotic pressure and *do not* affect the vapor pressure or the freezing point of water. Apart from being of an entirely negative character, these statements are true only in a very restricted sense; many crystalline substances can exist in the colloidal state, the vapor pressure and freezing point of gels differ greatly from those of their liquid, and the swelling pressure is not distinguishable in its action from osmotic pressure.

The size of the particles in a system has been used by Zsigmondy (1) and others as a criterion of colloidality. According, to this view, colloid systems contain particles much larger than molecules, yet below the limit of microscopic vision (10^{-5} to 10^{-7} cm. diam.). Wo. Ostwald has stressed the necessity of several phases being present in a colloid system and has pointed out the large amount of surface accompanying the state of fine dispersion. At the present time the orientation theory emphasizes the fact that colloid properties depend on a certain arrangement of the molecules; at the boundary of a phase, orientation always takes place to a greater or less extent. In elastic gels the orientation may be considered to occur in the interior of a liquid, independent of the presence of an interface, unless the oriented molecules themselves be considered to represent another phase (Bancroft (2)).

In this paper we shall follow the thermodynamic method, which is independent of any structural theory. Nevertheless, it will make the argument clearer if we indicate occasionally the picture we have in mind when discussing a given phenomenon. *It is convenient to imagine* that a system will have colloidal properties if it contains large polar molecules, or particles, more or less oriented. Such particles possess little or no energy of motion. There is, then, at one extreme the perfect gas composed of molecules which move haphazardly; its energy is a function of the temperature only. At the other extreme is the ideal colloid, a substance with large oriented molecules which have but little freedom of movement. The energy of the colloid is not, therefore, heat energy (irregular molecular motion), but another form of energy which will be shown later to be of an electrochemical nature.

The various definitions of colloids merely look upon the subject from different points of view: A high degree of dispersion (Zsigmondy, Alexander, Von Weimarn (3)) implies a large amount of interface (Ostwald), which in turn leads to the orientation of molecules (Harkins, Langmuir, Hardy (3)) and involves the presence of energy other than heat (Einstein (4)).

Colloids, it may be added, are not chemical compounds in the strict sense of the word. Their composition varies continuously with changes in physical conditions (see section on colloid energy). It would be convenient to designate them by the name *physical compounds.*

THE COLLOID VARIABLES

The state of a gas or of an ordinary solution depends upon various factors, such as pressure, volume, and temperature. By the application of certain fundamental principles which determine the relation between those factors, a great advance in our physico-chemical knowledge has taken place during the last few decades. If, however, we try to apply to colloids the thermodynamic relations which have been found so useful in the case of ordinary solutions, we are confronted with a difficult situation, because P, V, T, are no longer important variables where colloids are concerned. P, the osmotic pressure is, by definition, zero or negligible in the case of colloid solutions; in place of volume it is the surface which is important. The temperature too, must often be kept constant in a colloid system. This is shown by the fact that the colloids which form our body, and which probably come nearest to the ideal state, must be maintained at a constant temperature. All this is in accordance with our picture of the colloid as a substance in which energy is present in a form other than heat energy.

Since the thermodynamic variables, P, V, T, etc., are not suitable, we shall find another set of variables to take their place. For simplicity we shall denote these new variables by the corresponding letters, P', V', T', etc. Like ordinary pressure, volume, and temperature, these new variables are magnitudes that can be measured by experiment, and are *independent of any theories.*

The colloid pressure P': The swelling pressure of gels. When a sugar solution is enclosed in a semipermeable membrane, such as parchment paper, and immersed in pure water, the water penetrates into the sugar solution and builds up a certain pressure. This is called osmotic pressure. If a gelatine gel be used in place of sugar solution, it behaves in the same way; it absorbs water and exerts pressure, the so-called pressure of swelling of gels.

The great pressure exerted by colloids on swelling has been known from ancient times. The Egyptians used the pressure of swelling of wood to dislocate huge blocks of stone. Conversely, when shrinking owing to loss of water, gelatine pulls with sufficient force to chip the glass to which it is attached.[2]

Posnjack (5) has measured directly, in an osmotic cell, the pressure of swelling of gelatine, up to 6 atmospheres (fig. 1). The swelling pressure of gelatin may also be measured by balancing it against the osmotic pressure of crystalloid solutions. If a series of cubes of a gel (containing, say, 25 per cent dry gelatine) are placed in sugar solutions of different strengths, then the gelatine acts to a large extent as its own semipermeable membrane and according to the concentration of the surrounding sugar, water passes from the gel to the solution or vice versa (fig. 2).

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[2] The colloid pressure, it may be remarked, offers a simple mechanism for the rise of sap in plants. It is known that osmotic pressure due to the crystalloid substances in the plant cells is insufficient to account alone for the pressure necessary for that purpose.

Posnjak's original data were expressed in terms of concentration of gelatine per 100 grams of gel (fig. 1) and an exponential equation was fitted to represent the relation between concentration and swelling pressure, namely $P = P_0 C^n$ (n = nearly 3).

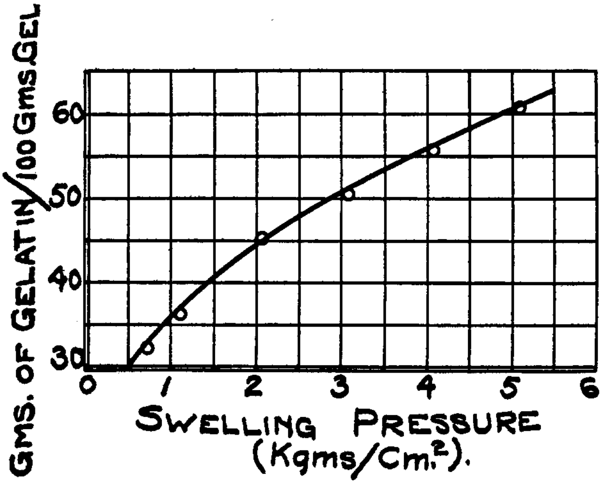

Fig. 1. Posnjak's Data on the Swelling Pressure of Gelatine

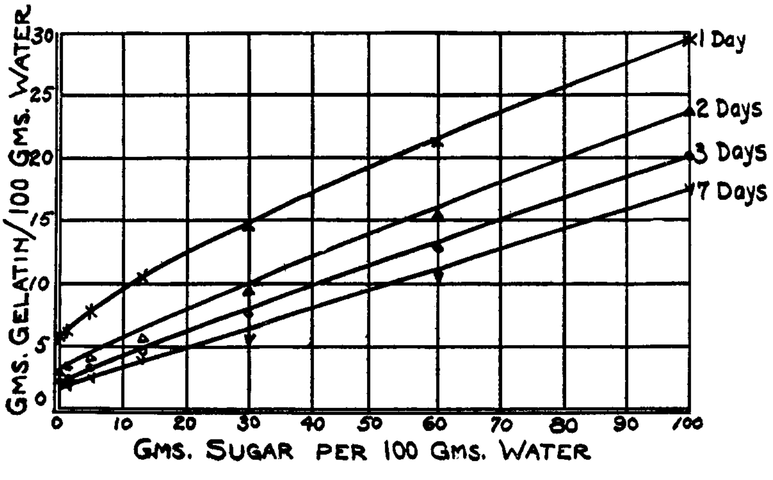

Fig. 2. Equilibrium between Osmotic Pressure and Swelling Pressure

It is customary, on the other hand, to express osmotic pressure results in relation to concentration of solute per 100 grams of solvent (6). By plotting Posnjak's data in the same way (fig. 3) it will be seen that the curves become much straighter than in figure 1. Further, it was assumed in deducing the exponential formula that C = 0 when P = 0; but it is well known that (below 20°) a gel will come to equilibrium with pure, or nearly pure solvent. This means that a formula of the type P = AC + const. would be more consistent with facts.

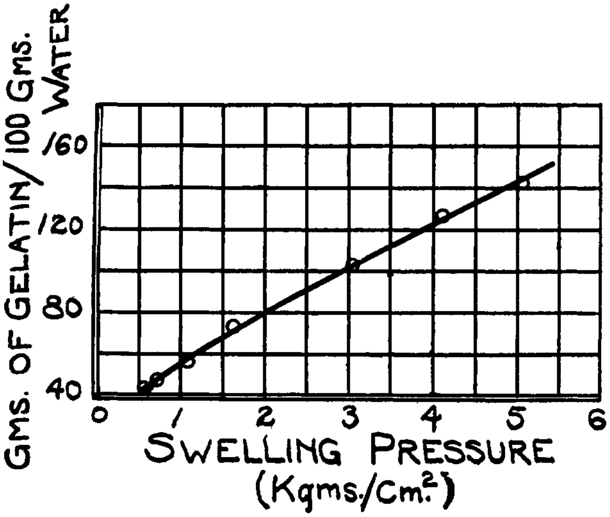

FIG. 3. DATA OF FIGURE 1 RECALCULATED IN TERMS OF CONCENTRATION OF GELATIN PER 100 GRAMS OF WATER

The experiments with sugar solution strongly suggest that whatever law connects concentration and osmotic pressure, also connects concentration and swelling pressure of gels. These experiments will have to be repeated with a real semipermeable membrane between the sugar and gelatin, in order to prevent completely the diffusion of sugar, before final conclusions can be drawn.

The general mathematical relations which we shall presently develop are independent of the particular law which governs pressure and concentration. Even when the "gas laws" are used, a linear relation need not be presupposed, if the "activity coefficient" (α) is introduced.

The surface pressure of adsorbed films. When a film of certain substances is present at the surface of a liquid, it exerts a pressure. This pressure is measured experimentally as the difference between the surface tension of the pure liquid and the surface tension of the surface contaminated with the adsorbed substance. Figure 4 shows a simple apparatus which may be used for the purpose: a shallow tray filled with water having a fixed barrier (paraffined copper plate or rod) at *A*, and a movable aluminum "float" at *B*. A monomolecular film of, say, oleic acid, lying on the water between *A* and *B* exerts a pressure on the float *B*, and this can be measured by placing weights on the balance at *C*. A more complete account of the behavior of thin films will be found in an article by N. K. Adam in this journal (7).

