and also the constancy of a, we must believe that nickel and sodium chloride behave in much the same way in adsorbing oxygen and nitrogen.

Further study of the phenomenon is needed before even an hypothesis for the mechanism can be made. In spite of the conflicts introduced by the ionic mechanism, it still seems more likely than an electronic mechanism.

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The Mechanics of the Condensation of Gases

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An attempt is made to explain the phenomenon of condensation of the gas, on the basis of the classical mechanical model of a gas. The condensation of the gas is connected with a change in the topological structure of the energy surface in the $6N$-dimensional phase space. This occurs when the total energy is zero. The agreement with experiment is satisfactory.

1. INTRODUCTION

THIS paper is based on the assumption of a classical model for a gas: It is composed of N point masses attracting and repelling each other; the force between two molecules is derived from a potential $ar^{-n}-br^{-m}$, where r is the distance between them; a, b, n, m are positive constants (which we will consider as known from experiment) with $n>m$. We neglect internal degrees of freedom of the molecules. The differential equations governing the motions determine a family of trajectories in the $6N$-dimensional phase space. If the total energy of the system is fixed, equal to c, the trajectories are restricted to a $(6N-1)$-dimensional manifold $M(c)$. It is to be remembered that, since in a gas there is never any information as to the initial conditions of the individual molecules, this manifold (and the volume, see Section 5) is the only thing that is physically given.

The structure of $M(c)$ is analyzed for varying c and it is found that, for $c\geqq 0$, $M(c)$ has one type of structure, while for $c<0$ the structure is quite different. Roughly speaking, at $c=0$, $M(c)$ collapses from an infinite manifold ($c\geqq 0$) to a finite manifold ($c<0$). It would seem appropriate to identify the energy value zero (where the structure of the manifold changes) with a state of transition of the whole system. This transition would be of the nature of a phase transition, like condensation, for the gas. Accordingly we could say that a transition will take place when the total energy is zero. This last hypothesis combined with the usual statistical method leads to results which can only partially be checked by experiment. One has to make additional assumptions in order to obtain explicit expressions for the transition temperatures. These computations have been made for a number of gases, and a good agreement with experiment is found.

2. ANALYSIS OF $M(c)$

We consider a gas of N particles (x_i, y_i, z_i), $(i=1, 2, \cdots N)$ in xyz space. All masses are assumed to be equal to m. The distance between particle i and particle j is denoted by r_{ij}. With the mutual interaction between the molecules given by $f(r)=ar^{-n}-br^{-m}$ the total potential energy is

$$V=\sum_{i\neq j}\left(\frac{a}{r_{ij}^n}-\frac{b}{r_{ij}^m}\right). \tag{1}$$

The energy integral is given by

$$\frac{1}{2m}\sum_i (p_{x_i}{}^2+p_{y_i}{}^2+p_{z_i}{}^2)+V(x_1,\cdots z_N)=c. \qquad (2)$$

Here $p_{x_i}=m(dx_i/dt)$, etc. Equation (2) defines the locus $M(c)$ in the $6N$-dimensional space of the variables $(x_1,\cdots z_N, p_{x1},\cdots p_{zN})$.

Since the p's appear here only as the sum of their squares, it follows that the structure of the locus $M(c)$ is determined by the structure of the locus $V\leqq c$ in the space of $(x_1,\cdots z_N)$. The word structure is meant here in the sense of topology, i.e., of properties invariant under a continuous one-to-one transformation with continuous inverse.[1, 2] However, we shall also remark on metrical properties.

To determine the structure of the locus $V\leqq c$ we first consider that of $V=c$, from which the former can be deduced. To that end we consider a ray from the origin in the $(x_1,\cdots z_N)$ space:

$$\begin{gathered} x_i=\lambda_i t, \quad y_i=\mu_i t, \quad z_i=\nu_i t, \\ \sum_i (\lambda_i{}^2+\mu_i{}^2+\nu_i{}^2)=1. \end{gathered} \qquad (3)$$

This ray meets the hypersurface $V=c$ in points determined by the equation

$$(\alpha/t^n)-(\beta/t^m)=c, \qquad (4)$$

where

$$\begin{gathered} \alpha=\sum a/\rho_{ij}^{\,n}>0, \quad \beta=\sum b/\rho_{ij}^{\,m}>0, \\ \rho_{ij}=[(\lambda_i-\lambda_j)^2+(\mu_i-\mu_j)^2+(\nu_i-\nu_j)^2]^{\frac{1}{2}}. \end{gathered} \qquad (5)$$

It follows that for $c\geqq 0$ there is in general exactly one intersection point, while for $c<0$ there may be two points or one or none. There are certain exceptional rays which will never meet the hypersurface $V=c$, namely, those for which at least one $\rho_{ij}=0$. These rays correspond to collision configurations, configurations in which two or more molecules coincide. Because of the energy integral, such configurations can never arise for any finite value of c. The family of exceptional rays forms a point set of $3N-3$ dimensions and will hence have only a slight effect on the structure of the $3N$-dimensional locus $V\leqq c$.

