PHYSICAL REVIEW VOLUME 63, NUMBERS 7 AND 8 APRIL 1 AND 15, 1943

A Statistical Theory of Liquids. II

GEORGE JAFFÉ
Louisiana State University, Baton Rouge, Louisiana
(Received February 6, 1943)

In continuation of Part I, vapor pressure, surface tension, and the neighborhood of the critical point are discussed. Section IX deals with the vapor pressure law. A comparison with experimental data shows that the experimental values of the heat of vaporization are, on the average, 55 percent higher than the calculated values for the ten liquids studied. This suggests association in the liquid phase. However, even for the noble gases and mono-atomic metal vapors there remains a discrepancy, though of less degree. In Section X the previously established expression for the surface tension is developed. The "number of molecules per sq. cm of surface" can be defined by the aid of integrals involving the potential of molecular interaction. If, then, a "molar surface S^*," is defined as a surface containing one mole of the liquid, the equation of state for the surface phase assumes the form $\gamma S^* = RT$. The value for mercury can be calculated quantitatively from the potential as established in Part I. In the case of the other nine liquids the potential has to be "cut off" at a distance of the order σ_1. Eötvös' law follows as a limiting law for sufficiently high temperatures.—In Section XI the potential in the surface layer is supplemented for the case that the density in the vapor phase becomes comparable with that in the liquid phase. Then the proof of the coexistence of the two phases (Section IV) is extended to the neighborhood of the critical point. For that neighborhood the rule of Cailletet and Mathias is deduced. Finally the Kamerlingh Onnes constant is deduced from the special form of potential introduced in Section VII. It comes out 25 to 33 percent too low.

THE following three sections deal with the application of the previously developed theory[1] (Part I), to vapor pressure, to surface tension, and to the neighborhood of the critical point.

IX.[2] VAPOR PRESSURE

The vapor pressure law is contained in our formula (3.18).[2] This formula was deduced under the restriction that the radii of curvature of the liquid boundary are large compared with the range of molecular action. Under this assumption the surface term in (3.18) is insignificant. Neglecting it and making use of (3.07) and (3.08) we obtain

$$n_2/n_1 = \exp\,(-(u_2-u_1)/kT), \qquad (9.01)$$

where u_1 and u_2 are given by (2.14) and (2.15), respectively.

We shall introduce molar quantities and shall not treat here the density in the vapor phase ρ_2, as small compared with that in the liquid phase ρ_1. If we call Avogadro's number N_0, the potential energy of the two phases per mole becomes

$$U_1^* = N_0 u_1, \quad U_2^* = N_0 u_2. \qquad (9.02)$$

Furthermore, the ordinary molar heat of vaporization L^* (which still contains the external work), is given by

$$L^* = -(U_1^* - U_2^*) + Mp(v_2 - v_1), \qquad (9.03)$$

where M signifies the molecular weight, and where v_1, v_2 represent the specific volumes. For $v_1 \ll v_2$ this is equivalent to our previous equation (6.10).

If, finally, we assume that the molecular constitution is the same in the two phases the ratio n_2/n_1 will be equal to the ratio ρ_2/ρ_1 of the densities, and (9.01) assumes the form

$$\rho_2/\rho_1 = \exp\,[-(L^* - Mp(v_2 - v_1))/RT]. \qquad (9.04)$$

It was pointed out before (p. 467, Part I) that the relation (9.01) might have been obtained directly from Boltzmann's theorem. This relation (9.01) is based on the fundamental principles of statistical mechanics, and the only specific assumption involved in (9.04) is the equality of molecular constitution in the two phases.

In principle Eq. (9.04) could serve to calculate the pressure of the saturated vapor as a function of temperature. Once the potential of molecular interaction is known completely, the dependence on temperature of all quantities involved in (9.04) is calculable, and then, from the equation of state (3.20), the pressure in the vapor phase

[1] G. Jaffé, Phys. Rev. **62**, 463 (1942).
[2] Section numbers and the numbering of equations and tables are continued from Part I.

can be evaluated. However, the determination of the potential of molecular interaction carried through in Part I claims to be valid only for the neighborhood of the chosen standard temperature, and it is not the object of the present investigation to calculate the quantities involved over a wide range of temperatures. As stated before (p. 475, Part I) this may necessitate a refinement in the choice of the potential.

However, the density law (9.04) can be tested without reference to any particular law of molecular interaction. If ρ_1 and ρ_2 are known for any temperature, L^* can be calculated and compared with the empirical value of L^* for that temperature. Equation (9.04) should hold for all temperatures lower than the critical. If, however, the temperature is so low that $v_1 \ll v_2$ and that the vapor may be treated as an ideal gas, we obtain from (9.04)

$$L^* = RT(\log(\rho_1/\rho_2)+1). \qquad (9.05)$$

We have calculated, from (9.04) and (9.05), L^* for the ten liquids discussed in Part I and over the range of temperatures where independent determinations of L^* are available. In Table III the ratios $Q = L^*_{\text{exp}}/L^*_{\text{theor}}$ are indicated together with the range of temperatures.

