

The Statistical Mechanics of Condensing Systems. II

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David von Seggern
(vsegger@seismo.unr.edu) University of Nevada
July 2012, page 10
DIGITAL OBJECT IDENTIFIER
<http://dx.doi.org/10.1063/PT.3.1619>
The article by Thorne Lay and Hiroo Kanamori is an interesting one. It compares the energy released by a 100-megaton explosion to a 100-megaton earthquake. This is not right. If the authors would have used the correct relationship between seismic moment and energy, they would find that the energy released by a 100-megaton earthquake is about 100 times as much energy as a 100-megaton explosion. The article does not have any references.

Comment on this article
By the act of hitting a ball with a bat, one calculates the force energy to deliver the ball to its new location, but one must also take into account that the ball extended its energy release to that which became struck by the ball as its momentum ceased and passed energy to the struck item. Therefore the parameters of the damage extend into the future when the received energy to that pushed upon later becomes released in a new event. Perhaps calculations of one added that in while another's calculations did not. E.M.C.
Written by Edgar McCarroll, 14 July 2012 19:59

The Statistical Mechanics of Condensing Systems. II*

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It is shown how the quantities entering into the equations for the thermodynamic functions of a saturated vapor, given in the previous article, may be calculated. It is necessary to evaluate certain integrals which enter into the final expressions as the terms of an (almost) infinite, but rapidly convergent series. The first two of these integrals have been evaluated with fair accuracy for a gas obeying the inverse seventh power law of force attraction. The third integral has been estimated. The coefficients with which these

integrals enter into the final expression have also been estimated. The results of the calculation have been compared with the experimental values for CO_2 and CH_4 . Specifically, the volume of the saturated vapor in units of the volume of the molecules, and the ratio $(PV)/(RT)$ for the saturated vapor have been calculated on an arbitrary temperature scale. The agreement between the calculations and the experimental values is not unencouraging.

IN the preceding article equations giving the thermodynamic functions of an imperfect gas, and in particular, a saturated vapor, were derived in terms of certain integrals over the coordinate space of varying numbers of molecules. In this paper we shall proceed to show how these integrals may be evaluated.

We seek the value of b_l , which is defined by the equation

$$b_l = \frac{1}{l!} \int \int \cdots \int \sum \left\{ \prod_{i \in \gamma} f_{ij} \right\} d\tau_1 \cdots d\tau_{l-1}, \quad (1)$$

(Sum over all products consistent with the existence of a single cluster.)

where $d\tau_i$ is the volume element of the i th particle, f_{ij} is a certain function of the difference in the coordinates of the i th and j th particle, and the sum is to be taken over all products of the f_{ij} 's in which every one of the l particles is linked (by means of an f) directly or indirectly to all other of the $l-1$ particles. The function f_{ij} is

$$f_{ij} = \exp(-v_{ij}/kT) - 1, \quad (2)$$

and in the following it will be explicitly assumed that v_{ij} , the mutual potential energy of the pair of particles i and j is a function only of the distance between their centers of gravity r_{ij} , so that $d\tau_i = dx_i dy_i dz_i$.

For small values of l we can consider the various b_l 's and the terms that go to make them up individually.

The smallest cluster is that of two particles. This cluster can be formed in only one way.

* Contribution from the Chemical Laboratory of The Johns Hopkins University.

The integral over the coordinates of one of the particles will be

$$b_2 = \frac{1}{2} \int_0^\infty 4\pi r^2 f(r) dr = \gamma_1/2, \quad (3)$$

since this integral will occur as a constituent of the terms making up the higher b_l 's we shall invest it with a new symbol, γ_1 .

The cluster of three particles can be formed in four ways by combining the three indices 1, 2, 3, in pairs in the following manner 1st (12)(13); 2nd (12)(23); 3rd (13)(23); 4th (12)(23)(13). In the first of these arrangements integration over the coordinates of particle 2, or of particle 3, gives γ_1 independently of the position of the remaining two particles. Subsequent integration over the volume of one of the remaining two particles again yields γ_1 . The value of the term is γ_1^2 . The same is true of arrangements 2 and 3. The contribution of all three of these arrangements to b_3 is then $3\gamma_1^2/6$ or $\gamma_1^2/2$. The integration of the fourth arrangement is more difficult and yields a new integral which we shall designate by γ_2 ,

$$\gamma_2 = \int \int f(r_{12}) \cdot f(r_{23}) \cdot f(r_{13}) d\tau_1 d\tau_2, \quad (4)$$

$$b_3 = \gamma_1^2/2 + \gamma_2/6. \quad (5)$$

The integrals of the type γ_1 and γ_2 we shall refer to as "irreducible integrals" and also as "constituent integrals." The irreducible integrals, which in general will be designated by two subscripts (km), will be integrals over the volume elements of k particles of a certain

definite product of the possible f_{ij} 's of $k+1$ particles. To be irreducible the product must be such that every one of the $k+1$ particles is connected by means of an f with at least two other particles, and in addition, of course, all $k+1$ particles must be at least indirectly connected with each other.

