On the Harkins—Jura's Adsorption Isotherm and Its Constants.

By Tomohiko SAKAKI

(Received August 27, 1952)

I. Introduction

W. D. Harkins and G. Jura⁽¹⁾ obtained experimentally the following equation of state for the condensed films spread on the surface of liquid:

$$\pi = b - a\sigma \qquad (1)$$

where π is the surface pressure, σ is the area per molecule of the film, and b and a are constants. They also found that the above linear relationship is applicable to adsorbed films on solids.

Equation (1) can be transformed into an adsorption isotherm expressed in terms of equilibrium pressure p and adsorbed volume v_a,

$$\log_{10}\frac{p}{p_0} = B - \frac{A}{v_a^2} \qquad (2)$$

with

$$A = \sigma\Sigma^2 V^2/2\times 2.303\,\boldsymbol{N}RT \qquad (3)$$

and

$$B = A/v_s^2$$

where Σ is the surface area of adsorbent, V the volume of one mole of ideal gas at N. T. P., $\boldsymbol{N}$ Avogadro number, p_0 the saturation pressure, and v_s the adsorbed volume at p_0.

Eq. (2) gives Type II isotherms which are in good agreement with the experimental curves up to $p/p_0 = 1/3$ or higher. Moreover, the surface area Σ is proportional to the square root of A;

$$\Sigma = kA^{1/2} \qquad (4)$$

Harkins and Jura regarded k in (4) as being characteristic to each adsorbate and independent of the adsorbents. Thus they have given the values of k to the four kinds of vapors, calculating from their isotherms on the anatase powder the area of which had been determined

---

(1) **W. D. Harkins and G. Jura**, *J. Am. Chem. Soc.*, **66**, 1366 (1944); *J. Chem. Phys.*, **11**, 430 (1943); ibid, **11**, 431 (1943).

Table 1

The H. J. Constants

Adsorbate	Temp. (°K)	k (m.²/cc.)	A (cc./gr.)²⁽ᵃ⁾	CAT (cal./mole·1/cm.⁴)⁽ᵇ⁾	σ_0 (Å.²)⁽ᶜ⁾	CAT σ_0^2 (cal./mole)
N_2	77.4	4.01	11.8	$159.\times 10^{30}$	16.2	417
H_2O	298.	3.83	12.9	$668.\times$ 〃	10.5	734
n-C_4H_{10}	273.	13.6	1.02	$48.4\times$ 〃	32.1	499
n-C_7H_{16}	273.	16.9	0.664	$31.5\times$ 〃	45.	640

(a) The value of 13.8 m.²/gr. was used for Σ.

(b) $C=\dfrac{\boldsymbol{N}^2R\ln_{10}}{V^2\Sigma^2}$

(c) The values of σ_0 for water and n-butane were calculated from the liquid densities according to B. E. T.. The value for n-heptane was determined from crystallographic data. (See Reference (1)).

by the "absolute method"(2) (Table 1). It is possible, therefore, to estimate the surface areas of solids using Eqs. (2) and (4) and Table 1 from the adsorption isotherms of these vapors on the solids, without the assumption of a molecular area of the adsorbate. This is called the "relative method" by the original authors.

There are, however, a few ambiguous points in the above-mentioned theory of adsorption. First, though Eq. (2) is considered to be applicable to multimolecular adsorption, the theoretical basis for this is not obvious. Secondly the assumption that the values of k are independent of adsorbents should be examined in more detail.

II. Thermodynamic Considerations

We shall begin by considering an adsorbed film composed of N_A molecules of the vapor adsorbed on a crystalline solid surface, having equilibrium pressure p at T°K below the critical temperature. If the same vapor has the saturation pressure p_0 in equilibrium with its liquid (or solid) at T°K, the difference in molar free energy between the film and the liquid, $\bar{F}$ is given by

$$\bar{F}=RT\ln\frac{p}{p_0} \qquad (5)$$

On the other hand $\bar{F}$ is formally written as

$$\bar{F}=(H_A-E_L)-T\bar{S} \qquad (6)$$

where H_A is the molar differential enthalpy of adsorption, E_L the enthalpy of condensation per mole, and S the difference in the molar entropy between the two states.