TABLE III. Comparison of theoretical and empirical data. (L = molar heat of vaporization, K = Kamerlingh Onnes constant.)

1	2	3	4	5	6	7
Liquid	t°C	$Q = L^*_{\text{exp}}/L^*_{\text{th}}$	t°C	$Q = L^*_{\text{exp}}/L^*_{\text{th}}$	K_{exp}	K_{theor}
Mercury	357	1.26				
Bromine	58.8	1.50				
Carbon disulfide	46.3	1.44				
Acetone	56.5	1.58	100	1.59	4.10	2.89
Carbon tetrachloride	76.8	1.55	280	1.52	3.68	2.80
Chloroform	61.2	1.57				
Ethyl ether	34.6	1.61	180	1.45	3.83	2.77
Benzene	80.1	1.56	280	1.52	3.76	2.86
Ethyl alcohol	78.4	1.91	240	1.71	4.02	2.86
Water	100	1.57	220	1.59	5.42	2.92

It will be noticed that the ratios Q are considerably larger than 1 in all cases, but that they depend comparatively little on the temperature (though the values of L^* change considerably in some cases). There does not seem to be any other explanation for this discrepancy except the assumption that the molecular constitution in the two phases is not the same. Now, some of the 10 liquids are definitely known to be "associating" (water, ethyl alcohol). Most of the others, even mercury, show the well-known rise of the boiling point upon energetic drying[3] which, again, indicates a complex constitution in the liquid phase. This makes the suggested explanation plausible.

The assumption of equal molecular constitution in the two phases is most legitimate in the case of monatomic vapors. We have, therefore, extended the calculations to the noble gases and to some metals. In the former group Q rises from 1.30 in the case of neon to 1.46 in the case of xenon (for the respective boiling points). Helium, it is true yields $Q=0.83$ but this must be accidental since classical statistical mechanics is not applicable to helium.[4]

For the 10 metals Na, K, Rb, Cs, Ag, Zn, Cd, Al, Pb, and Bi for which sufficiently reliable data are available Q rises from Al ($Q=0.985$) to Bi ($Q=1.35$) with an average value of 1.16.[5]

Thus, on the whole, the situation is more satisfactory for substances with monatomic vapors but it seems awkward to ascribe the remaining difference to molecular association, e.g., in the case of the inert gases. It should be pointed out, however, that this difficulty is not specific of our theory but would be the same in every theory which is based on classical statistical mechanics.

In performing the numerical calculations of Part I we made use of the empirical knowledge of the heat of vaporization at the ordinary boiling point. It might be mentioned that the systematic deviations recorded on p. 475, Part I could be reduced if the values of L^* calculated from (9.05) were used instead of the empirical values. We did not consider it worth while to repeat the lengthy calculations as there is very little gain if the error is thrown on the values of L^*.

X. SURFACE TENSION

In our formula (3.21) giving surface tension the corrective surface term can again be neglected. Introducing, then, the values (3.07) and (3.09) we obtain

$$\gamma = kTn_1 \int_0^\infty [1-\exp(-(u-u_1)/kT)]dh, \qquad (10.01)$$

[3] Brereton Baker, J. Chem. Soc. **101**, 2339 (1912); **121**, 568 (1922). For further references see A. Findlay, *The Phase Rule* (Longmans, Green and Company, London, New York, Toronto, 1931), seventh edition, p. 20.

[4] H. S. W. Massey and C. B. O. Mohr, Proc. Roy. Soc. **A141**, 434 (1933); **144**, 188 (1934).

[5] Mg makes a strange exception with $Q=2.31$. It seems that the experimental determination of L^* is at default in this case.

where u is given in general by (2.04), (2.07), and u_1 by (2.14). It should be mentioned that $(u-u_1)$ is always positive and γ, therefore, comes out positive. In the limit $(u-u_1)/kT\to 0$ the dynamic formula (10.01) reduces to a form which might be obtained by the usual static procedure.

In what follows we shall be satisfied to make use of the first approximation which assumes the molecular density n to be constant even in the surface layer. Then u takes the form given by (2.10), (2.11) and γ can finally be written in the form

$$\gamma = kTn_1\sigma^*, \tag{10.02}$$

where

$$\sigma^* = z\sigma_1. \tag{10.03}$$

Here z is a pure number given by

$$z = I_5 + I_6 \tag{10.04}$$

and I_5, I_6 represent the integrals

$$I_5 = \int_0^1 \{1-\exp[(\pi n_1/kT)(\psi(\sigma_1) - \xi\sigma_1\chi(\sigma_1))]\}d\xi, \tag{10.05}$$

and

$$I_6 = \int_1^\infty \{1-\exp[(\pi n_1/kT)(\psi(\sigma_1\xi) - \xi\sigma_1\chi(\sigma_1\xi))]\}d\xi. \tag{10.06}$$

It is easy to see that z will be of the order of 1, presumably somewhat larger than 1. For, I_5 is at the utmost equal to 1, and I_6 will depend on the distance up to which the molecular forces are noticeable and will tend towards zero as this distance becomes shorter. Altogether σ^* measures what might be called the "average thickness of the surface layer."