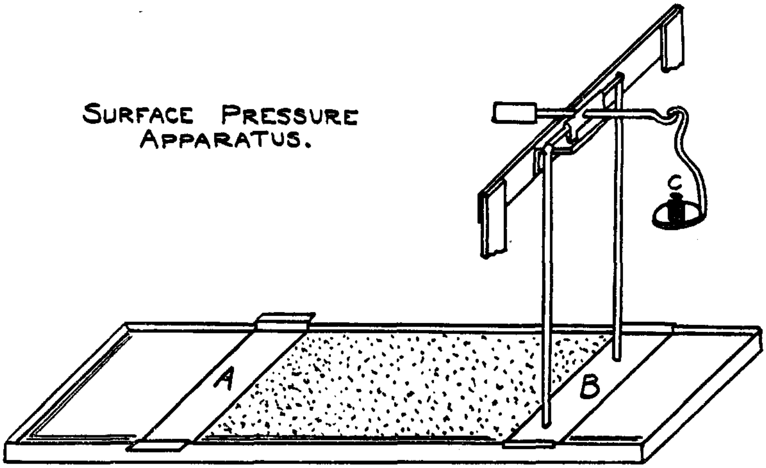

FIG. 4. SURFACE PRESSURE APPARATUS

The colloid volume V′ is the space within which the pressure P′ is active. In gels V′ may be taken to be the volume of the gel, or more correctly, the volume of the gel less the volume actually occupied by the colloid. This corresponds to the $(v-b)$ factor in van der Waals' equation of state for gases, and is necessary in order to obtain a simpler relation between pressure and volume, both in ordinary solutions and in gels (6).

In surface solutions V' is the volume of the surface region. In figure 5, XY represents the surface of a liquid which, when pure, has a surface tension σ represented by the inward pointed arrows. An adsorbed substance at the surface exerts an outward pressure, F, which opposes the surface tension. This pressure is similar to the osmotic pressure of ordinary solutions. It has been customary to express this "pressure" F in *dynes per cm.* The pressure, however, acts over a small but finite distance,

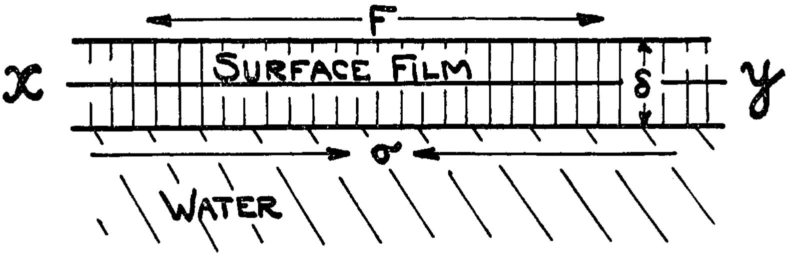

FIG. 5. OPPOSITE DIRECTIONS OF VECTORS FOR SURFACE PRESSURE AND SURFACE TENSION

δ, which is the thickness of the surface region. F/δ therefore represents the surface pressure and $A\delta$ the volume of the surface region, A being the area.

Returning for a moment to our structural idea, we may imagine that the concentration of oriented molecules becomes so great that they can "join hands," so to say, and form a continuous frame-work (8). Under those circumstances, when all the solvent is within the region where the force of orientation acts, the system becomes an elastic gel. On the assumption that the surface pressure and the swelling pressure are identical, we may write $P' = F/\delta$. On the same assumption, we may calculate the value of the thickness of the surface region, from the concentration of colloid per cm. square of surface, Γ, and from the minimum concentration of colloid that will give a gel C_m, because, assuming complete molecular orientation, we have $\delta = \frac{\Gamma}{C_m}$. The transition from gel to sol, however, is not sharp and δ will not be an exactly defined quantity; the result, nevertheless, may serve to indicate the order of magnitude of the surface region.

In the case of sodium oleate, C_m, the minimum concentration needed to give a gel is 0.24 grams per cubic centimeter (9). The "area per molecule" in a mono-molecular soap film has been calculated by Harkins and Zollman (10) from emulsion experiments to be about 47×10^{-16} cm.^{2}, which corresponds roughly to 1×10^{-7} grams of sodium oleate per square centimeter of interface. The writer, by a direct method, has found for the concentration of soap per square centimeter of foam surface a value of approximately 2×10^{-7} grams. The thickness of the surface layer is therefore of the order of magnitude

$$\frac{1.5 \times 10^{-7}}{0.24} = 6 \times 10^{-7} \text{ cm.}$$

or 60 Ångstrom units. The length of the oleic molecule itself has been computed to be 11 to 27 Å (from the thickness of surface films (11) and from x-ray measurements (12)).

The direct method for determining the concentration of sodium oleate in foam is as follows:

One cubic centimeter of a solution containing about 0.1 per cent sodium oleate and an equal amount of sodium carbonate (to keep the pH constant at about 10) is placed in a small glass tube and air free from CO_2 is forced through a capillary so as to form uniform bubbles of about 0.05 cm. diameter. Under these conditions, practically all the soap can be obtained in the form of a permanent foam of uniform bubbles. The surface area of this foam can be readily calculated, being equal to

$$\frac{\text{volume} \times 6}{\text{diameter of bubbles}}$$

In a series of experiments at 22°, 1 cc. of N/500 solution containing 0.06 per cent sodium oleate yielded on the average 35 cc.

of foam with uniform bubbles of 0.07 cm. diameter, representing a surface of

$$6 \times 35 \div 0.07 = 3000 \text{ cm.}^2$$

therefore the *maximum* amount of sodium oleate per square centimeter of surface is

$$= \frac{0.0006}{3000} = 2 \times 10^{-7} \text{ gms.}$$

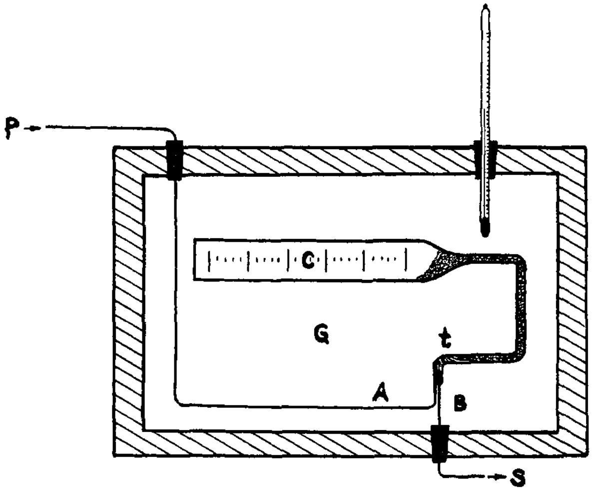

Fig. 6. Apparatus for Determining the Concentration of Soap in Foam

Corrections would have to be made for the amount of soap left in solution and for that present in the interior of the film, but these would both tend to decrease the value of δ. The above method can be employed for determining the foaming power of soaps in absolute units. Figure 6 shows how the apparatus can be arranged for convenient use:

The tube t containing the soap solution is connected with two capillaries, *A* and *B*. Through *A* air is introduced under a definite pressure, measured by the manometer attached to the inlet tube at P. The capillary B serves to introduce the solution at the beginning, and to withdraw it at the end of the experiment, also to clean the apparatus without having to remove it from the thermostat, *G*.

The writer wishes to emphasize the fact that the experiments described here, and elsewhere in this paper, were carried out in an industrial laboratory and that no attempt has been made to secure a high degree of accuracy. They are given here for the sake of the principles involved and not as exact quantitative determinations. The results obtained by other investigators are given for comparison wherever data are available.

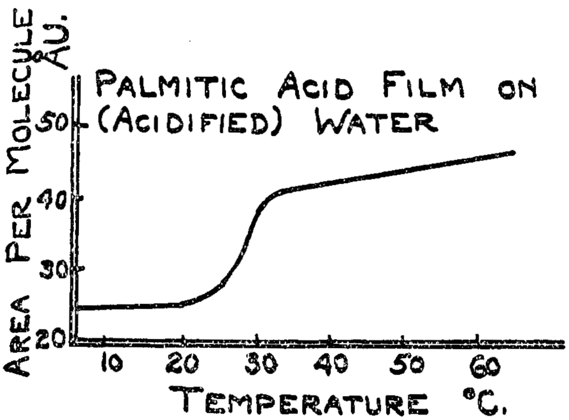

FIG. 7. INFLUENCE OF TEMPERATURE ON SURFACE FILM
(N. K. Adam. Proc. Roy. Soc. **101**, (A), 519 (1922))

The colloid "temperature" or potential T'. It has been stated above that the temperature should be considered a constant in colloid systems. By this it is not meant that temperature does not affect colloids, but only that the changes caused by heat are discontinuous. Figure 7 shows the effect of temperature on the area occupied by a surface film of palmitic acid. (13). When the temperature rises, little or nothing is observed up to a certain point, in the neighborhood of 25° to 30°, when a sudden change takes place; after that, further increase in temperature has but slight effect. Evidently in this case the relation between temperature and area (or colloid volume) cannot be expressed by a simple formula.

Consider now figure 8 which shows how the OH⁻ion concentration (pH = log OH⁻ion concentration + 14) affects the surface pressure of fatty acid films (14). (The latter is roughly proportional—or symbat—to the drop number). It is evident that there is a gradual, and in some cases almost a linear change. The surface pressure can therefore be expressed as a simple function of the pH.

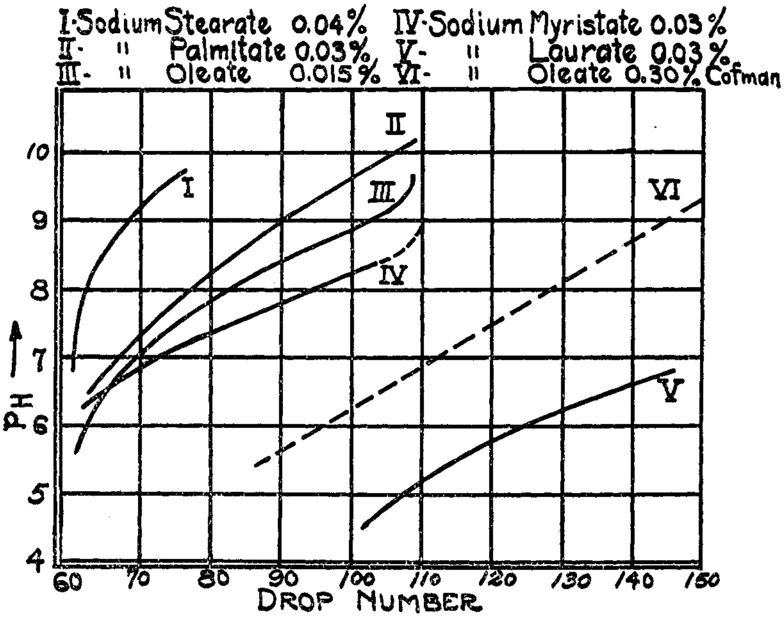

FIG. 8. INFLUENCE OF pH ON SURFACE TENSION OF SOAP SOLUTIONS
(S. Jarisch. Biochem. Zt. **134**, 163 (1922))

The variable T which causes the pressure and volume of gases to increase is called temperature or heat potential. The variable T′ which causes an increase in the colloid (surface) pressure and volume we shall denote by the name colloid potential. In the particular instance of fatty acid films, the pH is, within limits, a measure of the colloid potential, but it should be understood that this is not necessarily true for films of other substances.