3. STRUCTURE OF $M(c)$ FOR $c\geqq 0$

In this case the above analysis shows that the locus $V\leqq c$ has the structure of the exterior of a $(3N-1)$-dimensional sphere (minus certain exceptional rays, corresponding again to collision). It follows that the energy integral defines a locus $M(c)$ which is unbounded in all directions with respect to the configuration coordinates $(x_1,\cdots z_N)$. This type of manifold may be realized as follows:

Start with the $(6N-1)$-dimensional sphere

$$\sum (p_{x_i}{}^2+p_{y_i}{}^2+p_{z_i}{}^2)+\sum (x_i{}^2+y_i{}^2+z_i{}^2)=1. \qquad (6)$$

Now perform an inversion by reciprocal radii in the hypercylinder

$$\sum (x_i{}^2+y_i{}^2+z_i{}^2)=1.$$

That is, we replace each point $(x_1,\cdots z_N, p_{x1},\cdots p_{zN})$ by the point $(x_1',\cdots z_N', p_{x1}',\cdots p_{zN}')$, where

$$\begin{gathered} p_{x1}=p_{x1}',\ \cdots p_{zN}=p_{zN}'; \\ \frac{x_1}{x_1'}=\frac{x_2}{x_2'}=\cdots=\frac{z_N}{z_N'}; \\ x_1x_1'\geqq 0,\ \cdots z_Nz_N'\geqq 0; \\ (x_1{}^2+\cdots+z_N{}^2)(x_1'^2+\cdots+z_N'^2)=1. \end{gathered} \qquad (7)$$

Finally remove the points on the exceptional rays. The result is a locus having the same topological structure as $M(c)$ and having the same position[3] in the phase space as $M(c)$.

4. STRUCTURE OF $M(c)$ FOR $c\leqq 0$

Here we need a special lemma whose proof is omitted:

Lemma. *There is a constant* $-\delta$, $\delta>0$, *such that for* $-\delta<c<0$ *Eq.* (4) *has exactly two distinct roots on every non-exceptional ray. The least possible value of* $-\delta$ *is*

$$-\delta=\left(1-\frac{n}{m}\right)\left(\frac{m}{n}\right)^{n/(m-n)}\left(\frac{b^n}{a^m}\right)^{1/(n-m)}.$$

Suppose now $-\delta<c<0$. Then $V\leqq c$ holds between two hypersurfaces which are topologically equivalent to two concentric spheres. (Again exceptional rays must be removed.) Thus in this case the energy integral defines a locus which is essentially bounded. It becomes unbounded only

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[1] For references to topology, see P. Alexandroff and H. Hopf, *Topologie I* (Berlin, 1935), especially pp. 1–22.

[2] See W. Kaplan, Am. Math. Month. **59**, 316–323 (1942).

[3] See reference 1, p. 2.

in those directions which correspond to the exceptional rays. A further analysis shows that the structure of the manifold is the same as that of the topological product of a $3N$-dimensional sphere and a $(3N-1)$-dimensional sphere (minus certain exceptional points); that is, the same as the locus

$$\sum_{i=1}^{3N} u_i^2 = 1, \quad \sum_{i=1}^{3N+1} v_i^2 = 1$$

in the space of the variables $(u_1, \cdots u_{3N}, v_1, \cdots v_{3N+1})$. For $c \leqq -\delta$, $M(c)$ will collapse even further and shrink within itself until for $c=-\epsilon$, where $-\epsilon$ is a certain constant not yet determined, $-\epsilon > -\infty$, $M(c)$ disappears.

The value $-\delta$ is a second critical value for the manifold $M(c)$, but its physical significance has not been completely determined. Mayer and Mayer[4] in their statistical theory of condensation also obtain a second characteristic temperature. It is possible that our second change for $c=-\delta$ is related to their T_m.

5. $c=0$ AS A CRITICAL VALUE FOR THE ENERGY

The fundamental hypothesis introduced is that when the total energy of a gas changes from a small positive value to a small negative value a transition can occur. It is further assumed that this transition is the condensation of the gas. On the basis of the model assumed and these assumptions we can give the following description of the mechanism of condensation.