This statement suggests a different form for (10.02). The product $n_1\sigma^*$ defines the number of particles per cm^2 in the surface layer and we may look upon this surface layer as a separate phase with a surface density

$$\nu_1 = n_1\sigma^*. \tag{10.07}$$

The "equation of state" for this phase[6] will then be given by

$$\gamma = \nu_1 kT. \tag{10.08}$$

[6] M. Born and R. Courant, Physik. Zeits. **14**, 731 (1913) have stressed, long ago, the point that the Eötvös formula should be considered as an equation of state.

If, furthermore, we call a surface which contains one mole of liquid a molar surface S^*, we can write

$$\nu_1 = N_0/S^*, \tag{10.09}$$

and the equation of state assumes the form

$$\gamma S^* = RT. \tag{10.10}$$

It is known that Eötvös, in establishing his law, was led by the law of corresponding states. He, therefore, introduced a molar surface tension $\Gamma = \gamma(Mv_1)^{\frac{2}{3}}$, referring it to a spherical volume of liquid which would contain one mole. Our derivation shows that the true analogy with the gaseous phase is brought out, not if a volume containing a mole is considered, but if the surface phase itself contains one mole.

The equations (10.08) and (10.10), suggestive as they are, cannot be compared in significance with the corresponding laws for gases or solutions. This is due to the fact that ν_1 is not independently variable (as density in gases or concentration in solutions) but is an implicit function of the temperature. Therefore, neither ν_1 nor S^* are known *a priori*. They obtain a definite meaning only if defined by the integrals involved in the expression (10.04) for z. On the other hand, the argument may be reversed and the thickness of the surface layer determined from the experimental knowledge of the surface tension.

TABLE IV. Comparison of theoretical and empirical data* (γ = surface tension, k_E = Eötvös' constant.)

1	2	3	4	5	6	7	8
Liquid	σ_1 $\times 10^8$	σ^* $\times 10^8$ 20°C	γ_{exp} at b.p.	γ_{theor} at b.p.	$4a\Gamma/3$	k_E exp	k_E theor
Mercury	5.0	28.5	394	394	0.60	0.9–1.5	1.09
Bromine	6.7	8.8	34.7	34.6	0.80	2.00	1.95
Carbon disulfide	6.9	8.1	28.5	29.3	0.78	2.1	1.86
Acetone	7.5	7.2	19.1	26.4	0.71	1.90	2.13
Carbon tetrachloride	8.1	10.8	20.0	22.7	0.84	2.21	2.16
Chloroform	7.7	9.0	21.6	25.2	0.76	2.1	2.03
Ethyl ether	8.1	7.3	15.3	19.5	0.79	2.25	2.04
Benzene	7.9	10.7	20.0	24.0	0.86	2.22	2.27
Ethyl alcohol	7.3	5.13	17.5	34.5	0.50	1.15	2.55
Water	4.8	5.43	58.9	79.1	0.42	1.20	2.48

This procedure affords a first test for the correctness of our formula since reasonable values for the thickness of the surface layer should be obtained. Again it should be pointed out that this test is entirely independent of the special law of molecular interaction.

We have calculated σ^* for our ten liquids starting from the experimental values of the surface tension at 20°C. The values thus obtained are to be found in column 3 of Table IV. They are, without exception, of the order of magnitude which might have been anticipated.

Furthermore, if the values of σ^* are compared with the values of σ_1 as determined in Part I (Table IV, column 2) it will be seen that there is a remarkable agreement between the two series (except in the case of mercury where σ^* is five to six times as large as σ_1). This agreement suggests the interpretation that the surface phase, anyway in many cases, consists just of one molecular layer. However, we have pointed out previously (p. 475, Part I) that the values of σ_1 determined in Part I may be somewhat too large. If that is true the surface phase would consist of somewhat more than one layer. This is, of course, equally acceptable.

The situation becomes less satisfactory if an attempt is made to calculate the surface tension in a quantitative way from the potentials determined in Part I. This proves feasible, without serious modification of the potential, only in the case of mercury. In the case of the other nine liquids the potentials of the form (7.01) with the constants as given in Table II (Part I) do not fall off sufficiently quickly with larger distances. This calls for a general remark.