Temperature is measured in many ways: by the expansion of mercury, or of gas, by means of thermo-couples, radiation pyrometers, etc. Similarly, according to circumstances, in order to measure colloid potential we shall use the expansion of films and gels, hydrogen electrodes, color indicators, etc. If we had an ideal colloid whose volume V′ diminished continuously with decreasing colloid potential, finally becoming zero, then the colloid potential corresponding to zero volume would be the absolute zero of the colloid potential. Like the perfect gas (15) "the ideal colloid is an invented substance, defined by certain properties which are not possessed by any actual substance, but which are supposed to be approached by many actual colloids (at great concentration and high potential). We may state, then, that the perfect colloid is a substance which fulfills the two following conditions:

1. That its energy is a function of the colloid potential alone, or in other words that $\left(\frac{\delta E'}{\delta V'}\right)_{T'} = 0$.

2. That when its T′, P′, V′, are changed, these obey the relation $P' V' = M' R' T'$ where M′ is the mass of colloid."

Following the example of thermodynamics, we shall define later the colloid potential as a work function and also show its connection to entropy.

Spontaneous dispersion. An understanding of the factors described in the previous paragraphs, namely, colloid pressure, volume and potential, enables us to explain the phenomenon of spontaneous dispersion of liquids. At the plane of contact of two immiscible liquids a few minute particles of one of the liquids (diameter of the order 1×10^{-5} cm.) are generally seen floating in the other phase. The dispersion is greatly increased by the presence of certain electrolytes and in some cases it becomes so intense that an emulsion is produced. This happens, for instance, when a 5 per cent solution of ferric chloride in nitrobenzol comes into contact with water; the water enters the nitrobenzol in the form of minute droplets which, under a magnification of 100 diameters, are seen to be in violent movement. If a membrane of parchment paper be used to separate the two liquids water still penetrates into the nitrobenzol building up a certain pressure, as in the case of osmotic experiments. The emulsion thus formed is more stable than that obtained when no membrane is used.

Spontaneous emulsification of drops of rancid olive oil in alkaline water solution has been described by Gad (16). Maday (17) has observed the dispersion of oleic acid floating on aqueous ammonia. Gad also investigated the best conditions for the emulsification of oils containing fatty acids in aqueous solutions of sodium carbonate. The dispersion in these instances has been rightly attributed to the interaction between the fatty acid and the alkali, resulting in the formation of soap, which disturbs the equilibrium at the interface. According to Freundlich (18): "The soap formed at the interface by the interaction of fatty acid and alkali strongly depresses the interfacial tension and causes the formation of small drops. These drops do not coalesce, since the layer of soap at the interface acts as protective colloid. Indeed, the adsorbed layer of soap favors every increase in the interface; it fixes it, as it were; for the interfacial tension is small, and when by mechanical means depressions and contractions of form are produced in the liquid to be dispersed, they do not, on account of the low tension, disappear again. Indeed, one may, with Donnan, assume an influence which actually opposes the coalescence of the drops, and even divides them up further."

From the point of view of our new colloid variables, we are dealing here with a phenomenon analogous to the boiling of liquids. Oleic acid is adsorbed at the water-oil interface and exerts a pressure, lowering considerably the interfacial tension. (10). When it comes into contact with NaOH its potential increases, its pressure becomes greater than the interfacial tension, and dispersion occurs, just as a liquid boils when its vapor pressure becomes greater than the external pressure.

The energy needed for increasing the pressure of the adsorbed molecule is supplied in this case by the reaction between the acid and base. A chemical reaction does not seem to be always necessary, because in some cases good dispersion is obtained with one solute only: e.g., sodium benzoate in nitrobenzol and water. The energy is then obtained simply by the passage of a substance from one phase into another in which its potential energy is smaller.

It can be readily shown by a rough calculation that the energy from the reaction between the fatty acid adsorbed at the interface and the alkali is sufficient to account for the surface energy formed during emulsification.

The amount of oleic acid adsorbed per square centimeter of surface (in the form of a monomolecular film) is about 1.5×10^{-7} gm. When this combines with alkali to form soap it liberates about 300 ergs of energy, which is certainly more than the surface energy per square centimeter of interface in an emulsion (the total surface energy of water is 118 ergs / $cm.^2$ and that of nitrobenzol 77 ergs/$cm.^2$ (19)).

The subject is amenable to exact treatment as follows: Let the oleic acid be dissolved in nitrobenzol, and let

E_1 = energy of reaction (H Ol) Nb + (Na OH) Aq.
H = heat liberated during spontaneous emulsification; then
λ_s = energy used in surface formation = $E_1 - H$.

E_1 can be calculated from
H_1 = heat of reaction (H 0l)Aq. + (Na OH) Aq.
H_2 = heat of reaction H 0l + Nb.
H_3 = heat of reaction H 0l + Aq.
because $E_1 = H_1 + H_2 - H_3$.

λ_s can also be calculated from the formula $\lambda_s = T^1 \frac{dP'}{dT'}$ which corresponds to Clapeyron's equation for the latent heat of evaporation. $\frac{dP'}{dT^1}$ is the change in surface pressure with pH, provided the latter may be taken as a measure of the colloid potential T′ at the interface. The practical difficulties would probably consist in determining the extent of surface formed during emulsification.

It should be noted that λ_s, the energy of emulsification in the presence of a colloid, is *not* the same as the energy of formation of a new surface, which is given by the Kelvin equation,

$$\left(\frac{\delta E}{\delta A}\right)_T = \sigma - T\left(\frac{\delta \sigma}{\delta T}\right)_A$$

The former corresponds to the total heat of vaporization $T\frac{dP}{dT}$ (vapor), while the latter represents the energy used in the formation of a vacuum

$$\left(\frac{\delta E}{\delta V}\right)_T = P - T\left(\frac{\delta P_{gas}}{\delta T}\right)_V$$

δV being the volume of the vacuum formed and P the external pressure.

The colloid engine. The colloid potential T′ has already been defined in terms of the expansion of the ideal colloid, just as temperature is often defined as a function of the expansion of the perfect gas. There is, however, a more satisfactory definition of temperature, as a work function: *It is possible to obtain work whenever a difference in temperature exists.* This is the principle on which all heat engines are designed. It can be shown that the colloid potential T′ may be used as a work function in exactly the same manner. The apparatus for measuring surface tension, shown in fig. 4. will serve to show the principle of a colloid engine which transforms chemical energy into mechanical work, at constant temperature, given a difference in colloid potential.

If the film of oleic acid on the surface of the water, between A and B, has a concentration of one molecule per 40×10^{-16} cm.^{2}, it exerts a pressure of about 17 dynes/cm. on the float B (11). On adding carefully a drop of alkali to the film, or bringing over it some ammonia gas, the oleic acid is changed into soap and the pH (or − log. H-ion concentration) of the surface rises from 1.3 to 9.5, approximately. At the same time the pressure P′ increases from 17 to 44 dynes/cms. which is the surface tension lowering due to a saturated film of soap. This, of course, is only a momentary change, because the soap formed soon reacts with the acid in the interior of the liquid and the film returns to its original state.

The system shown in Figure 4 can therefore be made to work as an engine, the strip of aluminum B, being the movable piston. With every increase in pH (addition of alkali) the pressure P′ of the film increases and the piston is moved from B to a new position C. On removing the source of alkalinity the pH falls and the piston resumes its former position.

This represents a "colloid" engine in its simplest form. In order to deduce the efficiency of the above "colloid" engine, we may take it through a reversible cycle, by making the external pressure on the piston B differ from P′ only by an infinitely small amount dP, and assuming the usual frictionless piston and complete insulation.

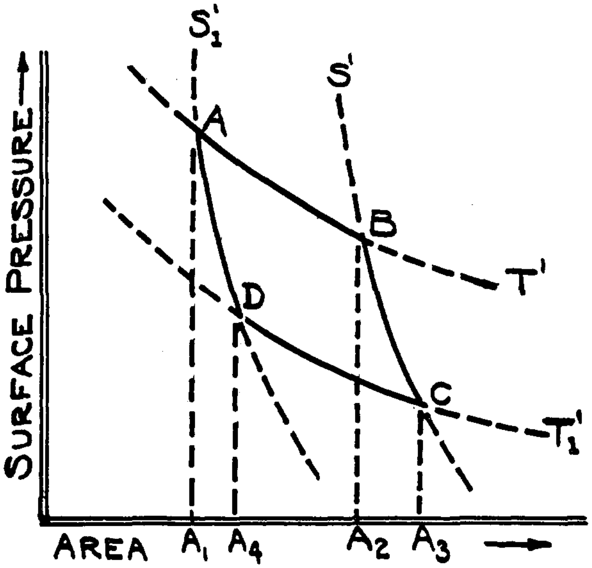

Fig. 9. The Colloid Analog of Carnot's Cycle

In figure 9 the coordinates represent the pressure and area of the surface solution of oleate we have just considered. The curves S′, S_1', represent adiabatic changes, the film being compressed or expanded without addition of energy. It is obvious that in expanding the film and doing work, the potential, T′, (or pH), of the oleate molecule will decrease, just as a gas cools when it expands doing work against outside pressure. Any one can convince oneself of this fact by blowing air (free from CO_2) through a soap solution, collecting the foam and comparing its pH with that of the original solution. Miss E. Laing, has measured the increase in acidity quantitatively (20).

The curves T' and T_1', are lines of equal potential, corresponding to isothermal changes in gases. We now carry the film through the following cycle: (*a*) expansion of surface from A_1 to A_2 at constant potential (with addition of alkali); (*b*) adiabatic expansion (without addition of alkali) from A_2 to A_3; (*c*) compression from A_3 to A_4 at constant potential (removal of alkali); (*d*) adiabatic compression from A_4 to A_1, back to the original state. The work done in this cycle is equal to the area *ABCD* the energy being derived from the transferrence of a certain amount of matter from a potential T' to a lower potential T_1'. By proceeding as in the case of Carnot's cycle, it can be shown that the maximum efficiency of the above engine is $\frac{T' - T'_1}{T'}$.

