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ADSORPTION ISOTHERM OF RARE GAS ON THE SURFACE OF ITS OWN BULK LIQUID

By

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Abstract

Preparatory to the investigation of multilayer adsorption, the adsorption isotherm of rare gases on a surface of its own bulk liquid was statistical mechanically worked out allowing for lateral, attractive interactions between adsorbate molecules in terms of the Bethe-Peierls' approximation. A quantity, γ_0, is defined as the Boltzmann factor of the increment of Helmholtz energy due to transfer of an adsorbate molecule from the gas phase to a definite, preliminarily evacuated site of adsorption, which is proportional to the concentration of adsorbate molecules in gas. The γ_0 was statistical mechanically calculated as a function of covered fraction, θ_0; the function has a single parameter of Boltzmann factor ξ of attractive potential between two adsorbate molecules with their spherical models in contact with each other. For $\xi<2.48$, γ_0 increased monotonously with increase of θ_0. For $\xi\geq 2.48$ the curve of $\gamma_0(\theta_0)$ revealed a loop passing, with increase of θ_0, a maximum and then a minimum; it followed thermodynamically from the loop that the adsorbate separates into coexistent two-dimensional vapour and liquid respectively with θ_0 equal to $\theta_{0,\mathrm{I}}$ and $\theta_{0,\mathrm{II}}(>\theta_{0,\mathrm{I}})$, insofar as the θ_0 of the original adsorbate lies between $\theta_{0,\mathrm{I}}$ and $\theta_{0,\mathrm{II}}$, which satisfy the condition that $\ln \gamma_{0,\mathrm{e}} = \int_{\theta_{0,\mathrm{I}}}^{\theta_{0,\mathrm{II}}} \ln \gamma_0 d\theta_0/(\theta_{0,\mathrm{II}}-\theta_{0,\mathrm{I}}) = (\ln \gamma_0)_{\theta_0=\theta_{0,\mathrm{I}}} = (\ln \gamma_0)_{\theta_0=\theta_{0,\mathrm{II}}}$.

The $\theta_{0,\mathrm{I}}$ and $\theta_{0,\mathrm{II}}$ shift toward zero and unity respectively with increase of ξ, which, as evaluated from thermodynamic data, indicates that the last-mentioned separation does occur at the boiling point of rare gases, except helium.

The approximation resorted to was verified to be numerically accurate enough as regards $\gamma_{0,\mathrm{e}}$, γ_0 for $\theta_0<\theta_{0,\mathrm{I}}$ and γ_0 for $\theta_0>\theta_{0,\mathrm{II}}$, *i.e.* γ over the whole range of θ_0, provided that ξ is sufficiently large, so that $\theta_{0,\mathrm{I}}$ and $\theta_{0,\mathrm{II}}$ are close to zero and unity respectively.

1. Introduction

It is well-known that the main fault of the BET theory of multilayer adsorption is the neglect of lateral interactions between adsorbate molecules. A number of attempts have been made to amend it but any of them appeared hardly to have offset the quantitative unsoundness of the method arising from

the fault. It is admitted,[1] on the other hand, that a sound theory of multilayer adsorption should comprize that of bulk liquid as its special case, where adsorbent it simply the liquid condensation of adsorbate. The present article is devoted, preparatoy to the treatment of multilayer adsorption, to the statistical mechanical formulation of the last-mentioned "adsorption" with particular reference to rare gases.

Based on a model presented below an isotherm of adsorbate molecules on a surface of the bulk liquid is formulated statistical mechanically allowing for the lateral interactions between adsorbate molecules. We thus derive the Boltzamann factor, γ_0, of the increment of Helmholtz energy due to transfer of a molecule from the gas phase to a definite, preliminarily evacuated site of adsorption apart from the interaction with surrounding adsorbate molecules; γ_0 is proportional to the concentration of molecules in gas phase in equilibrium with the adsorbate and is a function of covered fraction, θ_0, with a single parameter, ξ, which is the Boltzmann factor of attractive potential of a pair of molecules with their spherical models in contact with each other, irrespective of the kind of molecule and temperature. For $\xi \geq 2.48$, the $\gamma_0(\theta_0)$-curve reveals, along with increases of θ_0, a maximum and then a minimum, while for $\xi < 2.48$, γ_0 increases monotonously with θ_0. It follows thermodynamically from the former curve that the adsorbate separates, except for θ_0 close to zero and unity, into two-dimensional vapour and liquid coexistent with each other and with molecules in gas phase.

Regarding now the bulk liquid as a pile of layers of the two-dimesional liquid, parameter ξ is determined from the known thermodynamic data of rare gases. The ξ at the boiling point of rare gases, except helium, was found large enough to cause the separation.

2. Model

The model of bulk liquid is specified as below as an adsorbent on which basis the statistical mechanical theory is developed.

a) The adsorbent of bulk liquid and adsorbate consist of spherical molecules of the same kind, and the potential between them is attractive, additive and significant only for contacting pairs of them.

b) Molecules composing the surface of bulk liquid are arrayed in (111)-lattice and every three of them contacting one another furnish one of physically identical sites of adsorption. A molecule adsorbed on one of the sites contacts with the three underlying molecules which furnish the site. Molecules completely occupying the sites furnished by the underlying layer provide a fresh

array of sites which is identical with that provided by the underlying layer.

The sites mentioned in b) above are illustrated in Fig. 1; we see that adsorbate molecules compactly arrayed in a layer can occupy sites of either class indicated by ● or by ○ completely but not those of both the classes simultaneously.