The irreducible integrals of $k=3$ are the following

$$\gamma_{30} = \int \int \int f_{12} \cdot f_{23} \cdot f_{34} \cdot f_{14} d\tau_1 d\tau_2 d\tau_3, \quad (6)$$

$$\gamma_{31} = \int \int \int f_{12} \cdot f_{23} \cdot f_{34} \cdot f_{14} \cdot f_{13} d\tau_1 d\tau_2 d\tau_3, \quad (7)$$

$$\gamma_{32} = \int \int \int f_{12} \cdot f_{23} \cdot f_{34} \cdot f_{14} \cdot f_{13} \cdot f_{24} d\tau_1 d\tau_2 d\tau_3. \quad (8)$$

Each irreducible integral corresponds to a certain pattern of bonds between $k+1$ particles, the integral γ_1 corresponds to a line —, γ_2 to Δ , γ_{30} to \square , etc. In their additive contribution to b_{k+1} it can be seen that each irreducible integral γ_{km} occurs just as often as one can draw (in three dimensions) different patterns (km) between $k+1$ numbered points, i.e., γ_{30} occurs 3 times, γ_{31} , 6 times, and γ_{32} , once. If we call this number d_{km} , the number of ways that we can draw the pattern (km) between $k+1$ numbered points, and define as the "constituent integral" γ_k the sum $d_{km}\gamma_{km}$ over all values of m ,

$$\gamma_k = \sum_m d_{km} \gamma_{km}, \quad (9)$$

the contribution of γ_k to b_{k+1} will be just $\gamma_k/(k+1)!$

We need two other facts. Just as every irreducible integral corresponds to an irreducible pattern, so any one of the products, (Eq. (1)), making up b_l can be said to correspond to a certain configuration of bonds between l numbered points in space, and each configuration can be analyzed as a sum of singly connected irreducible patterns. The number of irreducible patterns (km) we shall designate by n_{km} . From the fact that the patterns are singly connected it follows that

$$\sum_{km} k n_{km} = l - 1. \quad (10)$$

It can also be seen that for every configuration in which the irreducible pattern km occurs once, there are $d_{km}-1$ other configurations exactly identical except that in the same $k+1$ particles the pattern km is drawn $d_{km}-1$ different ways, and there are also d_{km} other configurations identical with the first except that the pattern km' has replaced km , and in d_{km}' different ways. It follows from this that the sum of terms making up b_l contains only powers of the constituent integrals so that we can write, designating the general term $s = (n_1, n_2, \dots, n_k, \dots)$

$$b_l = (l!)^{-1} \sum_s C_s \prod_k \gamma_k^{n_k}. \quad (11)$$

Detailed analysis shows that

$$b_4 = 2\gamma_1^3/3 + \gamma_1\gamma_2/2 + \gamma_3/24, \quad (12)$$

$$b_5 = 25\gamma_1^4/24 + 5\gamma_1^2\gamma_2/4 + \gamma_2^2/8 + \gamma_1\gamma_3/6 + \dots, \quad (13)$$

$$b_6 = 9\gamma_1^5/5 + 3\gamma_1^3\gamma_2 + 3\gamma_1\gamma_2^2/4 + \gamma_1^2\gamma_3/2 + \gamma_2\gamma_3/12 + \dots, \quad (14)$$

$$b_7 = 2401\gamma_1^6/720 + 343\gamma_1^4\gamma_2/48 + 45\gamma_1^2\gamma_2^2/16 + \dots. \quad (15)$$

The next task is to obtain an asymptotic value for the general coefficient C_s , or at least for the logarithm of this coefficient, as l becomes very large.

From general considerations it can be seen that it will be possible to write the asymptotic value of the logarithm of C_s in the form

$$\ln C_s = l \ln l + \sum_k n_k [\ln (l/n_k) + \ln c_k - k + 1], \quad (16)$$

where c_k is a constant independent of l . If then the quantities β_k are defined as

$$\beta_k = c_k \gamma_k, \quad (17)$$

we can write Eq. (11) in the form

$$\ln b_l = \ln \left\{ \sum_{k \geq 1} (\beta_k^{n_k} l^{n_k} / n_k!) \right\}. \quad (18)$$

In the above, use has been made of the fact that $\sum k n_k = l$ in which the difference between l and $l-1$ for large values of l has been neglected.

We shall, for the moment, neglect the problem of determining the value of c_k , the ratio of β_k

to γ_k , and confine our attention to the problem of obtaining a more manageable equation for $\ln b_l$ from (18). The sum under the logarithm in Eq. (18) has as many terms as the "partitio numerorum" of l , a number whose logarithm is negligible for large values of l , compared to the logarithm of any single term (see preceding article, Eqs. (14) and (15)). For all values of β_k positive we could therefore, set the value of the logarithm of b_l equal to the logarithm of the largest term in the sum, and since the values of n_k maximum will obviously be proportional to l we would obtain, defining

$$\nu_k^* = n_k^*/l, \quad n_k^* = n_k \text{ (maximum)}, \quad (19)$$

$$\ln b_0 = (\ln b_l)/l = \sum_{k \geq 1} \nu_k^* (1 + \ln \beta_k - \ln \nu_k^*), \quad (20)$$

$$\text{with} \quad \sum_{k \geq 1} k \nu_k^* = 1. \quad (21)$$

The condition that ν_k^* be a maximum is obtained by setting the variation of Eq. (20) equal to zero, subject to the condition that the variation of (21) is also zero. Using the method of undetermined multipliers, multiply (21) by minus logarithm of ρ , and adding its variation to that of (20) we obtain that $(\nu_k^*/\beta_k)^{1/k}$ is independent of k , and equal to ρ , a value which we can then insert in Eqs. (21) and (20). We obtain

$$(\nu_k^*/\beta_k)^{1/k} = \rho, \quad \nu_k^* = \beta_k \rho^k, \quad (22)$$

$$\sum_{k \geq 1} k \beta_k \rho^k = 1, \quad (23)$$

$$\ln b_0 = \sum_{k \geq 1} \beta_k \rho^k - \ln \rho. \quad (24)$$

Eq. (23) can be used to determine ρ and Eq. (24) to determine $\ln b_0$. The above derivation assumes positive values of β_k , and is essentially the same as the method of obtaining q_r in the previous article. In the appendix of this article a derivation of the two equations (23) and (24) is given which is independent of the assumption of positive values of β_k , and which is essentially similar to the derivation of the equation for q_r given in the appendix of the preceding article.