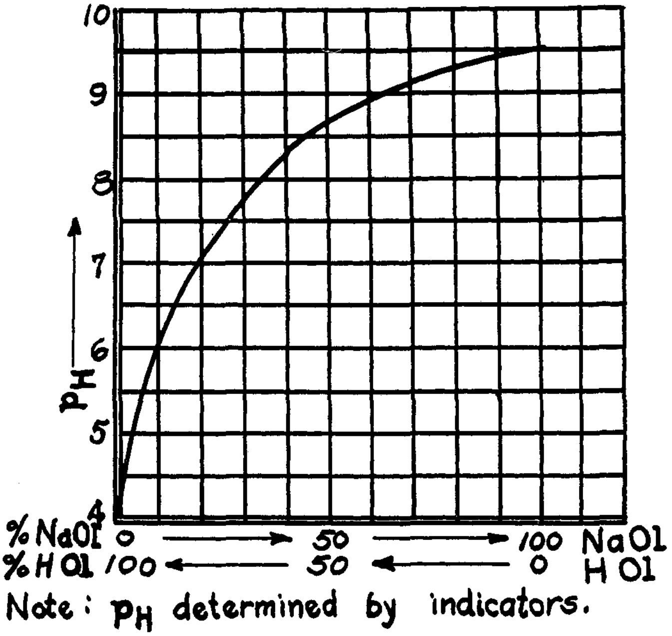

FIG. 10. pH OF 0.3 PER CENT SOLUTIONS CONTAINING VARIOUS PROPORTIONS OF NA Ol AND H Ol

That this formula agrees with the facts, at least qualitatively, will be evident from figures 10 and 11. Figure 10 shows the pH of a 0.3 per cent oleate solution, composed of different proportions of sodium oleate and oleic acid; Figure 11 represents roughly the variation of P′, the surface pressure of the oleate solution, with change in pH. It can be seen on comparing the two curves that by adding to an oleate solution of pH 5.5, one-fifth of its equivalent of sodium hydroxide, the pH will rise to 7.5 and the surface pressure from 21 to 34 dynes/cm. The same amount of alkali added to an oleate solution of pH 8.0 will increase its pH to 8.8, corresponding to an increase in surface pressure of 3.5 dynes cm. only. Since equal quantities of alkali added to the oleate solution at pH 5.5, and pH 8.0 represent (very nearly) equal amounts of energy, and since the pressure developed is a measure of the work obtainable, it follows that, other things being equal, the efficiency of the colloid engine is greater when it works at low potential.

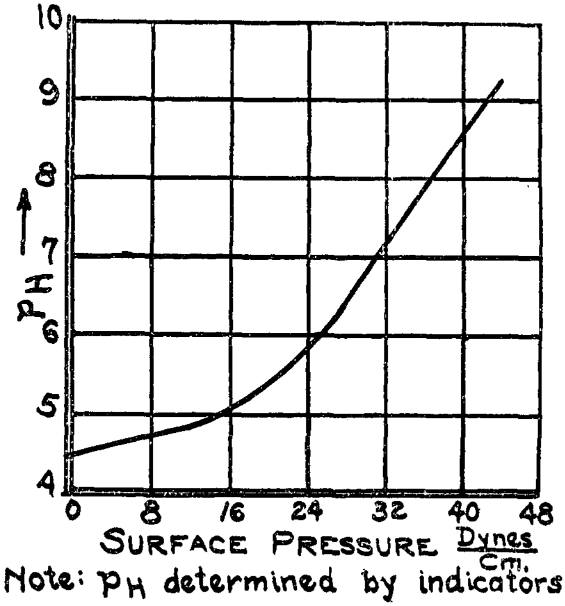

FIG. 11. CHANGE OF SURFACE PRESSURE WITH pH
(Analogous to change of gas pressure with temperature)

Colloid energy E′. The energy which causes the expansion and the pressure in the colloid system considered above is derived, in the light of accepted terminology, from the chemical reaction NaOH + oleic acid. We may leave it to linguistic experts to decide whether or not there are any grounds for speaking about a "chemical change" under colloid conditions, when no crystalline compound is present, when the "combination" between NaOH and oleic acid takes place in all proportions, and the change in properties is a gradual one. It is sufficient to point out that Krafft (21) has maintained that in soap solutions oleate radicles still exist as oleic acid, basing his opinion on the identity of the solidification points of soap sols and of the corresponding fatty acids. The present writer, as already mentioned, would prefer to describe colloids as "*physical compounds*," seeing that, in the case of surface films, for instance, the amount of sodium "combined" with the oleate radicle has been calculated by means of Gibbs' adsorption formula (22).

For our purpose all we need to bear in mind is that colloid systems store their energy not as heat energy, but as electrochemical energy; that a change in colloid volume or pressure will be accompanied *not by a thermal effect*, but by a "chemical" or electrical change. It has already been mentioned that when a soap film is expanded, it becomes more acid. Lord Kelvin (then William Thompson) calculated in 1859 that a soap film cools when it expands (23). Since the system is not "ideally" colloid a change in temperature may well occur, but if so, it is probably of secondary importance. Even when the increase in surface takes place in pure liquids, as in the spraying of water, electrical changes have been observed and measured (24). Again, when an ordinary insulating tape, which contains colloid material, is quickly unwound in the dark, there is no appreciable heat effect, but a distinct fluorescent light is emitted, due no doubt to the rapid extension and contraction of the colloid. Many other examples could be given showing the occurrence of electrical and chemical phenomena caused by sudden changes in the colloid variables P′ and V′.

Conversely, the electrification of a soap or saponin bubble causes an increase in its surface (24a), while the effect of temperature changes is either insignificant or causes the bubble to break. A potential difference across an interface leads to emulsification (24b) and chemical energy is transformed into surface energy in spontaneous dispersion.

Colloid Entropy S'. Following the example of thermodynamics the colloid potential T' has been defined by means of the ideal colloid, and also as a work function. Colloid entropy, S', like its thermal equivalent, may be defined by the integral $\int \frac{dE'}{T'}$. Its meaning may be gathered from the following material in quotation marks. It is a copy of a discussion of entropy to be found in Lewis and Randall's Thermodynamics (1923, p. 114) except that a soap film and two "reservoir solutions" at different pH have been substituted for Lewis and Randall's metallic spring and their two reservoirs at different temperatures.

"We will choose a standard system composed of a soap film and a reservoir of colloid energy. In employing this film-reservoir in conjunction with other systems, we are going to use the film as a source of work and the reservoir as a source or sink of colloid (electro-chemical) energy. It would be desirable to choose them so that the film will undergo no change in colloid potential (pH), and the reservoir will do no work during the processes we are about to consider.

"If the film is released and by some process gives up a part of its energy to the reservoir in the form of colloid energy, (e.g., transformation of oleic acid into sodium oleate, corresponding to an increase in pH due to contraction), we might measure the extent of this irreversible process by a pointer and scale attached to the film, or by the amount of energy given to the reservoir. We shall in fact take as the measure of the extent of this standard universal process a quantity which is proportional to the energy exchange, but not equal to it, for it is necessary to our purpose to consider also the colloid potential of the reservoir.

"To make this clear, we may consider a film, and two separate reservoirs, one at the colloid potential, (pH), T_1', and one at the lower colloid potential T_2'. If the film be released and a certain amount of colloid energy is given to the reservoir at T_1', and if then this same amount of energy is allowed to flow to the other reservoir at T_2', this latter is also an irreversible process. The net result is the same as if the energy developed by the film were given at once to the reservoir at lower pH. Now the sum of the degradation in two successive irreversible processes must be greater than that in either one alone; otherwise our definition would not be quantitative. Therefore, if we are to have a genuine scale of irreversibility, the transfer of energy from the film to the reservoir at higher pH must be regarded as a less irreversible process than the transfer of the same amount of energy from the film to the reservoir at lower colloid potential (pH).

"It will therefore be expedient to define the extent of irreversibility of our standard process by making it equal not to q, but to q'/θ', where q' is the energy transferred and q'/θ' is some quantity which quantitatively satisfies our definition of colloid potential. Moreover when the function is determined, it completes the quantitative definition of degradation. Let us consider a system composed of an ideal colloid in which, by definition

$$\left(\frac{\delta E'}{\delta V'}\right)_{T'} = 0$$

For such a colloid

$$P' = \theta' \left(\frac{\delta P'}{\delta \theta'}\right)_{V'}$$

and we see that at constant volume the pressure is proportional to T′, hence θ' is proportional to T′. This is all that we need to know in order to permit the complete identification of the "colloid-dynamic" scale with the ideal colloid scale."

In this particular system the transfer of energy is bound up with the transfer of ions, but we could construct a system involving a transference of electrons only, for instance involving an increase in the surface of a soap film on electrification. In that system no "matter" in the ordinary sense would pass from the higher to the lower colloid potential.

Some people may object to the introduction of several kinds of entropy, but Swinburne (25) has pointed out long ago that ordinary thermodynamic entropy is made up of a number of different entropies. When a perfect gas expands in vacuum its entropy increases and it is only by a stretch of imagination that we conceive this as an increase in *heat* entropy. Since we speak about several types of potential, we must also assume several entropies. The second law of thermodynamics, in the light of this extended entropy principle, is a special case of a more general statement, namely: *it is impossible to obtain work by transferring energy from a lower to a higher potential,* and is merely the negative of the definition of potential which states that "it is possible to obtain work by transferring energy from a higher to a lower potential."

Muscular action. The colloid engine enables us to understand the principle of muscular action. It has often been pointed out, that the contraction of a muscle is in some way connected with "surface" forces. Many theories have been put forward (26), but none in a form suitable for exact formulation. Galeotti's interpretation of the contraction mechanism as due to changes in pH is especially interesting. According to this author (27), "the anabolic phenomenon might consist in the formation of an organic acid within the contractile elements; the catabolic phenomenon in the dissociation of this acid and in the migration of the H-ions outside the contractile elements; with this mechanism the energy accumulated during the integrative period would be transformed into work. The H-ions, diffusing through the contractile elements and combining with the OH-ion of the sarcoplasma, would produce as heat of neutralization the heat which appears during the contraction of the muscle."