From (5) and (6) we get

$$\ln\frac{p}{p_0}=-\frac{\bar{S}}{R}+\frac{1}{RT}(H_A-E_L) \qquad (7)$$

Now H_A is the function of the adsorbed amount N_A, the form of which is determined experimentally. When $p\rightarrow p_0$, $H_A\rightarrow E_L$; hence $\bar{S}$ is a function of N_A as well, and approaches zero as p tends to reach p_0. If H_A and $\bar{S}$ are expressed as functions of N_A, $H_A(N_A)$ and $\bar{S}(N_A)$, the observed isotherm is

$$\ln\frac{p}{p_0}=-\frac{\bar{S}(N_A)}{R}+\frac{1}{RT}\{H_A(N_A)-E_L\} \qquad (8)$$

For convenience, introducing v_a in place of N_A,

$$v_a=V\cdot N_A/\boldsymbol{N}.$$

Eq. (8) can be written as

$$\ln\frac{p}{p_0}=-\frac{\bar{S}(v_a)}{R}+\frac{1}{RT}\{H_A(v_a)-E_L\} \qquad (9)$$

The dimensional consideration leads to the fact that H_A and $\bar{S}$ are the functions of degree of coverage, θ, given by

$$\theta=N_A/N_0$$

where N_0 is the number of molecules adsorbed on the surface when it is covered with a complete monomolecular layer. Thus Eq. (8) is rewritten as

$$\ln\frac{p}{p_0}=-\frac{\bar{S}(\theta)}{R}+\frac{1}{RT}\{H_A(\theta)-E_L\} \qquad (10)$$

When the degree of coverage reaches θ, the work required to evaporate all the molecules of the film is

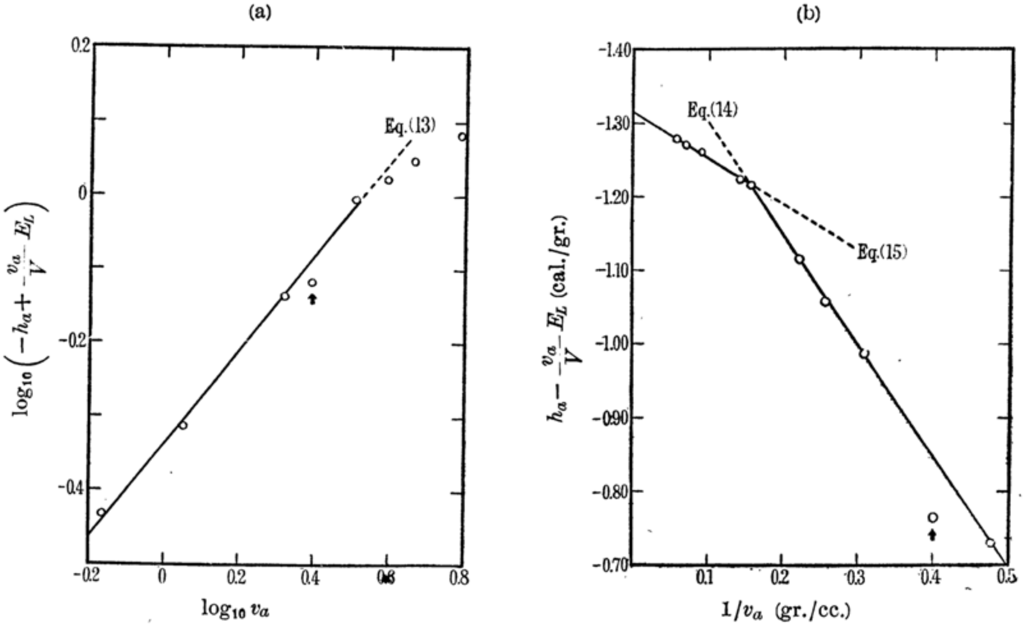
---

(2) W. D. Harkins and G. Jura, *J. Am. Chem. Soc.*, **66**, 1362 (1944).