In order that the integral (10.06) may become convergent the potential $\varphi(r)$ (p. 464, Part I) must fall off at least as $1/r^4$. For the calculations carried through in Part I it was only required that $\varphi(r)$ fall off at least as $1/r^3$. No attention was given to the more stringent requirement involved in the calculation of the surface tension, and most of the potentials tabulated in Table II are not in agreement with it.

However, this is no serious difficulty. It was stated (p. 474, Part I) that the theoretical values given in Table I (Part I) depend astonishingly little on the individual choice of the exponents λ or μ. The calculation of the surface tension, however, is strongly dependent on the individual value of μ (this μ determining the depth to which the molecular forces are sensible). It is, therefore, possible to introduce values of μ which make (10.06) convergent without sensibly affecting the agreement obtained for the other physical constants.

The theoretical value of γ can be increased indefinitely by letting the exponent μ approach its lower limit $\mu=4$. On the other hand, γ can be decreased only to a limiting value which is reached as λ and μ tend towards equality. The limiting value of the exponent is given with sufficient accuracy by $\lambda_0=\mu_0=(\beta/\gamma)^{\frac{1}{3}}+(\alpha/\gamma)$, in the notation of Section VIII. If, then, $\lambda=\lambda_0+\epsilon$ and $\mu=\lambda_0-\epsilon$ (with ϵ a small number) it is easy to develop formulae for all physical quantities including γ. They become independent of ϵ in the limit $\epsilon\to 0$ and agree closely with those tabulated in Table II, Part I. The values of λ_0 lie between 5.62 for Br_2 and 4.26 for H_2O.

However, the values of γ thus obtained are still too large by a factor which increases (in the order of our tables) from about 2 for Br_2 to at least 10 for H_2O. This discrepancy may be due to two reasons: the values of σ_1 as determined in Part I may be too large, and the potentials may fall off too slowly (even in the limiting case sketched above).

It was pointed out in Section VIII that the knowledge of σ_1 is not required for the determination of a, b, L, and c_v. Thus the agreement obtained for these constants would not be affected by a change of the values of σ_1. Only the relation (7.05) which has an approximate character would have to be modified. The knowledge of σ_1, on the other hand, is decisive for the calculation of γ and it would seem reasonable to determine σ_1 in such a way as to make γ fit the empirical data. However, such a procedure would necessitate changing σ_1 by more than seems reasonable from the uncertainty in σ_1.

Therefore, we prefer to make the potential itself responsible for the greater part in the observed discrepancy. A value of μ between 5 and 4.26 makes the surface layer extend over 3 to 10 molecular layers which is in contradiction to the direct evidence mentioned above. Thus, there can hardly be a doubt that μ should be at least 5 to make the surface tension fit empirical data. Consequently a potential of the form (7.01) does not seem adequate to describe the properties of liquids in a complete quantitative way: If the constants are determined by the elastic and thermal behavior of the liquid the potential will

fall off too slowly to give a quantitative agreement with observed surface tensions.

This situation is, after all, not astonishing. The elastic and thermal behavior of a liquid is determined by the form of the potential in the immediate neighborhood of a molecule, i.e., up to the distance σ_1. The surface tension, on the other hand, depends in a decisive way upon the decrease of the potential beyond that distance and a potential of the form (7.01) may not have sufficient flexibility to meet both exigencies.

A potential with an exponential decrease beyond σ_1 would, no doubt, be better fitted to give a quantitative description of most liquids. In order to avoid lengthy numerical calculations we have adopted, as a first very rough approximation, the procedure to "cut off," at the distance σ_1, the potentials as determined in Part I. Accordingly we assume that our potential $\varphi(r)$ is zero for $r>\sigma_1$. The same will hold, then, for $\psi(r)$ and $\chi(r)$ and the integral I_6 of (10.06) becomes zero. The numerical calculations show that the exponential in I_5 is sufficiently small for all liquids (except Hg) to make it negligible. The integral I_5 then has the value 1 and γ assumes the simple form

$$\gamma = kTn_1\sigma_1. \tag{10.11}$$

We have computed γ from this formula for our liquids (with the exception of Hg) for the chosen standard temperatures, i.e., the respective boiling points. The calculated values are compared with the empirical values in Table IV (columns 4 and 5). The empirical values had to be interpolated, and for Br_2 extrapolated, from the observed values. The agreement is about as good as might be expected from the rough approximation involved, except for the "associating" liquids alcohol and water.

It will be noticed that the theoretical values are, as a rule, too large. This would indicate that our values of σ_1 are, on the average, 30 percent too large. This is, of course, a lower limit for the deviation involved since a greater part of the error would fall on σ_1 if the potential were not to be cut off so abruptly.