The molecules are pictured as mass points. Because of the nature of the potential energy function, a collision in the strict sense, i.e., some $r_{ij}=0$, is impossible. (Collisions in the sense of molecules coming so close together that they exert considerable forces upon each other will of course occur. In statistical mechanics one sometimes represents such a collision by a discontinuous collision between non-interacting elastic spheres, of finite radius; this is useful for computations, but does not represent the actual physical state of a collision.) This means that, if the walls of the containing vessel were not present, the motion of the gas particles would be completely without singularity; any motion would be determined by analytic functions for all time. The motion of the system would be represented by a smooth curve on the energy surface and it would be natural to correlate the properties of the system with the properties of this curve as a whole.

In order to take the walls into account, we notice first that collisions with the walls do not change the energy of the colliding molecules, and hence the total energy remains unchanged. The only effect of the walls is a discontinuous one: Every particle on reaching the wall changes its direction continuously but conserves its energy. Since the collisions with the walls are isolated events, between collisions the system will move with regularity as before. On the energy surface this means the following: The surface is cut off by a certain boundary (corresponding to a certain volume) so that the allowed portion is finite in extent. (Note that the velocity coordinates are always bounded to start with, owing to the energy equation.) A trajectory now appears as a curve which is smooth until a collision with the wall takes place. Thus the trajectory jumps from one point of the boundary of $M(c)$ to another point and starts from there another continuous path until again a collision with the walls takes place, and this process is repeated *ad infinitum.* Thus one trajectory appears as a multitude of pieces of different trajectories, no two pieces intersecting. The effect of the walls may accordingly be described as one of continuously varying the initial conditions.

Now the question is how the structure of the whole manifold $M(c)$ is related to the character of this multitude of trajectories and, in turn, how these are related to the structure of the gas. The explanation offered is as follows: If $c \geqq 0$ the surface is infinite in extent in a very strong sense, while when $c<0$ the infiniteness occurs only in a small set of directions. It follows, therefore, that when $c \geqq 0$ the probability of any orbit's leaving the finite part of the energy surface in a given time interval is large. Hence for most initial conditions the probability of meeting the walls in a given time interval is large. If $c<0$, the orbits will wander around for a long interval before reaching the boundary. In fact there is a very large probability that in a given time interval the

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[4] J. E. Mayer and M. Goeppert-Mayer, *Statistical Mechanics* (John Wiley & Sons, Inc., New York, 1940), p. 308. J. E. Mayer and S. F. Harrison, J. Chem. Phys. 6, 87 (1938).

orbits remain completely in a bounded part of space, and never meet the boundary at all. Thus the discontinuous orbit is of a different nature, the system shows much less tendency to spread out, the gas condenses.[5]

It may be remarked that if the walls of the vessel are introduced as a force field, instead of in the qualitative way as above, the essential features of the argument are preserved. The case $c=0$ still appears as a critical value for the energy.

6. APPLICATION OF THE CRITERION

In order to test the validity of the assumptions made, a number of calculations have been made to compare the values obtained, on the basis of this theory, with the experimental values. In order to carry through the computation, one has to make some very strong additional assumptions, but it is reasonable to assume that at least the order of magnitude should be predicted correctly, if the proposed criterion has any value whatsoever.

We assume a gas of $N=M^3$ molecules in a cube of volume A^3 and we assume that the molecules form, as a first approximation (to be generalized below), a cubic lattice placed at the points $(h\alpha,\ k\alpha,\ l\alpha)$, where $h,\ k,\ l=0,\ \pm 1,\ \cdots$ and $\alpha=A/M$ is the nearest distance between molecules. We use the potential function V as given above, but now use numerical values for the constants: $n=9$, $m=6$, a, b as given for various gases in Table I.

The total potential energy of this lattice can then be written as

$$V=\frac{N}{2}\left(\frac{aB}{\alpha^9}-\frac{bC}{\alpha^6}\right) \tag{8}$$

with

$$B=\sum\frac{1}{(h^2+k^2+l^2)^{9/2}},\quad C=\sum\frac{1}{(h^2+k^2+l^2)^3}. \tag{9}$$

Assume now that we have one mole of gas of volume v, so that $N=N_0$, Avogadro's number. Then, since $\alpha=A/M$, the potential energy can be written as

$$V=\frac{N_0^3}{2v^2}\left(\frac{aBN_0}{v}-bC\right). \tag{10}$$

The total kinetic energy we assume to be $3N_0kT/2$; this assumption defines the temperature T for this theory. The condition: kinetic energy + potential energy = 0 then becomes

$$\tfrac{3}{2}N_0kT=\frac{N_0^3}{2v^2}\left(bC-\frac{aBN_0}{v}\right) \tag{11}$$

or

$$T=\sigma b\left(\frac{1}{v}\right)^2-\zeta a\left(\frac{1}{v}\right)^3 \tag{12}$$

where

$$\sigma=\frac{N_0^2C}{3k},\quad \zeta=\frac{BN_0^3}{3k}. \tag{13}$$

If we determine the numerical values of the constants σ and ζ assuming a cubic lattice, we find

$$\sigma=7.5117\times 10^{63},\quad \zeta=3.5939\times 10^{87}. \tag{14}$$

This leads to predictions of the critical temperature T_c from the known values of the critical volume v_c. The results are listed in column three of Table I.