3. Adsorption Isotherm

An adsorption isotherm is derived first, as there existed sites of class ● alone, which are marked in Fig. 1 by bold circles depicting orthographs of molecules adsorbed there. Site σ_0 is thus surrounded by six kindred sites, $\sigma_1, \cdots, \sigma_6$. The set of seven sites, $\sigma_0, \cdots, \sigma_6$, is symbolized by $\sum$ and indicated

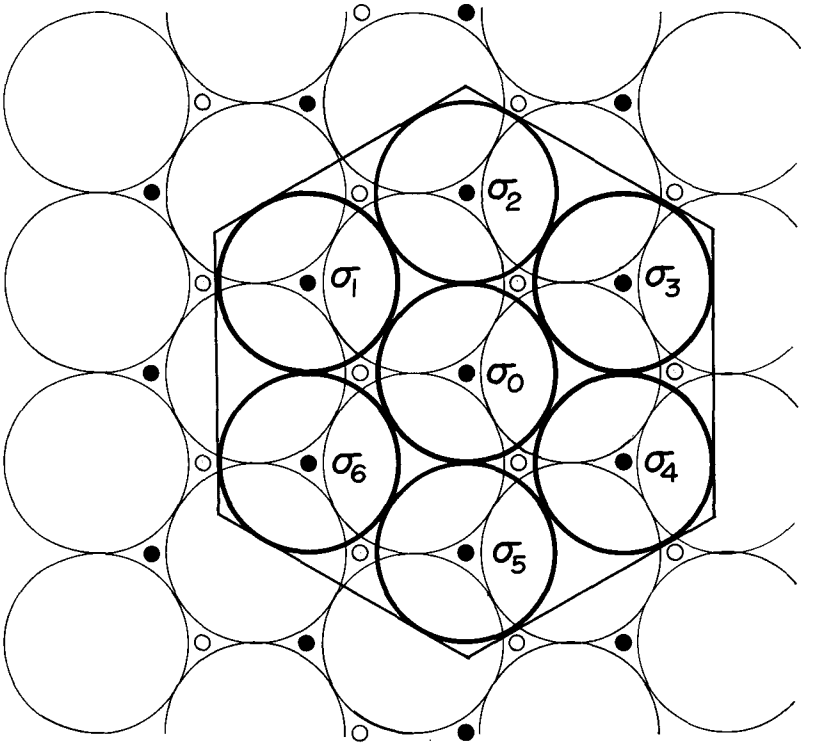


Fig. 1. Sites of adsorption on the surface of bulk liquid. ○ signifies an orthograph of a molecule composing the surface of bulk liquid, and O that of molecule adsorbed on the surface. ● denotes adsorption sites of a class and ○ that of the other, either of them being exclusively occupied by molecules closest packed in a layer; the set of sites, $\sigma_0, \cdots \sigma_5$, and σ_6, circumscribed by a regular hexagon is signified by $\sum$.

in Fig. 1 by a regular hexagon circumscribed about the orthographs of $\sigma_1, \cdots, \sigma_6$. Let $\mathfrak{A}$ be the assembly in equilibrium which consiste of an "adsorbent," "adsorbate" and molecules in gas phase. Partition function of $\mathfrak{A}$ is designated by $\Omega\mathfrak{A}$ and $\mathfrak{A}$ in a particular state by an appropriate suffix when necessary. The adsorption isotherm is given in terms of partition functions of $\mathfrak{A}$ in different particular states.

3.1. Partition functions

Partition functions of $\mathfrak{A}$ at different particular states are formulated, from which the adsorption isotherm is derived.

3.1.1. $\Omega\mathfrak{A}_{\sigma_0(0)}$

Let $\Omega\mathfrak{A}_{\Sigma(0)}$ be the partition function of $\mathfrak{A}$ in the particular state where $\sum$ is kept altogether unoccupied with certainty, and $\Omega\mathfrak{A}_{\sigma_0(0)}$ that in another particular state, where σ_0 is unoccupied with certainty. $\Omega\mathfrak{A}_{\sigma_0(0)}$ is given in terms of $\Omega\mathfrak{A}_{\Sigma(0)}$ as

$$\Omega\mathfrak{A}_{\sigma_0(0)} = \Omega\mathfrak{A}_{\Sigma(0)}(1+6\gamma_0\eta+6\gamma_0^2\eta^2\xi+6\gamma_0^2\eta^2+3\gamma_0^2\eta^2+6\gamma_0^3\eta^3\xi^2+6\gamma_0^3\eta^3\xi$$

$$+6\gamma_0^3\eta^3\xi+2\gamma_0^3\eta^3+6\gamma_0^4\eta^4\xi^3+6\gamma_0^4\eta^4\xi^2+3\gamma_0^4\eta^4\xi^2+6\gamma_0^5\eta^5\xi^4+\gamma_0^6\eta^6\xi^6), \tag{1. a}$$

where

$$\gamma_0 = q_0\xi^3/p_G\,; \tag{1. b}$$

p_G is the factor of multiplication of $\Omega\mathfrak{A}$ by addition of a molecule from outside $\mathfrak{A}$ to the gas phase of $\mathfrak{A}$; the multiplier, p, of this sort is connected with the appropriate chemical potential,[2] μ, as

$$\mu = -RT\ln p\,. \tag{2. a}$$

The ξ^3 is the Boltzmann factor of potential ε_0 of an adsorbate molecule due to three molecules in the underlying layer in contact with the adsorbate molecule in accordance with **a**) and **b**) in **2.**, hence

$$\xi = \exp(-\varepsilon_0/3kT)\,. \tag{2. b}$$

The $q_0\xi^3$ is another factor of multiplication of $\Omega\mathfrak{A}$ by addition of an adsorbate molecule from outside $\mathfrak{A}$ to a definite, preliminaily evacuated site[2]; q_0 is the relevant multiplyer of $\Omega\mathfrak{A}$ apart from the Boltzmann factor of the appropriate increment of potential energy of $\mathfrak{A}$. The $\gamma_0 = q_0\xi^3/p_G$ is in consequence the factor of multiplication of $\Omega\mathfrak{A}$ by transfer of a molecule from the gas phase

of $\mathfrak{A}$ to the definite, preliminarily evacuated site, hence is the Boltzmann factor of the relevant increment of Helmholtz energy, $-kT\ln q_0/p_G+\varepsilon_0$, according to Eq. (2. b) apart from the interaction with other adsorbate molecules.