For purposes of evaluation we shall find it convenient to introduce the dimensionless ratios between the various constituent integrals and the k th power of the first integral, namely,

$$r_k = \gamma_k / \gamma_1^k, \quad (25)$$

$$\text{and} \quad s_k = \beta_k / \beta_1^k = (c_k / c_1^k) r_k. \quad (26)$$

We can then write (23) as

$$x + 2s_2x^2 + 3s_3x^3 + \cdots = 1, \quad x = \beta_1\rho, \quad (27)$$

and (24) as

$$\alpha = e\beta_1/b_0 = x \exp(1 - x - s_2x^2 - s_3x^3 - \cdots). \quad (28)$$

We see that as $s_2, s_3, \cdots s_k$ approach zero, x and also α become unity, and b_0 becomes equal to $e\beta_1$.

We are finally forced to undertake the evaluation of the numbers c_k . To do this we must calculate the general coefficient C_s of the terms making up the sum of Eq. (11). This problem has not been solved satisfactorily. We can, in general, calculate a minimum value for the general coefficient C_s . For the term which we shall call $s=l-1$ for which $n_1=l-1, n_2=0, \cdots, n_k=0$ we can also calculate an upper limit to the value of C_{l-1} . The upper and lower limit bracket the value of the ratio c_1 between the values of $2/e$ and $e/2$, between two values, then, that differ by almost twofold. Fortunately it can be seen that the coefficient $C_{l-1}/l!$ for $l=2$ to 7 inclusive, the numerical coefficient of γ_1^{l-1} in Eqs. (3), (5) and (12) to (15), inclusive, obeys the equation

$$C_{l-1} = l^{l-2}, \quad (29)$$

from which, using Eq. (16), with $n_1=l$, and all other n_k 's=0, we would derive that $c_1=1$. Although the authors realize that a deduction of the general term in a series from the value of the first six members is not exactly in the highest tradition of mathematical rigor they feel that it is highly probable that this method gives the correct value of the ratio c_1 .

The bracketing process, referred to in the previous paragraph by which one obtains that c_1 lies between $e/2$ and $2/e$ is as follows. Firstly C_{l-1} , the number of ways that one can draw $l-1$ single bonds between l numbered points so as to have all the points indirectly connected to each other, but so as not to close any rings (which would lead to integrals other than γ_1), must be less than the total number of ways one can draw $l-1$ bonds between l numbered points. This total number is just the binomial coefficient, the coefficient of the $(l-1)$ th term in the ex-

pansion of $(1+x)$ raised to the $[l(l-1)/2]$ th power. Using Eq. (16) this leads to c_1 less than $e/2$.

In order to show that $c_1 > 2/e$ one may use the following argument. Consider l particles with $n-1$ bonds between them, making up a certain configuration. The configuration is not presumed to be such that only one cluster is formed, but it is presumed that no rings are closed, so that integration of the corresponding function would lead to γ_1^{n-1} . Assume that there are g_{n-1} such configurations. We now seek the ratio g_n/g_{n-1} . It is first apparent that any configuration of n bonds can arise from n different configurations of $n-1$ bonds. We shall determine the minimum number of ways that we can produce different configurations of n bonds out of any given configuration of $n-1$ bonds and divide this by n .

Assume we start with a configuration of $n-1$ bonds in which there are j clusters. There are then $n+j-1$ particles already in some way bonded, and $l-(n+j-1)$ particles which are not bonded. We have to pick 2 particles, but avoid closing a ring, which means only that we must avoid picking two particles out of the same cluster. We can pick two free particles, one bonded and one free, or two bonded particles, but from different clusters. The first we can do $[l-(n+j-1)] \times [l-(n+j)]/2$ ways, the second $(n+j-1) \times [l-(n+j-1)]$ ways, and the third *at least* $(n+j-1) \times 2(j-1)/2$ ways, since we can make our primary choice from any of the bonded particles and our second choice from any of the particles in the remaining $j-1$ clusters which have at least two particles per cluster. Summing these three ways, and dividing by n , we have

$$\begin{aligned} g_n/g_{n-1} &> (1/2n)[(l-n)(l+n-1) + j(j-1)] \\ &> (1/2n)[l-n][l+n-1], \end{aligned} \quad (30)$$

and since $g_1 = l(l-1)/2$, we find for $g_{l-1} = C_{l-1}$,

$$C_{l-1} > \frac{1}{2^{l-1}} \frac{(2l-2)!}{(l-1)!}, \quad (31)$$

$$S = \frac{(l-K-J+k)!}{(l-K-J-1)!(k+1)!} + \sum_{i=0}^{i=k} \frac{(l-K-J+k)!(K+J-k)m^i(J-1)!}{(l-K-J+i)!(k-i)!(J-1-i)!(i+1)!}. \quad (33)$$