If this were true the analogy between the muscle and the *special type* of colloid engine working between different H-ion concentrations would be complete, but the energy changes in the active muscle, as Galeotti himself points out, must be more complex. It is known that lactic acid is formed during contraction and that surface films of muscle protein contract when the H-ion concentration increases. Although Gorter and Grendel (28) have found that surface films of muscle protein expand when alkaline and contract when acid, Verzar (29) claims that in order to produce artificial muscular contraction the H-ion concentration must be increased to pH 3, a much higher acidity than can be detected in the normal muscle. This objection, according to Meyerhoff, (30), is not valid, the production of lactic acid in the muscle being localized so that the reaction of the muscle as a whole need not be materially affected. The accurate work of Hill and Meyerhoff (30) shows, however, that the energy changes in the muscle are derived from the transformation glycogen $\rightleftarrows$ lactate, and not merely from the reaction H + OH (lactic acid $\rightleftarrows$ lactate) which supplies but a fraction of the total energy.

It should be clearly realized that, for the understanding of the dynamic principle of muscular activity, we need not bring into discussion the chemical changes which supply the energy, any more than we should have to know what fuel is burnt in a locomotive in order to understand the expansion of steam and the movement of the piston. A change in pH is not essential, either; a reversible oxidation-reduction reaction (e.g. glycogen $\rightleftarrows$ lactate) can equally well serve as a source of energy. In this case the H-ion concentration would still be of great importance, because the value of an oxidation-reduction potential depends greatly on pH (31). Furthermore, the working of the muscle is not dependent upon "surface" tension or upon the existence of a monomolecular layer. All that need be postulated for a mechanistic explanation of muscular action is an oriented arrangement of polar molecules, the distance between which is regulated by the potential T′.

THE ADSORPTION EQUATIONS

In the light of the new colloid variables P′, V′, T′, the adsorption equation assumes a simpler and more general form which is, in fact, nothing more than the equilibrium equation.

$$V\,dP = V'dP' \qquad \text{(i)}$$

V, V′ and P, P′ being the specific volumes and pressures of a given substance in two different regions. This general relation tells us, for instance, how the vapor pressure of a liquid varies with the external pressure, or with the osmotic pressure of the liquid, or with the swelling pressure of a gel, and many other things (see section on generalized thermodynamics). The relation (i) may be expressed in the form

$$\frac{dP'}{dP} = \frac{V}{V'} = \frac{C'}{C} \tag{ii}$$

C′ and C being the concentrations of the adsorbed substance in the surface region and in the bulk of the solution respectively.

Gibbs' equation (32)

$$\Gamma = - C \frac{d\sigma}{dP} \tag{iii}$$

is readily obtained from (ii) because

$$\frac{\Gamma}{\delta} = C'; \frac{F}{\delta} = P' \text{ and } dF = - d\sigma$$

where δ is the thickness of the surface region.

There are several reasons for preferring equation (ii) to (iii):

(a) Gibbs' equation deals with concentration per square centimeter and with tension per line, while equation (ii) refers to concentration per cc. and to pressure per area, which are more readily visualized.

(b) Gibbs' equation does not tell us what happens after the surface tension has reached its lowest value and we continue to increase the concentration of the solution; equation (ii) leads us to believe that the thickness of the surface region will change under those conditions.

(c) Gibbs' equation leads to impossible results when the $\sigma - C$ curve has one or more minima, but the new equation can be adapted to such cases (see the effect of latent energy, λ, below). Equation (iii) is generally combined with the van't Hoff or "gas" law for dilute solutions PV = RTM or dP = RTdC so that

$$\Gamma = - \frac{C}{RT}\frac{d\sigma}{dC} \qquad \Gamma = - \frac{}{RT}\frac{d\sigma}{d\ln C} \tag{iv}$$

Gibbs himself never used the adsorption equation in this form (33).

The exponential equations. If we assume the "gas law" at the surface region as well as in solution then

$$dP = RT\,dC \text{ and } dP' = R'T'dC' \tag{v}$$

Substituting these values of dP and dP′ in equation (ii), we have

$$R'T'\frac{dC'}{C'} = RT\frac{dC}{C} \quad \text{or} \quad R'T'\,d\ln C' = RT\,d\ln C \tag{vi}$$

which on integration gives

$$R'T'\ln C' = RT\ln C + \text{constant} \tag{vii}$$

If we write λ for the constant of integration, we have,

$$C' = C^{\frac{RT}{R'T'}}\,e^{\frac{\lambda}{R'T'}} \tag{viii}$$

λ being the energy necessary to transfer one mol of the adsorbed substance to the surface region; it is a constant at constant T′, but may have different values according to the configuration of the adsorbed molecules. This, together with the variation of T′ on dilution, could account for the several minima observed in $\sigma - C$ curves (34).

Introducing the activity coefficient, α, which corrects for divergence from the gas law, we obtain

$$C' = \frac{\alpha}{\alpha'}\,C^{\frac{RT}{R'T'}}\,e^{\frac{\lambda}{R'T'}} \tag{ix}$$

a more general equation than (viii).[3]

Boltzmann's distribution law

$$C' = \frac{p_1}{p_2}\,Ce^{\frac{\lambda}{RT}} \tag{x}$$

has been applied by Langmuir (35) to the distribution of molecules between phases and interfaces, p_1 and p_2 being defined as the *a priori probabilities* of the molecules in the two states under

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[3] An even better formula would be one taking into consideration the influence of curvature.

consideration. Formula (x) becomes identical with (ix) when $R'T' = RT$ and $\frac{\alpha}{\alpha'} = \frac{p_1}{p_2}$.

The adsorption equation derived from Boltzmann's distribution law is free from the objections raised to the Gibbs' equation. The new formula (VIII) is preferable to the Boltzmann formula because it tells us how the concentration at the surface changes with the colloid potential (or pH in the case of fatty acids). This factor *must* be taken into consideration, for when a solution of sodium oleate is diluted beyond a certain point its alkalinity decreases (pH falls), and this greatly affects the adsorption. Any equation which ignores this change in pH cannot adequately represent the effect of dilution on surface concentration. Nor can it be maintained that the fatty acids are peculiar in this respect: surface active substances are, *par excellence*, hydrolyzable compounds and the pH of their aqueous solutions changes with dilution. Even if the pH were not a variable, e.g. in non-aqueous solutions, some other factor representing the colloid potential would have to be taken into account.

Freundlich's equation

$$C' = a\, C^{\frac{1}{n}}$$

can be obtained from (viii) by assuming $R'T'/RT$ = constant = n, and $e^{\frac{\lambda}{R'T'}}$ = constant = a. We may also mention here *J. J. Thomson's formula* (36) derived by means of generalized dynamics, using the Hamiltonian and Lagrangian functions. It has since been deduced thermodynamically by *Michaelis* (37) and has the form

$$C' = C\, e^{-\frac{1}{\delta RT}\frac{d\sigma}{dC}}$$

But

$$-\frac{1}{\delta}\frac{d\sigma}{dC'} = \frac{dP'}{dC'} = R'T'$$

and the formula reduces to

$$C' = C\, e^{\frac{RT}{R'T'}}$$

In the light of (viii) this equation obviously is incomplete, for (viii) would require R′T′ to equal RT, and RT to equal λ at the same time.

The "gas law" in colloid systems. Conflicting opinions have been expressed recently concerning the validity of the relation

$$\text{force} \times \text{area} = \text{constant}$$

for surface films. Marcelin (38) found this to hold true for oleic acid films; Delaplace (39), working with benzyl benzoate films even extended the formula to FA = KT. N. K. Adam (40) confirms Langmuir's deduction that FA = RT when the concentration of the substance at the surface is very dilute, but maintains that the law fails even at moderate concentrations.

From the point of view of colloid dynamics, very dilute films in which the molecules are free to vibrate and possess heat motion are of little interest; but the question of the behaviour of saturated or nearly saturated surface solutions is of great importance. It should be pointed out, however, that for the particular purpose of testing the gas laws in colloids, a film of fatty acid is a very unsuitable system; it corresponds to a gas at very low temperature, and under such conditions even permanent gases are apt to present anomalies. It has been shown, in fact, by Windisch and Dietrich (41) that dilute solutions of fatty acids may be surface active or not, according to conditions. This may account for the difference in the findings of N. K. Adam and of Marcelin.

In order to obtain definite proof whether the ideal gas law can be applied to colloids or not, it is necessary to work with a system at high colloid potential: for instance, sodium oleate, instead of oleic acid. The gas law states that the pressure of the system is directly proportional to (a) the concentration, and (b) the temperature or potential. The following facts are indications that in many instances this law applies (approximately) to surface solutions and gels.

(i) Freundlich (42) shows that by differentiating his equation $F = AC^{\frac{1}{n}}$ with respect to C, we obtain