The attraction of other adsorbate molecules is taken into account as follows. A molecule adsorbed on σ_0 is free from interaction with other adsorbate molecules, according to **a**), **2.**, if all peripheral sites, $\sigma_0, \cdots, \sigma_6$, of $\sum$ are unoccupied. Any adjacent pair of adsorbate molecules in $\sum$ contributes a term, $\varepsilon_0/3$, to the increment of Helmholtz energy due to formation of an arrangement inside $\sum$ or, accoding to Eq. (2. b), a factor ξ, to the relevant factor of multiplication of $\Omega\mathfrak{A}_{\Sigma(0)}$. An adsorbate molecule on one of the peripheral sites is subject, besides, to interactions with adsorbate molecules outside $\sum$, which is allowed for by a factor, η, to be subsequently determined by the BETHE-PEIERLS' method.[3] Every hexagon drawn below each term in Eq. (1. a) shows the appropriate pattern of occupied sites signified by dots.

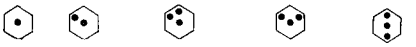
The first term in the parentheses is the multiplier of unity corresponding to none of adsorbate molecule inside $\sum$ and the second term, $6\gamma_0\eta$, is the multiplier of partition function due to transfer of a single molecule from the gas phase to one of the six peripheral sites inside $\sum$, the transfer to each site contributing the same multiplier, $\gamma_0\eta$, because of the hexagonal symmetry ; the third term, $6\gamma_0^2\eta^2\xi$, allows for the transfer of two adsorbate molecules to two adjacent peripheral sites, which has six different patterns of occupation, each contributing the same multiplier, $\gamma_0^2\eta^2\xi$. Factor, ξ, is absent in the fourth and the fifth terms because of lack of adjacent pair of adsorbed molecules inside $\sum$, whereas sixth term has two ξ-factors due to the two adjacencies inside $\sum$. Other terms are similarly derived from the appropriate patterns.

Numerical coefficients of terms sum up to the total sum of the binomial coefficients, *i.e.* $2^6=64$, which checks the formulation of terms in question.

3.1.2. $\Omega\mathfrak{A}_{\sigma_0(\delta)}$

Eq. (3) below gives the partition function of $\mathfrak{A}$ under a particular state that σ_0 is occupied with certainty, *i.e.* $\Omega\mathfrak{A}_{\sigma_0(\delta)}$; as seen readily, there sxists a one-to-one correspondence between terms of Eq. (1. a) and those of Eq. (3) such that every term of Eq. (3) is derived from a term in Eq. (1. a) by multiplying it into $\gamma_0\xi^{n_\eta}$, where n_η is the exponent to η of the latter term, *i.e.* the number of adsorbate molecules on the peripheral sites, which interact with that on σ_0.

$$\Omega\mathfrak{A}_{\sigma_0(\delta)}=\Omega\mathfrak{A}_{\Sigma(0)}\gamma_0(1+6\gamma_0\eta\xi+6\gamma_0^2\eta^2\xi^3+6\gamma_0^2\eta^2\xi^2+3\gamma_0^2\eta^2\xi^2$$



$$+6\gamma_0^3\eta^3\xi^5+6\gamma_0^3\eta^3\xi^4+6\gamma_0^3\eta^3\xi^4+2\gamma_0^3\eta^3\xi^3+6\gamma_0^4\eta^4\xi^7+6\gamma_0^4\eta^4\xi^6$$

$$+3\gamma_0^4\eta^4\xi^6+6\gamma_0^5\eta^5\xi^9+\gamma_0^6\eta^6\xi^{12})\,. \qquad (3)$$

$\Omega\mathfrak{A}_{\sigma_0(\delta)}/\Omega\mathfrak{A}_{\sigma_0(0)}$ gives now the ratio of probability that site σ_0 is occupied by an adsorbate to the probability that the same site is unoccupied; denoting the former probability by θ_0, we have

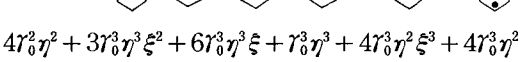
$$\frac{\theta_0}{1-\theta_0}=\frac{\Omega\mathfrak{A}_{\sigma_0(\delta)}}{\Omega\mathfrak{A}_{\sigma_0(0)}}\,. \qquad (4)$$

The θ_0 is identified with the covered fraction of sites on account of their physical identity postulated by **b**), **2**. The covered fraction, θ_0, is evaluated for any prescribed values of γ_0 and ξ, provided that η is determined.

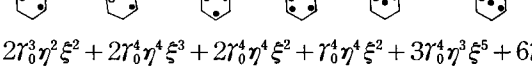
3.1.3. Determination of η.

The η is determined according to the BETHE and PEIERLS' approximation[3] by equating $\Omega\mathfrak{A}_{\sigma_0(0)}$ to $\Omega\mathfrak{A}_{\sigma_1(0)}$ on the ground of physical identity of σ_0 and σ_1, where $\Omega\mathfrak{A}_{\sigma_1(0)}$ is the partition function of $\mathfrak{A}$ in the particular state that site σ_1, instead of σ_0, is unoccupied with certainty; $\Omega\mathfrak{A}_{\sigma_1(0)}$ is formulated on the similar principle to that applied to $\Omega\mathfrak{A}_{\sigma_0(0)}$ and $\Omega\mathfrak{A}_{\sigma_0(\delta)}$, as

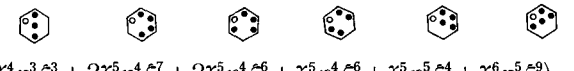
$$\Omega\mathfrak{A}_{\sigma_1(0)}=\Omega\mathfrak{A}_{\Sigma(0)}(1+5\gamma_0\eta+\gamma_0+5\gamma_0^2\eta\xi+4\gamma_0^2\eta^2\xi+2\gamma_0^2\eta^2$$



$$+4\gamma_0^2\eta^2+3\gamma_0^3\eta^3\xi^2+6\gamma_0^3\eta^3\xi+\gamma_0^3\eta^3+4\gamma_0^3\eta^2\xi^3+4\gamma_0^3\eta^2\xi^2$$



$$+2\gamma_0^3\eta^2\xi^2+2\gamma_0^4\eta^4\xi^3+2\gamma_0^4\eta^4\xi^2+\gamma_0^4\eta^4\xi^2+3\gamma_0^4\eta^3\xi^5+6\gamma_0^4\eta^3\xi^4$$



$$+\gamma_0^4\eta^3\xi^3+2\gamma_0^5\eta^4\xi^7+2\gamma_0^5\eta^4\xi^6+\gamma_0^5\eta^4\xi^6+\gamma_0^5\eta^5\xi^4+\gamma_0^6\eta^5\xi^9)\,, \qquad (5)$$

where the unoccupied site, σ_1, is signified by a circle and occupied sites by dots in every hexagon drawn below the appropriate term.