If now m is given its minimum value of 2 we can obtain a lower limit for the ratio g_s/g_{s-km} which leads to a lower limit for C_s and the c_k 's. Replacing m by 2, and doing some algebraic juggling in which

or finally, using (16), with $n_1 = l-1$, $n_k = 0$,

$$c_1 > 2/e. \quad (32)$$

The method which we use to obtain the general coefficient C_s is essentially similar to the method by which the equations (30), (31) and (32) were derived. It can be used to give a definite lower limit for C_s , or, by a slight alteration, to give an approximate probable value which we shall adopt to calculate the various c_k 's. We consider l numbered particles in space and assume that between these l particles a certain number of bonds are drawn making up a certain configuration, $s-(km)$ characterized by the numbers $n_1, n_2, \dots, (n_{km}-1)$, the numbers of the different irreducible patterns occurring in the configuration. The number of such configurations having the same characteristic numbers of irreducible patterns we shall call g_{s-km} . We now attempt to calculate g_s/g_{s-km} , g_s being the number of configurations with $s = n_1, n_2, \dots, n_{km}, \dots$ as the numbers of the different patterns. As before, any one configuration s may originate from n_{km} different configurations $s-(km)$, so we must divide the number of ways that we can make a configuration s out of one $s-(km)$ by n_{km} to obtain the desired ratio.

Assume that in a particular configuration $s-km$ there are J globs, so that if $K = \sum k n_{km}$ there are $K+J-k$ particles involved with bonds and $l-(K+J-k)$ free particles. The number of different configurations s we can make out of this configuration $s-(km)$ will be d_{km} times the number of ways that we can pick $k+1$ particles out of the configuration $s-km$ to add to it a single pattern km . We can pick all $k+1$ particles from the free particles, k from the free particles and one from any of the already bonded particles, $k-1$ free particles and two bonded particles, but from different globs, etc. Assuming that each glob has an average of m particles we find that to obtain the required number we must sum

the small integers i and k are neglected compared to the large, K and J values, so that the factorials are replaced by powers, one arrives finally at the equation.

$$g_s/g_{s-km} > d_{km}(l-K)^k(l+kK)/n_{km}(k+1)!. \quad (34)$$

If one remembers the definition of the constituent integrals as $\gamma_k = \sum_m d_{km} \gamma_{km}$, and uses

$$\sum_{n_{km}} (n_k! / \prod_m n_{km}!) \prod_m (d_{km} \gamma_{km})^{n_{km}} = \gamma_k^{n_k}, \quad (\text{with } \sum_m n_{km} = n_k) \quad (35)$$

one arrives at the expression for the general coefficient C_s

$$C_s > l! \prod_k [(k+1)^{1/k} l / e k!]^{n_k} / n_k!. \quad (36)$$

Use of this expression in Eq. (16) leads to

$$c_k > (k+1)^{1/k} / e k!. \quad (37)$$

This, of course, gives the same minimum value for c_1 that had been previously obtained, namely $2/e$.

We shall return to Eq. (33) and replace m , the average number of particles per glob by $K+J/J$, the ratio of the total number of bonded particles to the number of globs. We then obtain, in place of (34) Eq. (38), namely

$$g_s/g_{s-km} = d_{km} l^{k+1} / n_{km} (k+1)! \quad (38)$$

which leads to

$$c_k = e^k / (k+1)!. \quad (39)$$

This equation gives us $e/2$ as the value of c_1 , which was the upper limit previously found. We have already shown that there is reason to believe that c_1 is equal to unity. We shall then use $c_1 = 1$, but for c_2 and c_3 the values derived from (39), namely,

$$\begin{aligned} c_1 &= 1, & c_2 &= e^2/6, & c_3 &= e^3/24; \\ s_2 &= (c_2/c_1^2)r_2 = 1.23r_2, & s_3 &= (c_3/c_1^3)r_3 = 0.835r_3. \end{aligned} \quad (40)$$

The sum σ of the previous article, Eq. (44), was the sum over all values of l of $l b_l / b_0^{l-1}$. Using Eq. (40) for c_l , Eq. (17) and (27) and (28) for b_0 , and using the Eqs. (3), (5) and (12) to (15) for b_l from $l=2$ to 7, we can write the first few terms of σ . We obtain

$$\begin{aligned} \sigma &= \sum_{l \geq 2} l b_l / b_0^{l-1} = \sum (l b_l / \gamma_1^{l-1} e^{l-1}) \alpha^{l-1} = \alpha/e + \alpha^2(3/2e^2)(1+r_2/3) + \alpha^3(8/3e^3)(1+3r_2/4+r_3/16) \\ &\quad + \alpha^4(125/24e^4)(1+6r_2/5+3r_2^2/25+4r_3/25+\dots) + \alpha^5(54/5e^5)(1+5r_2/3+15r_2^2/36 \\ &\quad + 5r_3/9+5r_2r_3/36+\dots) + \alpha^6(3.334 \times 7/e^6)(1+15r_2/7+0.842r_2^2+\dots) \\ &= 0.368\alpha + 0.202\alpha^2(1+0.333r_2) + 0.133\alpha^3(1+0.75r_2+0.0625r_3) + 0.0955\alpha^4(1+1.20r_2+0.12r_2^2 \\ &\quad + 0.16r_3+\dots) + 0.0726\alpha^5(1+1.60r_2+0.417r_2^2+0.555r_3+0.139r_2r_3+\dots) \\ &\quad + 0.0579\alpha^6(1+2.14r_2+0.842r_2^2+\dots). \end{aligned} \quad (41)$$

The sum ϕ , Eq. (46) of the previous article is

$$\phi = \sum_{l \geq 2} b_l / b_0^{l-1}, \quad (42)$$

which can also be readily evaluated.