We have not discussed the case of mercury yet. This liquid presents special conditions in two regards. The theoretical value $\mu=6$ could be assigned (owing to the high bulk coefficient) and the thickness of the surface layer is much larger than in all other cases (Table IV, column 3). These circumstances render it possible to fit γ to the empirical value without cutting off the potential (7.01). We have evaluated for Hg the integral (10.06) by graphical methods (the evaluation of (10.05) is immediate). If the constants as given in Table II are used a value of $\gamma=306$ is obtained as compared with the measured value $\gamma=394$. Thus, in this case the theoretical value is even too small and μ must be lowered. With the assumption $\mu=5.32$ (which leads to $\lambda=12.86$) the agreement is complete and the constants of Table I are hardly affected.

Eötvös' Law

The temperature dependence of γ is rather involved according to our formula (10.08). At first sight it would seem that γ should increase with the temperature in contradiction to empirical facts. However, n_1 and σ^* decrease with rising temperature and a general decrease may result. We shall limit ourselves to showing that Eötvös' law follows from our formula as a limiting law for $\lim (u-u_1)/kT\to 0$.

Under this assumption the quantity Γ considered by Eötvös:

$$\Gamma = \gamma(Mv_1)^{\frac{2}{3}} = \gamma(N_0/n_1)^{\frac{2}{3}}, \tag{10.12}$$

can be written in the form

$$\Gamma = \pi N_0^{2/3} n_1^{4/3}\left\{\int_0^{\sigma_1}(h\chi(\sigma_1)-\psi(\sigma_1))dh + \int_{\sigma_1}^{\infty}(h\chi(h)-\psi(h))dh.\right. \tag{10.13}$$

Therefore we obtain

$$\frac{d\Gamma}{dT} = \frac{4}{3n_1}\frac{dn_1}{dT} + \frac{\pi}{2} n_1^{4/3} N_0^{2/3}\sigma_1^3\varphi(\sigma_1)\frac{\partial\sigma_1}{\partial T}. \tag{10.14}$$

This expression is always negative since $(1/n_1)(dn_1/dT) = -a$, and since $\varphi(\sigma_1)$ is positive and $\partial\sigma_1/\partial T$ is negative for the equilibrium distance.

If we now introduce the special potential (7.01) and make use of the approximate formulae

(7.04) and (7.12) we find

$$\frac{d\Gamma}{dT}=-\frac{4}{3}a\Gamma+\frac{R}{4N_0^{\frac{1}{3}}}\left(\frac{\delta}{2\pi}\right)^{\frac{1}{3}}\frac{\delta\varphi(\sigma_1)}{kT}\frac{\varphi(\sigma_1)}{\sigma_1\varphi'(\sigma_1)}. \quad (10.15)$$

Thus, in the limit $\varphi/kT\to 0$ the Eötvös constant, $k_E=-d\Gamma/dT$, should approach the value $4a\Gamma/3$. In this form the relation can be tested, without reference to the form of the molecular interaction, by the insertion of the experimental values for a and Γ. It will be seen from Table IV (columns 6 and 7) that $4a\Gamma/3$ has the correct order of magnitude but gives less than half of the experimental values.

Under actual conditions the second term in (10.15) is of the same order of magnitude as the first. We have calculated it making use of the values determined in Section VIII. This is a legitimate approximation since the second term in (10.15) has its origin in the first integral of (10.13). Hence the value of this term is not affected by the fact that the potential has to be modified *beyond* σ_1 in order to give correct values for γ itself.

Column 8 of Table IV contains the values which we have calculated from the complete expression (10.15), for the standard temperatures, using the empirical data for a and Γ. The agreement between observed (column 7) and calculated values is almost better than might have been anticipated since the assumption $(u-u_1)/kT\ll 1$ is not fulfilled for the standard temperatures. Under these circumstances it should be stressed only that $d\Gamma/dT$ comes out negative and of the proper order of magnitude. The main contribution in making $d\Gamma/dT$ negative comes from $\partial\sigma_1/\partial T$ as in the case of thermal expansion (see p. 474, Part I). It need hardly be mentioned that k_E is not a true constant but itself depends on temperature as is also shown by experimental evidence.

XI. NEIGHBORHOOD OF THE CRITICAL POINT

In deriving the potential for the surface layer we have assumed that the contribution on the vapor side can be neglected. As pointed out previously (p. 465, Part I) this assumption restricts our treatment, as far as surface terms have been considered, to the case where the molecular density in the vapor is small compared to that in the liquid. In order to obtain formulae which hold up to the critical point we must first generalize the expressions for the potential in the transition layer.

In doing so we shall not write down the formulae which correspond to (2.04) and (2.07) and which hold if the density is treated as variable within the surface layer. We shall be satisfied to establish the first approximation which assumes the densities in the two adjacent phases to be constant up to the geometrical boundary. Consequently there will be a discontinuity of the density in this boundary. Furthermore, we shall disregard the dependence of σ, the average distance of nearest neighbors, upon the change of potential within the layer (see p. 470, Part I). Then σ_1 and σ_2 become parameters independent of space within the respective phases and only dependent on the temperature and the average molecular density in the way established in Section V.