Equating $\Omega\mathfrak{A}_{\sigma_0(0)}$ to $\Omega\mathfrak{A}_{\sigma_1(0)}$ given respectively by Eqs. (1. a) and (5) and rearranging, we have

$$\gamma_0^5\xi^6\eta^6+(5-\xi^5\gamma_0)\gamma_0^4\xi^4\eta^5+\{6+4\xi-(2\xi+3)\xi^4\gamma_0\}\gamma_0^3\xi^2\eta^4$$
$$+(1+6\xi+3\xi^6)(1-\xi^3\gamma_0)\gamma_0^2\eta^3+(3+2\xi)(1-2\xi^2\gamma_0)\gamma_0\eta^2$$
$$+(1-5\xi\gamma_0)\eta-1=0\,, \qquad (6)$$

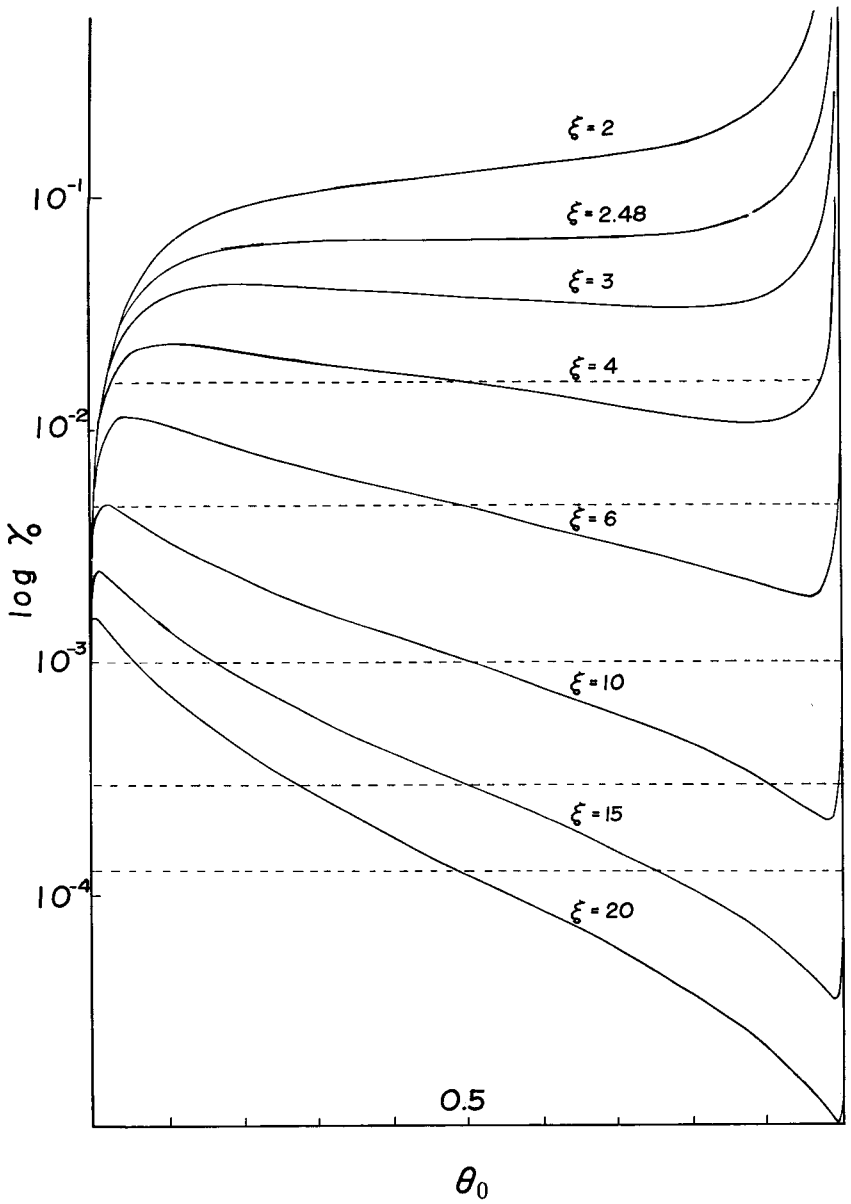


Fig. 2. log γ_0 *vs.* θ_0 for different values of ξ.

i.e. an equation of sixth degree with respect to η. The numerical values of η are worked out by solving Eq. (6) for different values of ξ and γ_0. It is thus found that there exist three real, positive roots of Eq. (6) for $\xi \geq 2.48$ over a certain range of γ_0 but for $\xi < 2.48$ only one positive, real root throughout.*) One or three real, positive values of η define so many such values of θ_0 by Eqs. (1. a), (3) and (4). The numerical calculation has been carried out with electronic computer, NEAC–2203 G. The $\log \gamma_0$ thus obtained is plotted against θ_0 as shown in Fig. 2.