If it is generally true that the coefficient of γ_1^{l-1} in b_l is $l^{l-2}/l!$ then the numerical coefficient multiplying α^{l-1} in the terms of σ will be $l^{l-1}/e^{l-1}l!$, which becomes asymptotically $e/l^3(2\pi)^{1/2} = 1.083l^{-1/2}$. In the last term given, for which $l=7$, the numerical coefficient has the value 0.0579 which is within about one percent of this asymptotic value. The use of this asymptotic value enables one to make

fairly accurate estimates of the sum of the contributions of the unevaluated terms in σ , and of course also in ϕ , which, however, converges appreciably more rapidly.

When all the r_k 's are zero, as has previously been noted, α becomes unity. σ has then the value 1.70, of which 0.772 is contributed by the terms beyond those evaluated. ϕ has the value 0.355 of which 0.032 is contributed by the unevaluated tail. The value of $(PV)_s/RT$ (see Eq. (52) of the previous article) is $(1+\phi)/(1+\sigma)$, which under the condition that all the r_k 's be zero, has the numerical value 0.501. This occurs, experimentally, in most gases, at a temperature slightly below the critical temperature, and we have chosen this temperature $T_{0.5}$ as a reference temperature from which to measure our temperature scale.

THE CONSTITUENT INTEGRALS

We now come to the problem of determining the constituent integrals, γ_k . To this problem there is, of course, no generally exact solution, since the exact form of the potential energy $v(r)$ as a function of the distance r between the centers of gravity of two molecules or atoms is not known. We shall assume a certain form

$$\begin{aligned} v(r) = v_1(z) &= 6u \{ (2/3z^6)(1/z^6 - 1) \}, \quad \text{for } (2/3)^{1/6} \leq z \leq \infty, \\ v_1(z) &= 75u - 72(3/2)^{1/6}uz, \quad \text{for } 0 \leq z \leq (2/3)^{1/6}, \\ z &= r/r_0. \end{aligned} \quad (43)$$

This function is of the general form $A/r^{12} - B/r^6$ in the range for which the exact value is of significance. The parameter r_0 is so chosen that $v(r) = 0$ when $r = r_0$, $z = 1$, and $-u$ is the minimum value of the potential which occurs at $z = (2)^{1/6}$ or $r = (2)^{1/6}r_0$. This potential function we shall refer to as the exact potential function, v_1 , and the subscript 1 will be used in the left hand lower side of any integrals derived from it. We shall find it convenient to express our integrals in terms of the volume

$$v_0 = 4\pi(r_0/2)^3/3 = \pi r_0^3/6, \quad (44)$$

which may be called the volume of the molecules. The quantity u/kT we shall call

$$\theta = u/kT. \quad (45)$$

Using Eqs. (2) and (3) we can evaluate ${}_1\gamma_1$ from this form of v_1 as accurately as we please. The integration is actually done directly from $z=0$ to $z=(2/3)^{1/6}$ and by expanding the exponential for larger values of z . The equation for ${}_1\gamma_1$ so obtained is

$$\begin{aligned} {}_1\gamma_1(\theta)/8v_0 &= -(2/3)^{1/6} \{ 1 - e^{-3\theta} (1/24\theta - 1/864\theta^2 + 1/62208\theta^3) + (1/62208\theta^3)e^{-75\theta} \\ &\quad - [3\theta + (69/70)\theta^2 + (9/770)\theta^3 + (5409/40040)\theta^4 \\ &\quad + 0.1504\theta^5 + 0.02108\theta^6 - 0.00726\theta^7 + 0.00273\theta^8 \dots] \}. \end{aligned} \quad (46)$$

The sudden occurrence of alternating signs is real.

This form of the potential function, however, leads to hopelessly complicated integrals in the determination of γ_2 . We shall therefore introduce a new potential function $v_2(z)$, such that

$$\begin{aligned} v_2(z) &= -kT \ln(1 + az^{-6}), & f_2(z) &= az^{-6}, & \text{for } 1 \leq z \leq \infty, \\ v_2(z) &= +\infty, & f_2(z) &= -1, & \text{for } 0 \leq z \leq 1. \end{aligned} \quad (47)$$

This function is also so chosen that $v(z)$ changes sign at $z=1$. The integration of ${}_2\gamma_1$ using this function is, of course, trivial. ${}_2\gamma_2$ can be obtained by using the coordinates r_{12}, r_{23}, r_{13} , with the volume element $d\tau_2 d\tau_3 = 8\pi^2 r_{12} r_{23} r_{13} dr_{12} dr_{23} dr_{13}$ and the integration limits for the first coordinate to be integrated, say

$$r_{12}, \quad |r_{13} - r_{23}| \leq r_{12} \leq |r_{13} + r_{23}|.$$

The integration is extremely tedious, even with so simple a function as $f_2(z)$, so the steps will not be shown here. The results are,

$${}_2\gamma_1(a)/8v_0 = a - 1, \quad (48)$$

$${}_2\gamma_2(a)/(8v_0)^2 = 4.5[0.014356a^3 - 0.075455a^2 + 0.10748a - 0.104167]. \quad (49)$$

It is now possible by numerically equating (49) to (46) to find the "best" value of a to correspond to any given value of θ . By this means we obtain γ_1 exactly, and γ_2 fairly satisfactorily in terms of the two parameters θ and r_0 (or v_0), of the "exact" potential function (46). This method is undoubtedly fairly satisfactory as a means of determining γ_1 and γ_2 in terms of two parameters of a potential function.