$$-\frac{d\sigma}{dC} = \frac{A}{n} C^{\frac{1}{n} - 1}$$

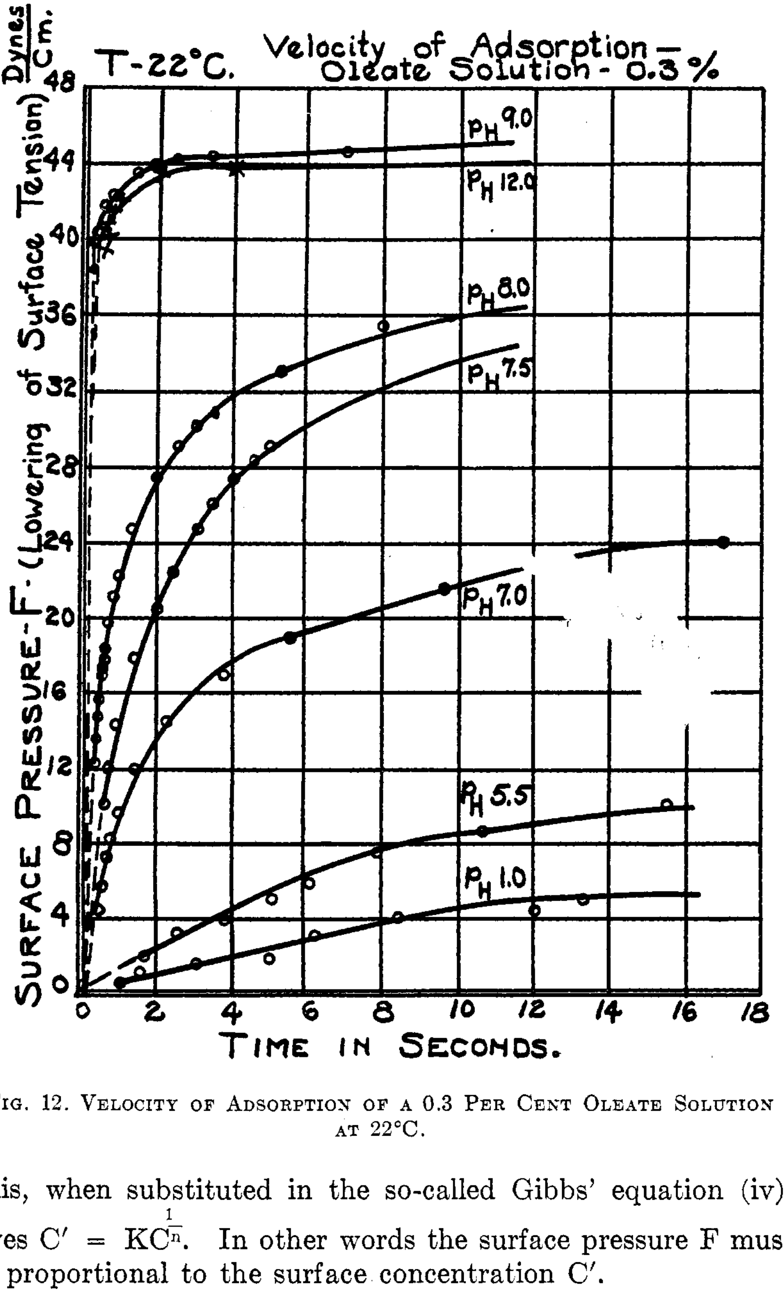

Fig. 12. Velocity of Adsorption of a 0.3 Per Cent Oleate Solution at 22°C.

This, when substituted in the so-called Gibbs' equation (iv), gives $C' = KC^{\frac{1}{n}}$. In other words the surface pressure F must be proportional to the surface concentration C'.

(ii) The change in the surface pressure of sodium oleate with time can be expressed by the formula

$$\frac{1}{t}\,\frac{F}{F_\infty - F} = \text{const.} \qquad \text{(xi)}$$

F_∞ being the maximum effect on the surface.[4] Differentiating with respect to time we have

$$\frac{dF}{dt} = k\,(1 - F)^2$$

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[4] Johlin (44) has investigated this phenomenon quantitatively by means of capillary rise measurements and has proposed a formula of the type $\sigma = \frac{a}{t^n}$, in which a is a constant. His results, when experimental conditions were such as to allow of accurate determinations, fit well with formula (xi). The capillary rise method is not quite suitable for adsorption-time measurements because at usual concentration (0.1 per cent) most of the total surface tension lowering takes place within the first few seconds, and it is impossible to take readings in that time; with dilute solutio[illegible]r per cent) on the other hand, long exposures to air are apt to modify t[illegible]ace film.

The curves sh[illegible]n figure 12 were obtained by Cofman and Sheely (unpublished data) by the "pressure in bubble" method. The apparatus used was the same as in figure 6, only in place of the bent tube used to measure the foam, a short vertical tube was substituted. The glass capillary had a radius of about $\frac{1}{200}$ cm. The air pressure was varied and the time between successive bubbles recorded.

The relation between radius of capillary, pressure, and surface tension of solution has been expressed in different ways (45). One of these is (46).

$$\sigma = \frac{r}{2}\,P\left(1 - \frac{2}{3}\,\frac{\rho\,r}{P} - \frac{1}{6}\,\frac{\rho^2\,r^2}{P^2}\right)$$

ρ being the density of the solution.

Since in our experiments $r = 0.0025$ cm. and p was never less than 100 dynes/cm. the correcting factors containing powers of r are insignificant and the formula reduces to

$$\sigma = \frac{r}{2}\,P$$

The sodium oleate solutions at lower pH were obtained by adding dilute hydrochloric acid. The curves with these solutions were not always exactly reproducible (see previous reference to surface active and surface inactive fatty acids).

Liepatoff (43) has found for the rate of change of adsorbed *mass* with time, for various substances, a general relation

$$\frac{dM}{dt} = k\,(a - \gamma\,M)^2,$$

γ being practically unity. This also supports the proportionality between concentration of adsorbed substance and colloid pressure.

(iii) The swelling pressure experiments bring further evidence pointing in the same direction.

(iv) If we measure the colloid potential in terms of pH, it appears to be proportional, within limits, to P', as indicated in Figure 11, provided the number of oleate molecules in a saturated film does not vary greatly with the pH.

All one can say at present, is that there exists some evidence in favor of the view that certain colloid systems are governed (approximately) by the law $P'V' = R'T'$. The ideal colloid, like the perfect gas, is non-existent.

CORRELATION OF COLLOID PROCESSES WITH ORDINARY PHENOMENA

Having shown that the new ideas may be used to derive exact laws which rule colloid systems, we shall proceed to discuss briefly a few other colloid phenomena and their equivalent crystalloid or thermal processes. It will be shown that the new concepts throw an interesting light on many obscure points, and open up new avenues of approach to many fields of inquiry.

Nerve conduction. This is not the place for discussing at length the physiological aspects of the new theory of colloids, but it may be pointed out that from the relations between the variables P', V', T', etc. it follows that a compression, or a chemical change, or other disturbance at a point in a colloid will cause a variation in pressure and potential. As Michaud (47) remarks: "one can hardly touch a gel without causing a difference in electric potential" which can be readily detected with a galvanometer. A disturbance produced in any manner in a colloid will propagate itself with a velocity depending on the elasticity and density of the medium. Just as in the case of propagation of sound-waves

$$\text{Velocity} = \sqrt{\frac{\text{Elasticity}}{\text{Density}}} \qquad \text{(xii)}$$

If the colloid is "ideal" and obeys the gas law $P'V' = R'T'$ we obtain by differentiating at constant T'

$$P' = -V'\frac{dP'}{dV'} = \text{Elasticity} \qquad \text{(xiii)}$$

Remembering that in colloids we must use surface instead of volume, we have

U, the area per unit mass, instead of 1/density.

Therefore

$$\text{Velocity of compression waves} = \sqrt{P'U}.$$

Both P' and U can be determined directly from measurements on surface films. No such determinations have yet been made apparently for the protein matter of the nerves, but for the proteins of the rabbit serum we have, from the data of du Noüy (34) $P' = 17$ dynes/cm. $U = 1.8 \times 10^6$ cm.^{2} Therefore

$$\text{Velocity} = \sqrt{17 \times 1.8 \times 10^6} = 56 \text{ m/sec. approximately.}$$

It is remarkable that the velocity thus calculated is of the same order of magnitude as the velocity of propagation of nerve stimuli in warm-blooded animals. This good agreement is no doubt largely fortuituous, there being large uncertainties in our calculation: (*a*) The values of P' and U for the protein matter of the nerve may be different from those of the serum, though Gorter and Grendel (28) have found the same value for U in the case of muscle protein; (*b*) the elasticity in formula (xiii) refers to conditions of constant potential. The wave of compression is probably an adiabatic phenomenon and a factor must be introduced in the calculation to take care of this, but this will not affect the order of magnitude of the velocity; (*c*) the colloid potential T' must be taken into consideration.

A critical survey of the literature on nerve conduction would fill a volume by itself. The reader may turn for information to Cremer (48) and Hallowell Davis' (49) recent review. It may be mentioned here that it is generally accepted by physiologists (50) that the nerve stimulus is propagated as "a molecular disturbance, wave-like in character.[5] Erlanger, Gasser and Bishop (51) by means of their cathode ray oscillograph have photographed the wave and shown it to be a potential wave. Sutherland (52) proposed the same formula (xii) for the velocity of transmission of stimuli, calculating the elasticity from Young's modulus for gels. Broemser (53) starting from quite different premises, reaches a similar formula in which the osmotic pressure of the liquid surrounding the nerve takes the place of the elasticity or the swelling pressure of gel. But we have seen that the osmotic pressure is identical with the pressure P' if the colloid is impermeable to the crystalloid constituents of the solution, which is assumed to be the case in nerves. Consequently the experimental support which Broemser brings for his formula serves to further strengthen formula (xii).

The semipermeable membrane. Theoretically, a semipermeable membrane is a thin wall separating two phases, allowing certain kinds of matter to diffuse through and not allowing others. Practically, a semipermeable membrane is a more or less ideal colloid (gel) or a rigid system having large surface, and therefore, possessing colloid properties.

Consider a gelatine gel such as was used in the swelling pressure experiments (fig. 3). If one side of the gel is in contact with a sugar solution and the other side with pure water then the gelatine acts as a semipermeable membrane.

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[5] The "all or none" principle which states that the stimulus traveling along a nerve has always the same intensity, is sometimes assumed to contradict the wave theory of transmission. In reality it is not incompatible with it, but requires additional hypotheses to account for the supply of energy on the way. A careful survey of the evidence in favor of the "all or none" principle shows that it is far from being completely verified. Many of the experiments which were originally supposed to prove this principle were shown by subsequent investigators to have been wrongly interpreted (54). At the present time the only support for the "all or none" principle, to the exclusion of all former "proofs" is that supplied by the experiments of Davis and his co-workers (54).

The immediate mechanism of semipermeability is here easily understood. The gelatin next to the sugar solution loses more water than that in contact with pure water. (Fig. 13). The swelling pressure in the membrane is therefore greater at A then at B and water flows from B to A. In consequence, water passes from the pure liquid to the solution. At equilibrium the sugar solution will be at a uniform pressure P_1, the water at another uniform pressure P_2. In the colloid region (membrane) the pressure will vary from P_1' at A, to P_2' at B. It is the rigidity of the colloid membrane allowing such a difference of pressure to exist in the colloid region which makes possible the measurement of osmotic pressure. What is measured in osmotic cells is not the osmotic pressure, but this difference in colloid pressure on the two sides of the membrane. Only when none of the solute particles pass through, which is seldom the case, is the difference in colloid pressure at A and B equal to the osmotic pressure. In the above experiment, where the semipermeable membrane is an elastic gel, the difference in pressure on its opposite sides is brought about by a change in the concentration of the colloid. If the semipermeable membrane is rigid, (e.g., ferrocyanide membrane) no change in concentration can occur The colloid potential T' or some other factor on which colloid pressure depends must then be different at A and B, in order to produce the necessary difference in pressure.