3. 2. Two-dimensional vapour and liquid.**)

Fig. 2 shows that any curve of $\log \gamma_0$ *vs.* θ_0 for $\xi \geq 2.48$ passes, along with increase of θ_0, a maximum and then a minimum, giving θ_0 as a three-valued function of $\log \gamma_0$ between the maximum and minimum. Any curve for $\xi \geq 2.38$ has thus the particular value, $\log \gamma_{0,e}$, of $\log \gamma_0$, which satisfies the equation

$$\ln \gamma_{0,e} = \int_{\theta_{0,I}}^{\theta_{0,II}} \ln \gamma_0 d\theta_0 / (\theta_{0,II} - \theta_{0,I}) , \tag{7}$$

where $\theta_{0,I}$ and $\theta_{0,II}$ are the lowest and highest values of θ_0 for $\gamma_0 = \gamma_{0,e}$. The chemical potential of molecules in gas phase, μ_0, defined as $\mu_0 = -RT \ln p_G$, which is expressed according to Eq. (1. b) as

$$\mu_0 = RT \ln \gamma_0 / q_0 \xi^3 . \tag{8. a}$$

Let $\mu_{0,e}$ be the particular value of μ_0 defined as

$$\mu_{0,e} = RT \ln \gamma_{0,e} / q_0 \xi^3 . \tag{8. b}$$

Eq. (7) is written according to Eqs. (8) in the form

$$\mu_{0,e} = \int_{\theta_{0,I}}^{\theta_{0,II}} \mu_0 d\theta / (\theta_{0,II} - \theta_{0,I}) \tag{9. a}$$

or

$$\int_{\theta_{0,I}}^{\theta_{0,II}} (\mu_0 - \mu_{0,e}) d\theta_0 = 0 ; \tag{9. b}$$

$\mu_{0,e}$ equals, by definition of $\gamma_{0,e}$ and Eq. (8. b), the value of μ_0, $\mu_{0,I}$, at $\theta_0 = \theta_{0,I}$ and that, $\mu_{0,II}$, at $\theta_0 = \theta_{0,II}$, *i.e.*

$$\mu_{0,e} = \mu_{0,I} = \mu_{0,II} . \tag{9. c}$$

It follows from Eqs. (8) and Fig. 2 that

*) Real and positive values of η and γ_0 are only significant by definition.

**) A similar treatment of isotherms as regards the coexistence of vapour and liquid is given in "*Chemical Thermodynamics*" by I. PRIGOGINE and R. DEFAY, translated by D. H. EVERETT, Chap. XVI, Longmans 1954.

$$\mu_0 > \mu_{0,e} \text{ for } \theta_{0,I} < \theta_0 < \theta_{0,m} \tag{10. a}$$

and

$$\mu_0 < \mu_{0,e} \text{ for } \theta_{0,m} < \theta_0 < \theta_{0,II}\,, \tag{10. b}$$

where $\theta_{0,m}$ is the third value of θ_0 between $\theta_{0,I}$ and $\theta_{0,II}$ for $\gamma_0 = \gamma_{0,e}$ or $\mu_0 = \mu_{0,e}$.

The above relations are transformed in terms of Helmholtz enery, F, of $\mathfrak{A}$ per mole of odsorption sites (irrespective as to whether occupied). F is connected with μ, as

$$\mu_0 = \partial F / \partial \theta_0\,, \tag{11. a}$$

hence derived by Eq. (11. a) from $\mu_0 = \mu_0(\theta_0)$ given by Fig. 2 with reference to Eq. (8. a) as shown in Fig. 3 by its excess over the linear function, $F_I + \mu_{0,e}(\theta_0 - \theta_{0,I})$, of θ_0, where F_I is the F-value at $\theta_0 = \theta_{0,I}$. Denoting the F-value at $\theta_0 = \theta_{0,II}$ by F_{II} we have from Eqs. (9. a) and (11. a)

$$(F_{II} - F_I)/(\theta_{0,II} - \theta_{0,I}) = \mu_{0,e}\,. \tag{11. b}$$

Let I and II be points on the F-curve, where $\theta_0 = \theta_{0,I}$ and $\theta_0 = \theta_{0,II}$ respectively and (I, II) a straight line which combines points I and II. (I, II) is now a tangent

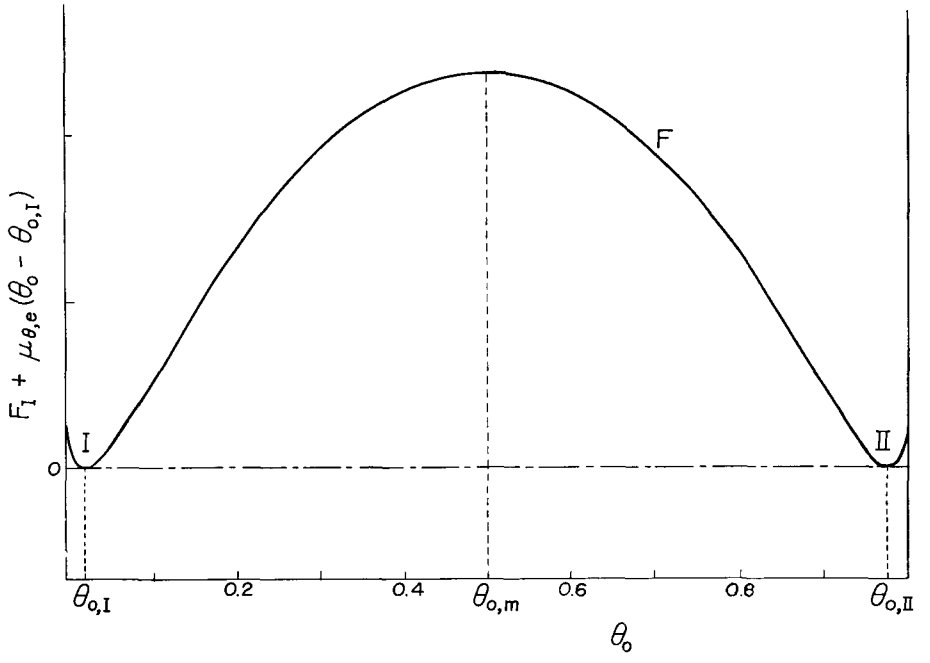


Fig. 3. Excess of Helmholtz energy of $\mathfrak{A}$ per mole of adsorption sites over $F_I + \mu_{0,e}(\theta_0 - \theta_{0,I})$ *vs.* covered fraction θ_n, for $\xi = 4$.

to F both at points I and II, since its slope, $\mu_{0,e}$, according to Eq. (11. b), equals the slope, $\mu_{0,I}=\mu_{0,II}$, of tangent to F at points I and II according to Eqs. (9. c) and (11. a).