Now the assumption of a cubic lattice is not justified by experimental evidence. A better assumption would be that for all gases the spatial distribution is a unique one up to a similarity transformation. This is really equivalent to assuming the law of corresponding states, which, in a sense, is already implicit in this computation since we work with a two-parameter potential function. It would follow that a formula like (12) would still hold, with the same σ and ζ for all gases; however, their values are no longer given by (14). [This follows by the same reasoning that led to Eq. (4).] What the exact spatial structure is remains to be determined; the values of σ and ζ of course depend on that structure.[6] It is interesting to note that Lennard-Jones and Devonshire[7] in a series of papers on the theory of dense gases and liquids have worked with a

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[5] A complete proof of the asserted properties of the orbits would require a delicate use of an ergodic-like hypothesis or one of metrical transitivity. See G. D. Birkhoff, Proc. Nat. Acad. Sci. **17**, 650–660 (1931), and J. C. Oxtoby and S. M. Ulam, Ann. Math. **42**, 874–920 (1941).

[6] In order to compute σ and ζ one must have some information about the distribution of the molecules in a dense gas. The actual computations would thus have to be along the lines indicated by Mayer and his co-workers. Cf. J. E. Mayer and E. Montroll, J. Chem. Phys. **9**, 2 (1941).

[7] J. E. Lennard-Jones and A. F. Devonshire, Proc. Roy. Soc. **A163**, 53–70 (1937); **165**, 1–11 (1938); **169**, 317–338 (1939); **170**, 464–484 (1939).

TABLE I. Compilation of results. Column 3 is based on a cubic lattice assumption. Columns 5 and 7 are based on the maximum point assumption.

	1 $a\cdot 10^{82}$	2 $b\cdot 10^{60}$	3 T_c pred.	4 T_c obs.	5 T_c pred.	6 v_c obs.	7 v_c pred.
Hydrogen	5.1	17.8	25	33.3	39	64.9	47.6
Helium	.51	2.37	4.4	5.3	9.3	57.8	35.8
Neon	3.5	14.5	43.6	44.5	45.1	41.7	40.0
Nitrogen	132	227	145	126	122	90.1	97.0
Argon	76.8	170	161	151	151	75.2	75.2
Krypton	193.6	346	219	211	200	107	93.5
Xenon	583	877	367	290	360	114	111

similar model and found it to give a consistent theory and good agreement with experiments.

In order to determine the best values of σ and ζ, we first note that according to our theory Eq. (12) should give the relationship between density and temperature of saturated vapor. According to (12) that temperature rises from zero to a maximum as the density increases, and then decreases. The first part of the curve is thus consistent with experiment; the second part has not as yet been explained. If the first part of the curve is correct, the maximum temperature should be T_c and the corresponding volume v_c. Using this we find

$$T_c=\frac{4}{27}\frac{\sigma^3 b^3}{\zeta^2 a^2},\quad v_c=\frac{3\zeta a}{2\sigma b}. \tag{15}$$

A simple way of determining σ and ζ would be to use the known values of T_c and v_c for one particular gas to compute σ and ζ by means of (15), and then use (15) further to compare the critical volumes and temperatures for other gases. The results are shown in columns 5 and 7 in Table I, with argon as the standard gas. The agreement so obtained is in general very satisfactory, especially when one considers the uncertainty in the force constants.

It should be remarked, however, that a very important factor contributing to this agreement is undoubtedly the fact that we use the law of corresponding states on the one hand, while we use some experimental data from the critical region to find σ and ζ on the other.[8] If we use the formula (15) for T_c and v_c directly, using for σ and ζ the cubic lattice values and for a and b values as given from experiment, we have a much more *a priori* theory. If this is done, values are obtained having the right order of magnitude; they are, however, not so close to the observed values as the ones computed in the other way. This is to be expected, since in this computation the cubic lattice assumptions enter explicitly. We can conclude that, in general, the agreement with experiment is satisfactory.

In a paper to follow a more detailed account will be given of the method. The connections with other theories of condensation will be given, and a more refined comparison with experiment will be undertaken.

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[8] This point was first remarked to us by Professor G. E. Uhlenbeck.