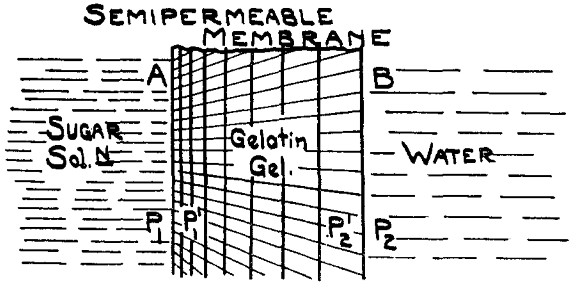

FIG. 13. ACTION OF A GELATINE GEL AS A SEMI-PERMEABLE MEMBRANE

Electro-osmosis and "thermo-osmosis." An obvious instance, where the difference in pressure on the opposite sides of the semipermeable membrane is caused by a difference in colloid potential, is electro-osmosis.

We have seen that the colloid potential depends on the electrochemical potential; an applied e.m.f. will, as a rule, produce a difference in colloid potential. This in turn will cause a difference in pressure on the two sides of the colloid region and liquid will flow across the membrane.

In order to fix our ideas, let the semipermeable membrane consist of a gel of sodium oleate, firmly fixed in a tube so that its volume cannot change (fig. 14). If a sufficiently high e.m.f. is applied, alkali will be liberated on that side of the membrane facing the positive pole and acid on the opposite side (55). The swelling pressure P′ will increase on the alkaline side (higher colloid potential) and will decrease on the acid side, thus producing the necessary conditions for osmotic flow.[6]

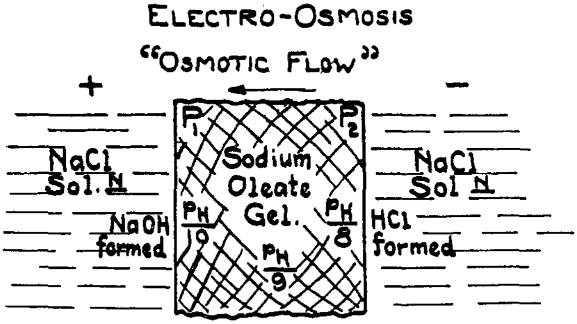

FIG. 14. ELECTRO-OSMOSIS

An analogy with a crystalloid system will make the matter clear. Suppose that a sugar solution is divided by a semipermeable membrane into two compartments, maintained at different temperatuess. The osmotic pressure will be greater on the warmer side ($P \infty T$) and pure solvent will flow from the cold to

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[6] In a gelatine gel water will flow from the positive to the negative side or vice-versa, according as the gelatine is on the acid or on the alkaline side of the pH.

the warm section. This is clearly the thermodynamic equivalent of electro-osmosis and might be termed thermo-osmosis.[7]

Stream potential and "stream temperature." If we reverse the procedure in the above experiment, that is, if the temperature in the two compartments is equal to begin with, and pure solvent is caused to flow across the semipermeable membrane by applying pressure on one side, then a difference in temperature will develop. This is accounted for in terms of "heat of dilution": we may call it "stream temperature," to conform with the name applied to the same phenomenon in colloid systems: the difference in colloid potential produced on the two sides of the membrane, measured as an electrical potential difference is called "stream potential."

Electrophoresis and "thermo-phoresis." When colloid particles are placed in a non-uniform electric field, they acquire, in general, a different colloid potential at front and rear and move according to circumstances, either with or against the impressed electric field. For reasons given in the paragraph on "imperfect colloids," it is not easy to give a simple colloid-dynamic interpretation of this phenomenon. However, even here it is possible to draw attention to an equivalent thermodynamic phenomenon:

A light body whose opposite sides are at different temperatures will move one way or the other. This happens for instance to the vanes in Crook's radiometer. The conditions in the two instances are not identical, but it is possible to construct an even closer analogy: Consider a small amount of sugar solution enclosed in a semi-permeable membrane. A temperature gradient in the surrounding liquid will set such a system in motion because, as in thermo-osmosis, water will penetrate at one end and be eliminated at the other.

The opposite phenomenon, namely the existence of a difference in temperature between the front and rear of an object moving in a gas or liquid, can hardly be doubted. The movement of a

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[7] In Soret's experiments—in the absence of a semipermeable membrane—a difference in temperature produced differences in the concentration of the solute present in solution. [Ch. Soret: Ann. Chim. Phys., **22**, 293 (1881); J. van't Hoff: Zt. Phys. Chem., **1**, 487 (1887)].

body produces compression ahead and rarefaction behind, and this must give rise to opposite temperature effects.

The colloid dynamic phenomenon that corresponds to the last mentioned thermodynamic effect is the potential difference due to falling particles.

The imperfect colloids. The new variables have not yet been applied to the subject of lyophobic colloids (such as gold sols). These systems may be described as "imperfect" colloids and are subject to more complicated changes. They can be compared with vapors as contrasted to permanent gases. A vapor, in a vacuous enclosure provided with a movable side, is an extremely unstable system: a slight change in temperature or pressure may cause the formation of a mist, or complete liquefaction (large decrease in volume).

Lyophobic colloids similarly are very sensitive to slight changes in the conditions of the dispersing medium. A trace of electrolyte may cause partial or complete precipitation of a suspension (large decrease in surface, or colloid volume).

The water-vapor analogy can be carried yet further: The presence of a permanent gas in an enclosure "stabilizes" the vapor. For instance, consider a cylinder provided with a movable piston, and which contains air mixed with water vapor in contact with liquid water. It is possible for the cylinder to contain water vapor under conditions of temperature and pressure which would condense pure water vapor. In the same way, a lyophilic (permanent) colloid may stabilize a lyophobic system.

The laws which define imperfect colloid systems are naturally more complex than those which apply to permanent or ideal colloids. It is perhaps because most of the work on colloids has dealt with those difficult systems, that the simple laws of colloid dynamics have for so long escaped detection.

One other factor complicates lyophobic systems, namely, the curvature of the surface, which apparently has an influence similar to that of gravitation in ordinary systems. For instance, any particle floating on the surface of water in a beaker is "attracted" towards the greater curvature near the edge, if only it approaches close enough to the sides of the beaker. The concentration of an adsorbed substance is also greater in the curved region. This is indicated by the following experiment which incidentally demonstrates the reversibility of the adsorption phenomenon. If a little foam (obtained by blowing air through a capillary into sodium oleate solution) is placed on the surface of pure water, it breaks immediately; if placed on soap solution of concentration greater than 0.02 per cent (at pH 10) the foam lasts a long time, but when the soap concentration is decreased, a point is reached when the bubbles on the flat portion of the surface break immediately while those near the edge persist.

Many of the considerations in the last sections are of a qualitative nature only, and must await quantitative confirmation. In view of their simplicity and symmetry the writer is confident that quantitative proof will be forthcoming and possibly in some cases can be obtained from existing data. It is pertinent to remark that one of the most widely quoted surface "laws," the Gibbs' equation, has had so far only semi-quantitative confirmation (33).

Extensive use has been made above of the analogy between colloid and crystalloid or thermal systems. Analogies are often deceptive and the fact that in this instance it has been possible to carry them so far without coming across obvious incompatibilities, leads one to suspect that there is some "natural law" which causes the variables P' V' T' to behave in the same manner as P V T etc. This point of view will be further enlarged in the next section on generalized thermodynamics.

GENERALIZED THERMODYNAMICS

Consider Gibbs' fundamental equation (56)

$$dE = TdS - PdV + F_n dM_n \qquad \text{(i)}$$

M_n and F_n stand for different kinds of substances and their corresponding "partial molal free energies." Although dE has no subscript it also stands for various kinds of energy; similarly P and V may represent either the pressure and volume of gas, or osmotic pressure and its corresponding volume. We have seen, too, that there are several T's and S's therefore we may write formula (i) more consistently

$$dE_n = T_n dS_n - P_n dV_n + F_n dM_n \tag{ii}$$

where n stands for any number of variables of the same type For instance M_n may represent the mass of gas, colloid, electrons, etc.; P_n may refer to gas pressure, colloid pressure, osmotic pressure, electromotive force, and so on.

The practical value of this scheme is best shown by an example: We may express a large number of apparently unrelated physical "laws" by simply combining the gas law $PV = RT$ with the general equilibrium condition

$$P_x dV_x = P_y dV_y$$

where x and y refer to different types of systems (electronic, molecular, macroscopic). For instance:

Vapor pressure and total pressure on the liquid

$$\frac{dP_v}{dP_l} = \frac{V_l}{V_v} \qquad \text{or} \qquad (VdP)_l = (VdP)_v$$

Vapor pressure and osmotic pressure. The osmotic pressure P_o corresponds to a decrease in internal pressure of liquid P_l; therefore

$$-dP_o = dP_l$$

Now,

$$-P_o = \frac{RT}{V_l} \ln P_v + \text{const.} \qquad \text{or} \qquad -dP_o = dP_l = \frac{RT}{V_l}\frac{dP_v}{P_v}$$

hence

$$(VdP)_l = (VdP)_v$$

Vapor pressure and swelling pressure of gels. The formula is identical with that for osmotic pressure (57).

The adsorption formula

$$\Gamma = -\frac{C}{RT}\frac{d\sigma}{dC}$$

has already been shown to be a special case of $(VdP)_l = (VdP)$ surface.

Nernst's equation for electromotive force. In a cell with a hydrogen electrode the relation between e.m.f. and gas pressure is

$$E = E_0 + \frac{RT}{Fr} \ln p \quad \text{or} \quad Fr.dE = \frac{RT}{P} dP \quad \text{or} \quad (Fr.dE) = (VdP)_{gas}$$

Here Fr. stands for one Faraday of electricity and, in this formula, it is apparently a volume and not a quantity factor.

Atmospheric pressure and altitude (h)

$$\frac{1}{P}\frac{dP}{dh} = -\frac{g}{RT} \quad \text{or} \quad -VdP = gdh \quad \text{or} \quad (PdV) = (gdh)$$

In the same way the Clapeyron equation, the Gibbs-Helmholtz equation for the temperature coefficient of e.m.f., the Richardson thermionic equation (58), and the equation giving the latent energy of emulsification, can all be expressed by the general formula

$$\frac{\lambda}{dV_n} = T\frac{dP_n}{dT_n} - P_n$$

λ being latent energy.

No doubt the time is not distant when all physical laws will be conveniently tabulated in groups instead of being expressed in many different ways, as it is now the custom.

Formula (ii) also throws light on the 3rd law of thermodynamics. The total entropy of a system will be zero only when *all* its potentials, not temperature alone, become zero. If any kind of difference of potential exists at the absolute zero of temperature the equalization of that potential difference will cause an "increase in entropy."