We see, on the other hand, from Inequalities (10) that $\int_{\theta_{0,I}}^{\theta_0}(\mu_0-\mu_{0,e})\,d\theta_0 = \int_{\theta_{0,I}}^{\theta_0}\mu_0 d\theta_0-\mu_{0,e}(\theta_0-\theta_{0,I})$ increases from zero at $\theta_0=\theta_{0,I}$ steadily with increase of θ_0 up to $\theta_{0,m}$ and then decreases steadily, with further increase of θ_0, down to zero at $\theta_0=\theta_{0,II}$ in accordance with Eq. (9. b). It follows that the F-value on curve F, *i.e.* $F_I+\int_{\theta_{0,I}}^{\theta_0}\mu_0 d\theta_0$, is for θ_0 between $\theta_{0,I}$ and $\theta_{0,II}$ constantly greater than that on (I, II), *i.e.* $F_I+\int_{\theta_{0,I}}^{\theta_0}\mu_{0,e}d\theta_0$ or by Eq. (11.b), $F_I+\frac{\theta_0-\theta_{0,I}}{\theta_{0,II}-\theta_{0,I}}(F_{II}-F_I)$, which is identical with $F_I\frac{\theta_{0,II}-\theta_0}{\theta_{0,II}-\theta_{0,I}}+F_{II}\frac{\theta_0-\theta_{0,I}}{\theta_{0,II}-\theta_{0,I}}$; the latter is F of the adsorbate composed of the fraction, $(\theta_{0,II}-\theta_0)/(\theta_{0,II}-\theta_{0,I})$, of the homogeneous adsorbate with $\theta_0=\theta_{0,I}$ and $F=F_I$, and the fraction, $(\theta_0-\theta_{0,I})/(\theta_{0,II}-\theta_{0,I})$, of another homogeneous adsorbate with $\theta_0=\theta_{0,II}$ and $F=F_{II}$ respectively per mole of sites, wihch are in equilibrium with each other according to Eq. (9.c). The number of moles of adsorbate per mole sites is now $\theta_{0,I}\frac{\theta_{0,II}-\theta_0}{\theta_{0,II}-\theta_{0,I}}+\theta_{0,II}\frac{\theta_0-\theta_{0,I}}{\theta_{0,II}-\theta_{0,I}}=\theta_0$. A homogeneous adsorbate represented by a point on curve F at θ_0 between $\theta_{0,I}$ and $\theta_{0,II}$ has thus the same amount of a dsorbate per mole of sites as the last-mentioned heterogeneous adsorbate relevant to a point on (I, II) at θ_0, but a higher value of F; F-value of the heterogeneous adsorbate is now the lowest possible one for a state the same total amount of adsorbate per mole of sites, insofar as any homogeneous adsorbate is exclusively represented by a certain point on curve F.

It follows that the conversion of adsorbate from a point on curve F to that on (I, II) at the same θ_0 may take place spontaneously or a homogeneous adsorbate of θ_0 between $\theta_{0,I}$ and $\theta_{0,II}$ may separate spotaneously into the two coexistent two-dimensional phases to attain a stable equilibrium. The homogeneous adsorbate of covered fraction $\theta_{0,I}$ or $\theta_{0,II}$ will be called the two-dimensional vapour or liquid respectively. It is assumed in what follows that $\mathfrak{A}$ is always in a stable equilibrium, hence the last-mentioned separation results with certainty for θ_0 between $\theta_{0,I}$ and $\theta_{0,II}$.

The log $\gamma_{0,e}$ is shown by broken lines in Fig. 2, which indicates that $\theta_{0,I}$ and $\theta_{0,II}$ tend to approach zero and unity respectively with increase of ξ.

3.3. Bulk condensation and vaporization.

The chemical potential, μ_0, in the coexistence of the two two-dimensional phases in equilibrium is kept sharply constant at $\mu_{0,e}$ according to **3.2.**. If μ_0

of molecules in gas phase exceeds $\mu_{0,e}$ at the coexistence, there occurs a spontaneous conversion of molecules in gas phase into the adsorbate, increasing the two-dimensional liquid. A layer of the two-dimensional liquid, when thus completed, furnishes now, according to **b**), **2.**, a new array of physically identical sites of adsorption, on which a new layer is formed in the same way. The layers are thus completed one after another unlimitedly to result in a bulk condensation, insofar as μ_0 keeps above $\mu_{0,e}$.

If, on the other hand, μ_0 keeps beolw $\mu_{0,e}$ the above process is exactly reversed resulting in a continuous vaporization of bulk liquid until exhaustion.

It follows that molecules in gas phase is in equilibrium with bulk liquid just at $\mu_0=\mu_{0,e}$. It may be noted that the adsorption of θ_0 between 0 and $\theta_{0,I}$ or between $\theta_{0,II}$ and unity is not realized unless the evaporation of the surface layer of the bulk liquid or the formation of the layer over that just completed is metastably suppressed.

3.4. Extreme values of γ_0 and θ_0.

Factors q_0 and ξ in Eq. (1. b) of γ_0 are respectively definite at a constant temperature, whereas p_G in the same equation is expressed for a monoatomic molecule of mass M and concentration N as[2)]

$$p_G=(2\pi MkT)^{3/2}/Nh^3\,; \tag{12}$$

γ_0 is thus proportional to N according to Eq. (1. b) as mentioned in **1.**, hence varies with N from zero to infinity.

It follows, on the other hand, from Eq. (6) that $\eta\to 1$ or ξ^3 according as $\gamma_0\to 0$ or ∞ respectively. The η comes, however, never to less than unity or greater than ξ^3 by definition in accordance with the model described in **2.**, or η lies between unity and ξ^3. We have from Eqs. (1. a), (3) and (4)

$$\frac{\theta_0}{(1-\theta_0)\gamma_0}=$$

$$\frac{1+6\gamma_0\eta\xi+3\gamma_0^2\xi^2\eta^2(2\xi+3)+2\gamma_0^3\xi^3\eta^3(3\xi^2+6\xi+1)+3\gamma_0^4\xi^6\eta^4(2\xi+3)+6\gamma_0^5\xi^9\eta^5+\gamma_0^6\xi^{12}\eta^6}{1+6\gamma_0\eta+3\gamma_0^2\eta^2(2\xi+3)+2\gamma_0^3\eta^3(3\xi^2+6\xi+1)+3\gamma_0^4\xi^2\eta^4(2\xi+3)+6\gamma_0^5\xi^4\eta^5+\gamma_0^6\xi^6\eta^6}\,.$$

It follows from the above equation that

$$\theta_0\to\gamma_0 \text{ as } \gamma_0\to 0$$

and that

$$\theta_0\to 1 \text{ as } \gamma\to\infty\,,$$

in as much as $\theta_0/(1-\theta_0)$ tends to infinity, while the right-handside of the above

equation remains finite.