If we now call h_1 the normal distance from the boundary in the liquid the potential of a point at the depth h_1 becomes, by straight forward integrations,

$$u=\pi n_1[\psi(\sigma_1)+h_1\chi(h_1)]+\pi n_2[\psi(\sigma_2)+(h_1/\sigma_1)(\psi(\sigma_1)-\psi(\sigma_2))-h_1\chi(h_1)],\quad 0\leq h_1\leq\sigma_1, \quad (11.01)$$

and

$$u=\pi n_1[2\psi(\sigma_1)-\psi(h_1)+h_1\chi(h_1)]+\pi n_2[\psi(h_1)-h_1\chi(h_1)],\quad \sigma_1\leq h_1<\infty. \quad (11.02)$$

These formulae reduce, of course, to (2.10) and (2.11) if n_2 is negligibly small compared with n_1.

Counting h_2 in the analogous way from the boundary into the vapor phase we obtain

$$u=\pi n_1[\psi(\sigma_1)-h_2\chi(\sigma_1)]+\pi n_2[\psi(\sigma_2)+h_2\chi(\sigma_2)],\quad 0\leq h_2\leq\sigma_1, \quad (11.03)$$

$$u=\pi n_1[\psi(h_2)-h_2\chi(h_2)]+\pi n_2[\psi(\sigma_2)+h_2\chi(\sigma_2)],\quad \sigma_1\leq h_2\leq\sigma_2, \quad (11.04)$$

and

$$u=\pi n_1[\psi(h_2)-h_2\chi(h_2)]+\pi n_2[2\psi(\sigma_2)-\psi(h_2)+h_2\chi(h_2)],\quad \sigma_2\leq h_2<\infty. \quad (11.05)$$

These expressions make the potential a continuous function across the boundary, varying from the negative value (2.14) in the interior of the liquid to the negative value of smaller amount (2.15) in the interior of the vapor (see reference 7, Part I). In the geometrical boundary we have

$$u_0=\pi[n_1\psi(\sigma_1)+n_2\psi(\sigma_2)]. \qquad (11.06)$$

It should be noticed that, on the vapor side u is different from u_2 even if the contributions of n_2 are neglected. For $n_1=n_2$ the potential (11.01) to (11.05) becomes constant throughout as it should.

With the potential thus generalized the partition function leads to an expression for the "work function" identical with (3.10) if only (3.06) is replaced by

$$q_\tau=\Pi=\Pi_1V_1+\omega_1S+\Pi_2V_2+\omega_2S. \qquad (11.07)$$

Here, Π_1 and Π_2 are defined by (3.07) and (3.08) and the two surface terms are given by

$$\omega_i=\int_0^\infty[\exp(-u/kT) - \exp(-\mu_i/kT)]dh_i, \quad i=1,2. \qquad (11.08)$$

It should be mentioned that ω_1 is negative whereas ω_2 is positive.

S, of course, refers to the common surface of the two phases. This will be spherical under our assumptions, as previously proved (p. 467, Part I). The vapor phase will necessarily have an exterior surface S_2 and this should give a contribution to q_τ depending on the interaction between the vapor and the walls of the containing vessel. We are not interested here in this surface effect and have disregarded it.

With the new form of Π, (11.07), most of the formulae of Section III take slightly modified forms which are easy to establish. The changes regard the corrective surface terms which are of negligible influence anyway. The only significant change concerns the surface tension. Instead of (3.21) we obtain

$$\gamma=-kTn_1\frac{\omega_1}{\Pi_1}\Big/\left(1+\frac{\omega_1S}{\Pi_1V_1}\right) - kTn_2\frac{\omega_2}{\Pi_2}\Big/\left(1+\frac{\omega_2S}{\Pi_2V_2}\right). \qquad (11.09)$$

If this expression is evaluated as in the preceding section our final formula (10.02) is augmented by additional terms which do not vanish even if all terms involving n_2 are neglected. However, it can be shown that the additional terms are numerically irrelevant as long as the density of the vapor is small compared to that of the liquid. Thus the procedure adopted in Part I and in Section X is legitimized. The corrected form of γ, (11.09), vanishes, as do ω_1 and ω_2, if n_1 and n_2 become equal.