However, the authors had no desire to continue the integration of $f_2(z)$ to obtain γ_3 . With sufficient patience this could be done, but the chore is rather tedious. Considerable time was spent in integrating the three parameter function

$$f_3(z) = \beta[(z/R) - 1] \exp(-z/\alpha R). \quad (50)$$

As long as $f_3(z) \geq -1$ this corresponds to the potential

$$v_3(z) = -kT \ln [1 + \beta\{(z/R) - 1\} \exp(-z/\alpha R)]. \quad (51)$$

This function is much too "soft," that is it has no sufficiently pronounced deep minimum but a rather broad band where $v_3(z)$ is negative and $f_3(z)$ positive. The only use which we wish to make of the integrals obtained from this function is to point out the qualitative fact that most reasonable choices for the parameters give the ratio ${}_3\gamma_2/{}_3\gamma_1^2 = {}_3r_2$ as very much smaller than ${}_2\gamma_2/{}_2\gamma_1^2 = {}_2r_2$. With these values ${}_3r_3 = {}_3\gamma_3/{}_3\gamma_1^3$ is, in general, over the range in which we wish to work, very much smaller than ${}_3r_2$. If the parameters are so chosen that the ratio ${}_3r_2 = {}_2r_2$ we find that ${}_3\gamma_3$ and r_3 remain negative to much lower temperatures than γ_2 and r_2 . The general impression obtained from attempting to work with this function $f_3(z)$ is that for the "soft" function γ_3 remains negative to lower temperatures than γ_2 (which with any function chosen is negative at lower temperatures than γ_1) and that r_3 is smaller than r_2 except at extremely low temperatures when both are greater than unity.

We then attempted to investigate

$$\begin{aligned} f_4(z) &= -1, & v_4(z) &= \infty, & \text{for } 0 \leq z \leq 1, \\ f_4(z) &= a/3\delta, & v_4(z) &= -kT \ln [(a/3\delta) + 1], & \text{for } 1 \leq z \leq 1 + \delta, \\ f_4(z) &= 0, & v_4(z) &= 0, & \text{for } 1 + \delta \leq z \leq \infty, \end{aligned} \quad (52)$$

in which δ is regarded as an infinitesimal. This function is too "hard" in contradistinction to the "soft" $v_3(z)$, and should show deviations in the opposite direction from the true integrals. The integrations are relatively simple for γ_1 , γ_2 , γ_{30} and γ_{31} . γ_{32} was obtained by making a few approximations which are of no great importance to discuss here since it contributes relatively little to $\gamma_3 = 3\gamma_{30} + 6\gamma_{31} + \gamma_{32}$. The equations obtained are

$${}_4\gamma_1(a)/8v_0 = a - 1, \quad (53)$$

$${}_4\gamma_2(a)/(8v_0)^2 = a^3/6 - 3a^2/4 + 15a/16 - 15/32, \quad (54)$$

$${}_4\gamma_{30}(a)/(8v_0)^3 = a^4/6 - 2a^3/3 + 6a^2/5 - 34a/35 + 34/105, \quad (55)$$

$${}_4\gamma_{31}(a)/(8v_0)^3 = a^5/36 - a^4/4 + 11a^3/16 - 39a^2/40 + 0.70837a - 0.2361234, \quad (56)$$

$${}_4\gamma_{32}(a)/(8v_0)^3 = 0.001805a^6 - 0.064815a^5 + 0.2882a^4 - 0.4862a^3 + 1.25a^2 - 0.885a + 0.295, \quad (57)$$

$${}_4\gamma_3(a)/(8v_0)^3 = 0.001805a^6 + 0.101852a^5 - 0.7118a^4 + 1.6388a^3 - a^2 + 0.885a - 0.295. \quad (58)$$

Numerical comparison shows that a is to be identified with the a of $v_2(z)$. ${}_4\gamma_2$ becomes positive at much higher temperatures than ${}_2\gamma_2$, and ${}_4\gamma_3$ is positive at all reasonable temperatures, but very small in numerical value until about the temperature at which ${}_4\gamma_2$ becomes positive. For lower temperatures than this it increases rapidly in value, with decreasing temperature. The fact that ${}_4\gamma_3$ is positive at high temperatures may be due to an error in estimating ${}_4\gamma_{32}$, but if so this will make little difference at the lower temperatures at which it is unimportant. Plotting ${}_4\gamma_2$ and ${}_2\gamma_2$ against a shows that a shift of scale of a in ${}_4\gamma_2$ will bring the two curves into remarkably good agreement. The shift is by a factor of 1.31 such that

$${}_4\gamma_2(a/1.31) \cong {}_2\gamma_2(a). \quad (59)$$

We have therefore chosen, as an empirical estimate of γ_3 to use Eq. (59) but with substitution of $a/(1.31)^2$ for a in the equation. We shall not trust any numerical calculations in temperature ranges where s_3 is large, and since we are entirely omitting s_4 in any event this rather crude estimate of γ_3 is probably sufficient for our purposes. It will at least give us a rough indication of the temperature range for which we can make calculations with some degree of confidence in the results.