The converse of the a bove proposition applies as well, as shown below. We see that the right-hand side of the above equation remains finite irrespective of the value of γ_0, which varies from zero to infinity. It follows that as θ_0 tends to zero, γ_0 must as well, hence the right-hand side approaches unity, so that γ_0 approaches θ_0, as θ_0 tends to zero. As θ_0 nears unity, on the other hand, $\theta_0/(1-\theta_0)$ tends to infinity ; γ_0 should then tend to infinity as well, since otherwise the left-hand side of the above equation tends to infinity, while the right-hand side remains finite.

The converse is thus true at the extremities of θ, where the separation of the two-dimensional phase does not occur as seen from **3. 2.**.

3. 5. Isotherm at extremely low coverage.

We have according to **3. 4.** at the lower extremity of θ_0

$$\theta_0 \to \gamma_0 .$$

Sites of both the classes are then available, which counts $2N_L$, *i. e.* twice the number of constituent molecules of a completed layer, N_L. The number of adsorbate molecules, N_A, is in consequence

$$N_A = 2\theta_0 N_L = 2\gamma_0 N_L .$$

We have hence according to Eqs. (1. b) and (12)

$$N_A = 2N_L q_0 \xi^3 Nh^3/(2\pi MkT)^{3/2} . \qquad (13)$$

4. Examination of the Approximation

Approximations comprized in the present calculation are revealed and the inaccuracies there by introduced investigated.

4. 1. Approximations comprized.

Approximations comprized in the present calculation are :

a) Sites of either class, ● or ○, indicated in Fig. 1 are taken exclusively into account. This is justified when sites are nearly completely occupied, but not otherwise : in case of sparse coverage, sites of both the classes are simultaneouly avilable for adsorption.

b) Molecules adsorbed on adjacent peripheral sites inside $\sum$ interact with each other not only directly as allowed for by factor ξ in **3. 1.**, but also indirectly through adsorbate molecules outside $\sum$; one of the adjacent molecules inside causes to increase adsorbate molecules outside resulting in an additional

attraction upon the other, which is not taken into account by factor $\eta=\eta(\theta_0)$ in Eqs. (1. a), (3) and (5).

Inaccuracies involved with these approximations, if any, tend, however, to vanish with increase of coverage, for approximation **a**) comes then to be exact and **b**) as well, since the η approaches the fixed value, ξ^3, as shown in **3. 4.** leaving little room for the indirect interaction to be operative.

In accordance with the above consideration an exact adsorption isotherm is obtained at extremely low and high coverages. The present calculation of $\gamma_{0,e}$, which involves γ_0-values at intermediate coverages, is now checked in the next section.

4. 2. Accuracy of $\gamma_{0,e}$.

The value of $\gamma_{0,e}$ or $\mu_{0,e}$ is an average of γ_0 or μ_0 over the range of θ_0 from $\theta_{0,I}$ to $\theta_{0,II}$ according to Eq. (7) or Eq. (9. a); the inaccuracies of isotherm at the intermediate coverages should in consequence more or less affect the values of $\gamma_{0,e}$ or $\mu_{0,e}$ thus calulated. This point is examined by comparing the value of $\gamma_{0,e}$ or $\mu_{0,e}$ obtained by the method described in **3. 2.** with its value inferred alternatively in the following particular case.

Consider the process of forming a new completed layer of the two-dimensional liquid consisting of N_L molecules over the surface of a bulk liquid. Helmholtz enery of the bulk liquid increases by $-kT\ln q_0\xi^3$ by seating a molecule on a definite, unoccupied site apart from the lateral interactions. This increment sums up to $-N_L kT\ln q_0\xi^3$ for the new complete layer. The total increment of Helmholtz energy is obtained by adding to the latter the mutual potential of lateral interactions. Each molecule is surrounded by six adjacent molecules in a completed layer, hence its potential due to the latter is $2\varepsilon_0$ by definition of ε_0 in **3. 1. 1.**; this potential sums up to $2N_L\varepsilon_0$ over N_L constituent molecules, which includes, however, twice the potential of every contacting pair. The mutual potential of lateral interactions is thus $N_L\varepsilon_0$, hence the total increment is $-N_L kT\ln q_0\xi^3+N_L\varepsilon_0$ or, by Eq. (2.b,) $-N_L kT\ln q_0\xi^6$.

It follows that the partition function of the bulk liquid is multiplied into $(q_0\xi^6)^{N_L}$ by addition of the new complete layer consisting of N_L molecules to occupy sites of class either ● or ○ exclusively. Since sites of either class may be occupied equally probably, the multiplier of partition is twice the above value, *i. e.* $2(q_0\xi^6)^{N_L}$.

This multiplier is given alternatively by $p_L^{N_L}$, admitted that p_L, *i. e.* p of liquid molecule remains sufficiently constant throughout the addition of N_L molecules. Equating these alternative expressions, we have

$$p_L = q_0\xi^6 \tag{14}$$

for N_L great enough to reduce $2^{1/N_L}$ practically to unity. In equilibrium we have

$$p_L = p_G , \tag{15}$$

hence from Eqs. (1. b), (14) and (15)

$$\gamma_{0,e}\xi^3 = 1 , \tag{16}$$

specifying γ_0 in Eq. (1. b) to be $\gamma_{0,e}$ for the equilibrium of molecules in gas phase with bulk liquid according to **3. 3.**, noting that $\gamma_0=\gamma_{0,e}$ as $\mu_0=\mu_{0,e}$ according to Eqs. (8).