We are now prepared to study the equilibrium of the two phases in the neighborhood of the critical point. Proceeding in exactly the same way as in Section IV we obtain, instead of (4.06) and (4.05) the following two conditional equations:

$$\Omega_1=\Omega_2=\Omega \qquad (11.10)$$

and

$$\Pi_1-n_1\Omega+2\omega S/3V_1=\Pi_2-n_2\Omega. \qquad (11.11)$$

Here we have introduced the notations

$$\omega=\omega_1+\omega_2 \qquad (11.12)$$

and

$$\Omega_i=\frac{\partial\Pi_i}{\partial n_i}+\frac{S}{V_i}\frac{\partial\omega}{\partial n_i}, \quad i=1,2. \qquad (11.13)$$

The conditional equations (11.10) and (11.11) now hold for all values of n_1 and n_2, including the critical region. It can be proved that, with the assumptions regarding $\varphi(r)$ which we made in the beginning (p. 464, Part I), a critical point will exist.[7] The critical data will be given, in the usual way, by the equation of state[8] together with the two conditions

$$\frac{\partial p_1}{\partial V_1}=0, \quad \frac{\partial^2 p_1}{\partial V_1^2}=0. \qquad (11.14)$$

It will be seen presently that the relative size of the two phases in the immediate neighborhood of the critical point is fixed by the conditions of equilibrium. However the solution for the critical data will still involve corrective surface terms. In a strict sense, therefore, one should speak of a "critical region." However, the critical data can

[7] See Appendix I, this paper.

[8] The exact expression for the pressure in the liquid phase is now given by the left-hand side of (4.05) with ω substituted from (11.12). The pressure in the vapor phase is given by a similar expression with the last term missing.

be obtained with sufficient accuracy by the use of the abbreviated equation of state (6.04). If required, the exact data could, then, be calculated by a procedure of successive approximations.

For what follows we assume the critical data n_c, p_c, and T_c to be determined. For the neighborhood of the critical point we set

$$n_1=n_c+\nu_1, \quad n_2=n_c+\nu_2, \quad T=T_c+\tau, \quad (11.15)$$

and develop the conditional equations (11.10) and (11.11) with regard to the small quantities ν_1, ν_2, and τ. The zero-order terms yield

$$\frac{S}{V_1}\left(\frac{\partial\omega}{\partial n_1}\right)_c=\frac{S}{V_2}\left(\frac{\partial\omega}{\partial n_2}\right)_c, \quad (11.16)$$

where the subscript c refers to the critical point. This equation determines the relative size of the two phases. The first-order terms yield

$$\begin{aligned}\nu_1\Big[\left(\frac{\partial^2\Pi_1}{\partial n_1^2}\right)_c+\frac{S}{V_1}\left(\frac{\partial^2\omega}{\partial n_1^2}\right)_c \\ -\frac{S}{V_2}\left(\frac{\partial^2\omega}{\partial n_2\partial n_1}\right)_c\Big]-\nu_2\Big[\left(\frac{\partial^2\Pi_2}{\partial n_2^2}\right)_c \\ +\frac{S}{V_2}\left(\frac{\partial^2\omega}{\partial n_2^2}\right)_c-\frac{S}{V_1}\left(\frac{\partial^2\omega}{\partial n_1\partial n_2}\right)_c\Big] \\ =-\Big[\frac{S}{V_1}\left(\frac{\partial^2\omega}{\partial n_1\partial T}\right)_c-\frac{S}{V_2}\left(\frac{\partial^2\omega}{\partial n_2\partial T}\right)_c\Big]\tau \quad (11.17)\end{aligned}$$

and

$$\begin{aligned}\nu_1\Big[\frac{1}{3}\left(\frac{\partial\omega}{\partial n_1}\right)_c\Big]-\nu_2\Big[\left(\frac{2}{3}+\frac{V_1}{V_2}\right)\left(\frac{\partial\omega}{\partial n_2}\right)_c\Big] \\ =\frac{2}{3}\left(\frac{\partial\omega}{\partial T}\right)_c\tau. \quad (11.18)\end{aligned}$$

From these equations ν_1 and ν_2 can be determined as functions of τ.

We shall not attempt to investigate the solution of (11.17) and (11.18). However, one point is of interest. From the form of the equations it is evident that ν_1 and ν_2 will be proportional to τ, and the same result, therefore, will hold for $\nu_1+\nu_2$. This expresses the rule of the "rectilinear diameter" established by Cailletet and Mathias. Our deduction, of course, holds only for the neighborhood of the critical point and there is no indication, without the study of higher terms, why the rule holds over a comparatively wide domain of temperatures. This fact, however, appears connected with the corresponding fact that the surface tension is practically a linear function of the temperature.

Finally we shall derive the value of the Kamerlingh Onnes constant K under the assumption of the special potential (7.01). The complete knowledge of the critical point requires, besides the determination of n_c, p_c, and T_c, that of the equilibrium distance σ_c at the critical point. The necessary four equations are given by the equation of state, the two conditions (11.14) and the equation (5.05) which is characteristic of our theory and which connects σ, T, and n.