NUMERICAL RESULTS

In Table I the most important steps in the evaluations, and the values of some of the observable properties of the saturated vapor are

given. In column 1 the value of a is given for which the subsequent values in the same row are calculated. In column 2 are the values of $\gamma_1/8v_0$ calculated from Eq. (48), namely $a-1$. In column 3 the values of $\theta=u/kT$ are given, calculated from Eq. (46). r_2 obtained from Eqs. (49) and (48), and r_3 from (59) and (48), as well as s_2 and s_3 are listed in columns 4, 5, 6 and 7, respectively. $x=\beta_1\rho$, Eq. (27), and α , Eq. (28), as well as b_0/v_0 are in columns 8, 9 and 10. It is to be noted that from Eq. (28), $\partial\alpha/\partial x=0$ when (27) is fulfilled, so that the error introduced into α and b_0 by the omission of s_4 and subsequent terms may be expected to be of the order of magnitude of s_3x^3 rather than of $3s_3x^3$. For the row $a=6.5$ we have $s_3x^3=0.026$ and for the last row, $a=9$, $s_3x^3=0.035$. The sums σ , Eq. (41), and ϕ , (42), are tabulated in columns 11 and 12. Finally v_s/v_0 , the ratio of the volume per molecule of the saturated vapor to the volume of the molecules as defined by Eq. (44), is given in column 13, $(PV)_s/RT$, which is $(1+\phi)/(1+\sigma)$, a measure of the degree by which the saturated vapor deviates from the perfect gas law, is listed in column 14. In the last column an arbitrary linear scale of temperature is given. The scale is so chosen that the temperature, $T_{0.5}$, at which PV/RT is 0.5 is chosen as unity.

On this scale of temperature, the temperature at which $\gamma_1/8v_0$ becomes zero is 3.562. One predicts then, that for gases obeying an A/r^7 attractive law of force between the molecules, the temperature at which the second virial coefficient changes sign, the Boyle temperature, should be

TABLE I.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
a	$\gamma_1/8v_0$	$\theta=u/kT$	$r_2=\gamma_2/\gamma_1^2$	$r_3=\gamma_3/\gamma_1^3$	$s_2=\beta_2/\beta_1^2=1.23r_2$	$s_3=\beta_3/\beta_1^3=0.836r_3$	$x=\beta_1\rho$	$\alpha=e\gamma_1/b_0$	b_0/v_0	σ	ϕ	v_s/v_0	$\frac{PV}{RT}=\frac{1+\phi}{1+\sigma}$	$T/T_{0.5}$
1.0	0.0	0.286												3.562
2.0	1.0	0.606												1.681
3.0	2.0	0.857												1.190
3.5	2.5	0.960	-0.027		-0.034									1.064
3.8	2.8	1.020	0.000	δ	0.000	δ	1.000	1.000	60.9	1.70	0.35	22.5	0.502	1.000
4.0	3.0	1.056	0.019	0.02	0.023	0.02	0.915	0.961	67.8	1.13	0.32	31.8	0.620	0.967
4.5	3.5	1.140	0.060	0.04	0.074	0.03	0.841	0.919	82.8	0.94	0.29	42.7	0.667	0.895
5.0	4.0	1.220	0.095	0.06	0.117	0.05	0.784	0.882	97.5	0.84	0.27	53.0	0.690	0.837
5.5	4.5	1.294	0.130	0.07	0.160	0.06	0.746	0.859	114	0.79	0.26	63.7	0.706	0.790
6.0	5.0	1.358	0.166	0.08	0.205	0.07	0.717	0.833	130	0.74	0.25	75.0	0.719	0.753
6.5	5.5	1.411	0.201	0.09	0.248	0.07	0.690	0.820	146	0.71	0.24	85.2	0.725	0.723
7.0	6.0	1.466	0.234	0.10	0.288	0.08	0.668	0.797	164	0.67	0.23	98.0	0.736	0.697
8.0	7.0	1.556	0.301	0.14	0.371	0.12	0.625	0.763	199	0.62	0.22	123	0.754	0.652
9.0	8.0	1.636	0.379	0.20	0.467	0.17	0.583	0.729	239	0.57	0.21	152	0.773	0.624

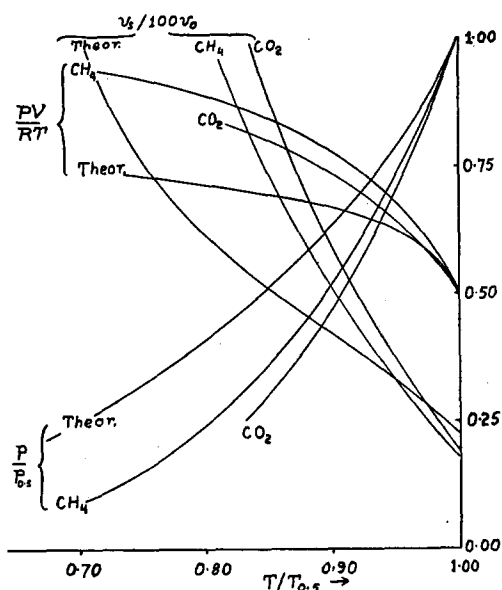


FIG. 1. PV/RT , P and $v_s/100v_0$ for the saturated vapor plotted against $T/T_{0.5}$. The temperature scale is so chosen that unity is the temperature at which PV/RT of the saturated vapor is equal to 0.5. The pressure scale is so chosen that P is unity when T is unity. The volume ratio is obtained by assuming that in liquid CO_2 and CH_4 the volume per molecule is 2.5 times v_0 .

about 3.5 times the temperature for which PV/RT of the saturated vapor is one-half. Experimentally it appears that this ratio is about 3.5 in N_2 .