Eq. (16) is based on the two approximations, that p_L keeps constant throughout the addition of N_L molecules and that $2^{1/N_L}$ equals unity, which hold practically for a macroscopic bulk liquid. Eq. (16) thus provides a criterion upon which the accuracy of calculation in **3. 2.** is tested. The value of $\gamma_{0,e}\xi^3$ with $\gamma_{0,e}$ calculated according to **3. 2.** is thus the ratio of the latter value of $\gamma_{0,e}$ to its value derived from ξ by Eq. (16). Every value of $\gamma_{0,e}$ calculated according to **3. 2.** is in close accordance with Eq. (16), verifying the numerical accuracy of the former calculation.

We see thus that a sufficient accuracy coherent to the model described in **2.** is secured by expressing $\gamma_0(\theta_0)$ by Eq. (13) from $\gamma_0=0$ to $\gamma_0=\gamma_{0,e}$, calculating $\gamma_{0,e}$ by Eq. (16) and working out $\gamma_0(\theta_0)$ for $\gamma_0>\gamma_{0,e}$ according to **3.**, provided that $\theta_{0,I}$ and $\theta_{0,II}$ are respectively sufficiently close to zero and unity.

5. Parameters in Theoretical Equations

Parameters, q_0 and ξ, comprized in theoretical equations, (1. b), (13) and (14), are evaluated by fitting them to thermodynamic data preparatory to the treatment of multilayer adsorption.

5. 1. Relation of parameters to the heat of vaporization.

Heat of vaporization, ΔH, is the excess of molar enthalpy of molecules in gas phase $\bar{H}_G$, over that of the coexistent liquid, $\bar{H}_L$,$\bar{H}_G$ and $\bar{H}_L$ are connected with μ_G and μ_L respectively as

$$\bar{H}_G = \mu_G - T(\partial\mu_G/\partial T)_P , \qquad \bar{H}_L = \mu_L - T(\partial\mu_L/\partial T)_P , \tag{17. G), (17. L}$$

where μ_L is the chemical potential of liquid and P the pressure to be kept constant at the differentiation. We have from Eqs. (12) and (14) with reference to Eqs. (2)

$$\mu_G = -RT\ln\frac{(2\pi MkT)^{3/2}}{Nh^3}, \qquad \mu_L = -RT\ln q_0 + 2\varepsilon_0, \tag{18. G), (18. L}$$

hence according to Eqs. (17) and (18), noting that $N=P/kT$ and admitting that ε_0 is constant independent of temperature,

$$\Delta H = \bar{H}_G - \bar{H}_L = (5/2)RT - RT^2(\partial \ln q_0/\partial T)_P - 2\varepsilon_0 . \tag{19}$$

The valuation of the parameters thus depends on q_0.

5.2. Classical approximation.

The q_0 and ξ are evaluated approximating q_0 classically for the rare gases in accordance with its definition in **3.1.1.** as

$$q_0 = v_L(2\pi MkT)^{3/2}/h^3 , \tag{20}$$

where v_L is the volume of space available for the classical motion of an adsorbed molecule of mass M. We have from Eqs. (19) and (20), ignoring the temperature change of v_L,

$$\Delta H = RT - 2\varepsilon_0 , \tag{21}$$

which determines ε_0 on the base of observed value of ΔH, hence ξ by Eq. (2. b); q_0 is now determined by the equation,

$$q_0\xi^6 = (2\pi MkT)^{3/2}/N_{0,e}h^3 , \tag{22. q_0}$$

derived from Eqs. (12), (14) and (15), and v_L by the equation,

$$v_L N_{0,e}\xi^6 = 1 , \tag{22. v_L}$$

obtained by substituting q_0 from Eq. (20) into Eq. (22. q_0).

Table 1 shows ξ, q_0 and v_L evaluated from thermodynamic data by Eqs. (21) and (22) with reference to Eq. (2. b); T_B is the absolute temperature of boiling point under one atmospheric pressure.

TABLE 1 ξ, q_0 and v_L of rare gases

Rare gases	He	Ne	Ar	Kr	Xe	Rn
T_B °K[4]	4.216	24.57	87.29	119.93	165.1	211
ΔH kcal/mole[4]	0.020	0.43	1.558	2.158	3.021	3.92
ξ	1.26	3.67	3.78	3.83	3.93	4.02
q_0	1.87	0.63	157	983	3694	12955
V_L Å^3	143	3.19	4.06	5.18	6.12	6.79

6. Conclusive Remarks

The statistial mechanical calculation in **3.** leads to the conclusion that two-dimensional vapour and such liquid coexist over the range of θ_0 from $\theta_{0,\mathrm{I}}$ to $\theta_{0,\mathrm{II}}$ for $\xi \geq 2.48$, where γ_0 keeps sharply constant at $\gamma_{0,\mathrm{e}}$; for $\gamma_0 < \gamma_{0,\mathrm{e}}$ two-dimensional vapour of $\theta_0 < \theta_{0,\mathrm{I}}$ exists alone, and for $\gamma_0 > \gamma_{0,\mathrm{e}}$ two-dimensional liquid of $\theta_0 > \theta_{0,\mathrm{II}}$ does instead provided that the evaporation and condensation are respectively metastably suppressed.

Approximation comprized in the present calculation may possibly introduce inaccuracy of γ_0 over intermediate θ_0, hence into that of $\gamma_{0,\mathrm{e}}$ as commented upon in **4. 1.**, whereas at higher extremity of θ_0 the calculation is based accurately upon the model described in **2.** as accounted for in **4.**. At lower extremity of θ_0, on the other hand, γ_0 is calculated accurately as a function of θ_0 as developed in **3. 5.**. The calculation of $\gamma_{0,\mathrm{e}}$ turned out to be numerically accurate enough on the ground of its coherence with that inferred alternatively in a special case. The latter accurate value of $\gamma_{0,\mathrm{e}}$ assures the precise evaluation of function $\theta_0(\gamma_0)$ over the whole range of θ_0, provided that $\theta_{0,\mathrm{I}}$ and $\theta_{0,\mathrm{II}}$ are sufficiently close to zero and unity respectively, which is the case for sufficiently large ξ as mentioned in **3. 2.**.

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