Neglecting surface terms we start from the equation of state in the form (6.04), with U_1 given by (6.03) and (7.03). The combination of the two equations (11.14) yields σ_c:

$$\sigma_c^{\lambda-\mu}=f\lambda^2(\lambda+3)(\mu-3)/(g\mu^2(\mu+3)(\lambda-3)). \quad (11.19)$$

Substitution of this value into either of Eqs. (11.04) gives a relation between the critical temperature and critical density

$$kT_c=(2\pi/9)n_cf\sigma_c^{-\lambda+3}\lambda(\lambda+3)\times(\lambda-\mu)/(\mu(\lambda-3)), \quad (11.20)$$

and if this is substituted into the equation of state, an expression for K is obtained:

$$K=RT_c/p_cV_c=(\lambda+3)(\mu+3)/\lambda\mu. \quad (11.21)$$

Here V_c stands for the molar volume at the critical point. Lennard-Jones and Devonshire[9] have derived, by the "cell method," a formula for K which is equivalent to (11.21). The exponents introduced by these authors refer, however, not to the intermolecular potential but to a function defining, in an arbitrary way, the average volume occupied by each atom.

We have compared the expression (11.21) with the experimental critical data as far as they are

[9] J. E. Lennard-Jones and A. F. Devonshire, Proc. Roy. Soc. **A163**, 53 (1937).

available for our ten liquids. The calculated and the observed values of K are given in columns 6 and 7 of Table III. The calculated values are consistently too small by 25 to 33 percent (if H_2O is excluded). This suggests a systematic error as in the case of the heat of vaporization. However, the discrepancy is hardly larger than one would expect with the special form of potential adopted if it is taken into account that the coefficients involved (Table II, Part I) have been determined from measurements at the ordinary boiling point.

If we want to summarize the results we should distinguish between the general theory and the deductions based on the special form of potential (7.01). The general theory seems satisfactory in the following regards: It reestablishes a random distribution of the molecules and gives the liquid a shape determined by surface tension. Furthermore, it proves the possibility of coexistence of vapor and liquid within certain limits of temperature and it leads automatically to kinetic expressions for the vapor pressure and for the surface tension.

As to the special form of the potential (7.01) it has been shown that it represents the behavior of liquids of widely variable character in a general way. In the one case of mercury the representation covers the thermal and elastic behavior as well as the surface tension. In all other cases the potential has to be modified for larger molecular distances if it is to include surface tension quantitatively. Furthermore, there remain discrepancies of a systematic nature in the determination of the heat of vaporization and in the critical data. It has not been investigated how far association in one or both phases may be responsible for these deviations. However, even with these deficiencies, it seems satisfactory that the simplified assumption of extensionless mass points, with the very special form of potential (7.01), gives our model practically all properties of real liquids with an almost quantitative agreement.

APPENDIX I

It has to be shown that, for sufficiently high values of the temperature, the equations of state for the two phases admit of only one solution for the molecular density n. The proof proceeds in two steps. First surface terms are neglected. In the limiting case $\varphi/kt \to 0$ the parameter σ becomes independent of T and assumes the geometrical value $\sigma=(1/2\pi n)^{\frac{1}{3}}$ of Hertz (p. 470, Part I). From this fact, and from the assumed form of $\varphi(r)$ (p. 464, Part I), it follows that p, as determined from (6.04), increases monotonically with decreasing V. This proves the point in the absence of surface terms. To complete the proof we call the unique solution which exists for sufficiently high values of T, in the absence of surface terms n_0 and investigate whether two solutions of the form $n_1=n_0+\nu_1 S/V_1$ and $n_2=n_0+\nu_2 S/V_2$ can be obtained. If these expressions are introduced into the formulae for the pressure[8] it follows that $n_1=n_2$ *to all orders of approximation.* Hence there is only one solution and no surface of separation can exist. As it has been proved previously (Appendix I, Part I) that there are at least two solutions for sufficiently low temperatures there must be an upper limit of temperature (eventually depending on surface terms) for which more than one solution can be obtained.

In Appendix I, Part I we have given two forms for the conditional equations, either Eqs. (a) and (c) or Eqs. (d) and (e). As surface terms were not considered in Appendix I, Part I, it should be mentioned that both sets yield only a zero approximation for a procedure of successive approximations. Furthermore, it should be pointed out that the two sets are *not* equivalent. Eqs. (d) and (e) are a necessary consequence of Eqs. (a) and (c) but not vice versa. The reason for this situation is that the transition from (a) and (c) to (d) and (e) involves a differentiation. For the calculation of the exact critical data the set (d) and (e) represents a much more adequate zero solution than (a) and (c) since (a) makes the pressure zero.

Letters to the Editor

Nuclear Energy Levels in Fe^{56} from the Decay of Mn^{56} and Co^{56}

L. G. Elliott and M. Deutsch
Massachusetts Institute of Technology, Cambridge, Massachusetts
March 25, 1943

THE radiations accompanying the radioactive decay of Mn^{56} have been studied by a number of authors.[1] However, no consistent energy level scheme could be con-