In Fig. 1 a plot showing the agreement, or disagreement, between the results of these calculations, and the experimentally observed values for the two gases CO_2 and CH_4 is shown. The temperature scale is so chosen that $PV/RT = 0.50$ at $T = 1.00$. The pressure scale is also chosen so that $P = \text{unity}$ at this temperature. The volume scale is, however, not arbitrary: It was assumed that the volume of a liquid at ordinary temperatures, (P_s about 1 atm.) would be about 2.5 times our v_0 , per molecule. It is to be remembered that the v_0 which we chose is the volume of a sphere the diameter of which is equal to the distance of the centers of two molecules when their mutual potential just changes sign. This volume is some $\sqrt{2}$ fold less than the volume corresponding to the minimum of the potential energy curve. The value 2.5 then assumes that the volume of the liquid is about 25 percent greater than "close packing." The free energy of the gas changes by only about $RT \ln 2$ for a two-

fold change in pressure or volume. The fact that, from $T = 1.00$ to about $T = 0.8$ the ratio v_s/v_0 appears to agree within 2-fold with the experimental values indicates that within this temperature range our equations should give the free energy of the liquid to within about $RT \ln 2$. This appears to the authors to indicate some degree of success. It is, however, obvious from the plot of Fig. 1 that considerable improvement can be made before the agreement with experiment can be said to be excellent.

CONCLUSION

It is obvious that the present paper shows lacks, both in the rigor of some of the proofs and in the accuracy of the numerical evaluations. The value $c_1 = 1$ is probably exact, but certainly not proven, the values of other c_k 's, c_2 and c_3 are extremely uncertain, in fact it can be safely said that they are rather certainly inexact. Although the value of γ_1 can be said to be exactly correct for a gas of molecules with the mutual potential given by Eq. (43), the value of γ_2 is certainly somewhat in error, and that of γ_3 is little more than a guess. Better evaluations of these integrals is largely a matter of patience, although considerable patience was needed to go as far as has been done!

In addition to these faults the question of the volume dependence of b_i at small volumes has been entirely neglected as yet. The discussion of the slightly complicated behavior of the gas in the neighborhood of the critical point has been avoided in this paper.

The authors hope that some of these questions will be handled in later papers.

In conclusion the authors wish to thank Dr. M. Goeppert Mayer, who has listened patiently, but critically, to many false theories, and has offered many constructive suggestions.

Note added in proof: P. G. Ackermann has discovered that the value of the general coefficient C_s (Eq. (36)) appears to be

$$C_s = (l!/l^2) \Pi(l/k!)^{n_k} (1/n_k!)$$

which leads to $c_k = 1/k!$. This can probably be proven. Work on the integrals γ_3 by S. F. Harrison indicates that the values chosen in this article are too small. It is to be hoped that

better numerical agreement with experiment can now be obtained. Harrison and Mayer have also observed that Eqs. (22), (23) and (24) contain an explanation of the phenomena of fusion, a prediction of a second change of phase, highly temperature dependent, arising in a manner similar to the condensation phenomena.

APPENDIX

We seek a more satisfactory form for $\ln b_l$, than Eq. (18) of the text. We define a function B , as $B(l, \beta_1, \dots, \beta_k, \dots, x, j)$

$$= \sum_{n_k} \{ \Pi \beta_k^{n_k} x^{kn_k} j^{n_k} / n_k! \}, \text{ with } \sum_k n_k = l, \quad (1)$$

and obtain, by direct differentiation of the sum

$$\beta_k \frac{\partial B}{\partial \beta_k} = \beta_k x^k j B(l-k, \beta, x, j), \quad (2)$$

$$x \frac{\partial B}{\partial x} = \sum_k k \beta_k \frac{\partial B}{\partial \beta_k} = l B, \quad (3)$$

$$j \frac{\partial B}{\partial j} = \sum_k \beta_k \frac{\partial B}{\partial \beta_k}. \quad (4)$$

The introduction of b_0 , with $x=1$,

$$\ln b_0(l, \beta, j) = (1/l) \ln B(l, \beta, j), \quad (5)$$

allows us to transform (3) into

$$\sum_k k \beta_k (\partial \ln b_0 / \partial \beta_k) = 1, \quad (6)$$

and (4) into

$$\partial \ln b_0 / \partial j = (1/j) \sum_k \beta_k (\partial \ln b_0 / \partial \beta_k). \quad (7)$$

Taking the logarithm of (2), setting $x=1$ and $j=l$, and using $\ln b_0(l-k, \beta, j) = \ln b_0(l-k, \beta, (j-k) + k(\partial \ln b_0 / \partial j))$ we obtain, after neglecting one term which is multiplied by k/l ,

$$\ln (\partial \ln b_0 / \partial \beta_k) = -k \ln b_0 + k \sum_k \beta_k (\partial \ln b_0 / \partial \beta_k) + l \{ \ln b_0(l-k, \beta, j-k) - \ln b_0(l, \beta, j) \}. \quad (8)$$

The last term in this expression is negligible, since it is just $-k(\partial \ln f(l) / \partial l)$ which is of the order of magnitude $(k/l) \ln f(l)$ and negligible compared to $\ln b_0$. We find that $(\partial \ln b_0 / \partial \beta_k)^{1/k}$ is independent of k , and can abbreviate it with the symbol ρ , in which case (6) and (8) become

$$\sum_{k \geq 1} k \beta_k \rho^k = 1, \quad (9)$$

$$\ln b_0 = \sum_{k \geq 1} \beta_k \rho^k - \ln \rho, \quad (10)$$

identical with Eqs. (23) and (24) of the text.

Errata: The Role of Molecular Orientation in Photochemical Reactions in Monolayers

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(J. Chem. Phys. 4, 725 (1936))

ON page 727 of my article with the above title, the last sentence of the paragraph preceding the paragraph headed "General Features of the Absorption of Light by Monolayers," should read "For any value of θ_0 , the deviation of the observed ϕ_a from that calculated on the assumption of negligible thermal oscillation is proportional to the absolute temperature, but owing to the usual variation of θ_0 with molecular area, it is only at and near the limiting area that such an effect could be detected."