Entropy and time. One of the chief drawbacks of thermodynamics has been its neglect of the time variable. This may be readily overcome by multiplying the left side of the equation (ii) with $\frac{dt}{dt}$, t standing for *time*. In the equations that follow we shall, for convenience, drop the n's. We have

$$\frac{dE}{dt} dt = T\,dS - P\,dV + F\,dM \qquad \text{(iii)}$$

dE/dt, which we shall denote henceforth by X, is a "power" function. Equating (iii) to zero, we obtain

$$(F\,dM - P\,dV) + (T\,dS - X\,dt) = 0 \qquad \text{(iv)}$$

This is a *symmetrical* equation, with time as a variable. The first thing to be noted is that the relation between entropy and time corresponds to that between mass and volume: *entropy extends in time, just as mass extends in space. The events which compose our four-dimensional world can be separated into a space component (matter), and a time-component (entropy).*

A little reflection will show that, looked at in this way, the concept of entropy becomes more rational and easy to grasp, and fits in with all that is known about it. Entropy is always associated with an *event,* extending in *time.* The attempt to associate entropy with a body, or system, is responsible for the great difficulties which still surround that subject. The entropy of a system has been expressed in terms of the logarithm of probability. It may be possible to express the mass of an hour of time at a given place, in terms of the logarithm of probability, but such a concept would not be a simple one.

The entropy of the world is constant. This is a restatement of the 2nd law of thermodynamics in a new and preferable form—placing it in the same category as the first law—the conservation of energy. Naturally, moving along the time axis we come across more and more entropy in the same way as we encounter more and more matter as we move along in space. At a given time there are places in the world where there is no matter, and equally, at a given place there are times at which there is no entropy: the system in that space is at rest.

Living and lifeless systems. The great value of equation (iv) lies in its simplicity and symmetry, which should prove valuable in deducing new relations among its constituent variables. In the first place, it supplies a simple thermodynamic distinction between animate and inanimate processes.

When dealing with inanimate systems, provided we know the *usual* variables involved, it is possible to predict what will take place. An entropy-time curve, showing the amount of entropy in each unit of time, may then be plotted in advance.

The curve AC (fig. 15) may represent, for instance, the entropy-time curve of a simple chemical reaction, and the irregular line DEFGH (or rather the area under it) may tell us the behaviour of a more complicated system. It may be said in such instances that *entropy is fixed in time* or at least its position is determinable with our present limited knowledge. Their counterpart is a material system at equilibrium in space. But, as we know, matter can change its position in space and the question arises, what would happen if entropy changed its position in time? Obviously, if entropy were shifted along the time axis, removed from one moment and heaped on to another, then the course of events would be changed.

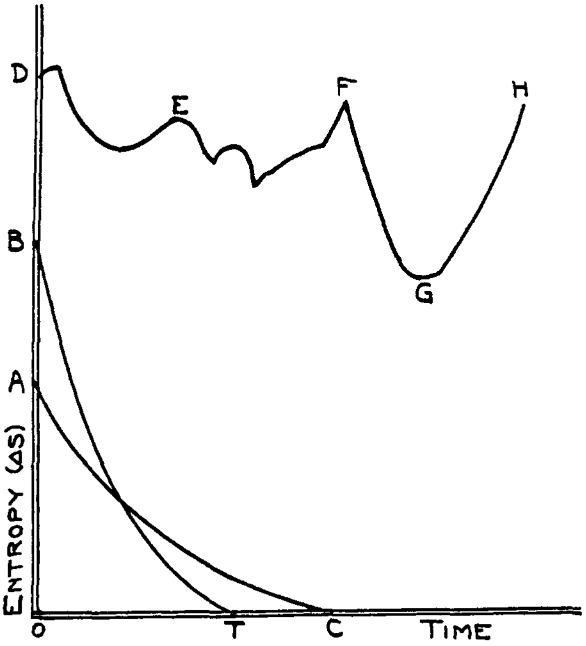

FIG. 15. ENTROPY-TIME DIAGRAM; ENTROPY FIXED IN TIME

Consider, for instance, a watch: The gradual unwinding of its spring during a period of time, say 24 hours, is an irreversible event with which is associated a definite amount of entropy. Let the horizontal line BKL (fig. 16) represent the distribution of entropy in time when the watch is left by itself. If at a moment, K, the watch is stopped by an external agency, it comes instantly to equilibrium and the entropy change falls to zero. At another moment, N, one may set the watch-spring loose, so that the whole of its energy is liberated at once. The entropy of the event will at that instance jump up (NFP) and then quickly fall to zero as the energy is dissipated into heat.

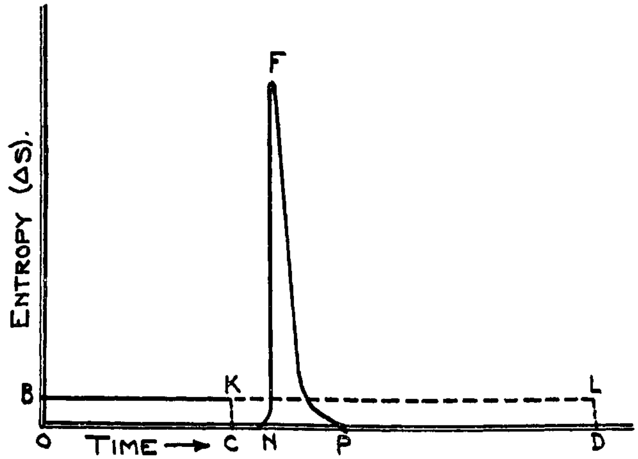

FIG. 16. ENTROPY-TIME DIAGRAM FOR A WATCH SPRING, AS AFFECTED BY EXTERNAL FORCES

In the event just considered the distribution of entropy in time was changed by the intervention of external forces. Suppose, however, that the movement of entropy were to take place in an isolated system. Such a system could defer its movement and its action and behave in an entirely erratic manner, judged from the point of view of ordinary inanimate systems, in which entropy is fixed in time. *It would be said to possess life.*[8]

If a catalyst were present in the system undergoing the chemical change whose entropy is represented by area under the curve *AC*

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[8] From the psychological angle, memory and foresight are in some way connected with the movement of the *life function* along the time axis and should be compatible with such a system.

(fig. 15), then the rate of reaction would be increased. The entropy-time distribution would be expressed by the steeper curve *BT*, instead of the curve *AC*. The areas under the two curves denote the total entropy of the reaction and are therefore equal; only the distribution of entropy in time is changed by the presence of catalyst. A system containing catalysts or enzymes appears to be intermediate between living and lifeless; its entropy may be considered to move in a simple manner. The increase in the rate of reaction can be taken (under given conditions) as a measure of the "activity" or mass of active catalyst present. This would be expected from the symmetry of equation (iv) since we know that (under given conditions) the change of matter in time and space is a function of the entropy (Δs).

Going one step further, it may be assumed that the more complicated shifting of entropy along the time axis, which distinguishes living systems, is also predictable in terms of a function M_x, which has the dimension of mass, but is not matter in the ordinary sense of the word. The practical aspect of this reasoning lies in the suggestion of a quantitative measure of the *life factor*. Life may be measured quantitatively by its effect on the entropy of a system. In two systems otherwise identical, but one containing life the entropy-time distribution will differ and from this difference the amount of "life" may be deduced. The subject is evidently one for experimental investigation. For simple changes which take place in the presence of both living and lifeless organic matter, e.g., yeast fermentation or liquefaction of gelatine by bacteria, some data bearing on this point should not be difficult to obtain. Even in higher animals if the nerve of one limb were severed or anaesthesized and the other not, the difference in the entropy-time distribution for the two limbs would give an indication of the amount of "life" transmitted by the intact nerve. Blood circulation would have to be prevented and other precautions taken to keep the conditions of the two limbs identical, except for the nerve impulse received by the one and not by the other. This method would not work if the reactions which supply muscular energy were of an "explosive" nature, as it has sometimes been suggested. The method presupposes that the reactions are reversible, which is very likely, from what we know of the transformation glycogen ⇄ lactate.

It is not within the province of thermo-dynamics, or generalized dynamics, to give a "mechanical" interpretation of the variables involved in its formulae. Nevertheless, those who like to have a pictorial representation of abstract factors, and who wish to speculate as to the possible "nature" of the life function, M_x will find the following passage from Eddington's Mathematical Theory of Relativity, of interest. "A particle of matter is a structure whose linear extension is time-like. We might perhaps imagine an analogous structure ranged along a space-like track. That would be an attempt to picture a particle traveling with a velocity greater than that of light; but since the structure would differ fundamentally from matter as known to us, there seems no reason to think that it would be recognized by us as a particle of matter, even if its existence were possible. For a suitable chosen observer a space-like track can lie wholly in an instantaneous space. The structure would exist along a line in space at one moment; at preceding and succeeding moments, it would be non-existent. Such instantaneous intrusions must profoundly modify the continuity of evolution from past to future. In default of any evidence of these space-like particles, we shall assume that they are impossible structures (59)."

In our daily experience, is there indeed default of "structures" not recognized by us as matter, "instantaneous intrusions non-existing at preceding and succeeding moments, which profoundly modify the continuity of evolution from past to future"?

> "Bist du beschränkt, dass neues Wort dich stört?
> Willst du nur hören, was du schon gehört?
> Dich störe nichts, wie es auch weiter klinge,
> Schon längst gewohnt der wunderbarsten Dinge"
> —Goethe's "Faust" (pt. II, Dark Gallery Scene).

ACKNOWLEDGMENTS—AND AN APOLOGY

The writer wishes to thank Mr. J. R. Powell, Assistant General Manager, Armour and Company 31st Street Auxiliaries, for permission to publish some of the results of work carried out in

the Armour Research Laboratory. He is greatly indebted to Prof. W. P. Davey, of The Pennsylvania State College, without whose prompting this article would not have been written.

An apology is undoubtedly due to the reader. The writer feels that he has covered rather hastily a large unexplored region, and has often ventured into strange fields with many pitfalls awaiting him; in consequence, his views are probably not entirely free from errors. The only excuse he can offer for this recklessness is that he has always tried to submit his deduction to experimental proof and that the method used requires intrinsically few arbitrary assumptions; moreover, if there be serious mistakes in his deductions, the writer feels confident that, in view of the fact that he is not yet an authority, they will not be accepted as gospel truth, but will be exposed forthwith, as a warning to all rash theorizers thereafter.

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