Table 2

The Enthalpy Functions in the System of H_2O-Anatase

Range	Integral Enthalpy, h_a	Molar Differential Enthalpy, H_A
v_a, 0.68—3.25 cc./gr. p/p_0, 0 —0.10 〃	$h_{a1}=-0.461(v_a)^{5/8}+\frac{v_a}{V}E_L$ Eq. (13)	$H_{A1}=-6460(v_a)^{-3/8}+E_L$ Eq. (16)
v_a, 2.09—6.16 〃 p/p_0, 0.02—0.55 〃	$h_{a2}=-1.446+\frac{1.50}{v_a}+\frac{v_a}{V}E_L$ Eq. (14)	$H_{A2}=-\frac{33600}{v_a^2}+E_L$ Eq. (17)
v_a, 6.16—∞ 〃 p/p_0, 0.55—1.00 〃	$h_{a3}=-1.315+\frac{0.634}{v_a}+\frac{v_a}{V}E_L$ Eq. (15)	$H_{A3}=-\frac{14200}{v_a^2}+E_L$ Eq. (18)



The arrowed point $\left(v_a=2.49\text{ cc./gr.},\ h_a-\frac{v_a}{V}E_L=0.762\text{ cal./gr.}\right)$ lies neither on the line of (a) nor on that of (b).

Fig. 1.—The Variation of the Integral Enthalpy of Adsorption with v_a in the System of H_2O—Anatase

$$F_a=\frac{1}{N}\left\{-T\int_0^{N_A}\bar{S}(N_a/N_0)dN_A+\int_0^{N_A}H_A(N_A/N_0)dN_A+KN_A\right\} \quad (11)$$

where K is a constant.

By definition the surface pressure of the film is given by

$$\pi=-\left(\frac{\partial F_a}{\partial\Sigma}\right)_{T,\ N_A}=-\frac{1}{\sigma_0}\left(\frac{\partial F_a}{\partial N_0}\right)_{T,\ N_A} \quad (12)$$

π is calculated from the isotherm, using Eqs. (11) and (12).

III. The Isotherm and Heats of Adsorption in the System of H_2O—Anatase

Harkins and Jura⁽³⁾ measured the heats of immersion into water of the anatase samples, on which various quantities of water vapor had been adsorbed. The integral enthalpies, h_a's, of this case are known from the results of this experiment.

The formulae listed in column 2 of Table 2 correctly represent the original data⁽⁴⁾ written in terms of cals. per one gram of the adsorbent as illustrated in Fig. 1 (a) and (b). The variation of the molar differential enthalpy H_A with v_a, derived from these formulae, are

---

(3) W. D. Harkins and Jura, *J. Am. Chem. Soc.*, **66**, 919 (1944).

(4) Table I in the reference (3).

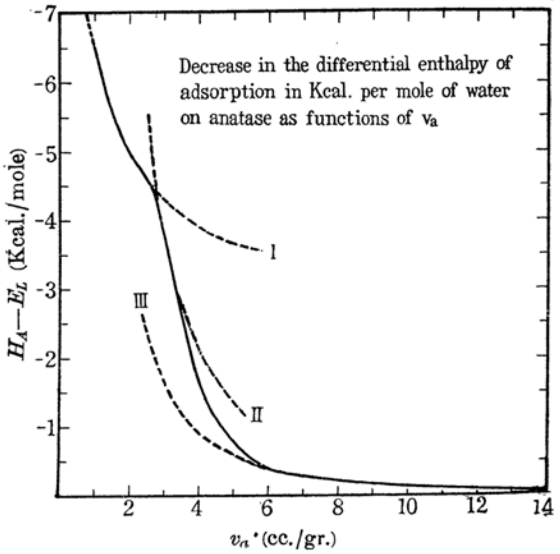


Fig. 2.

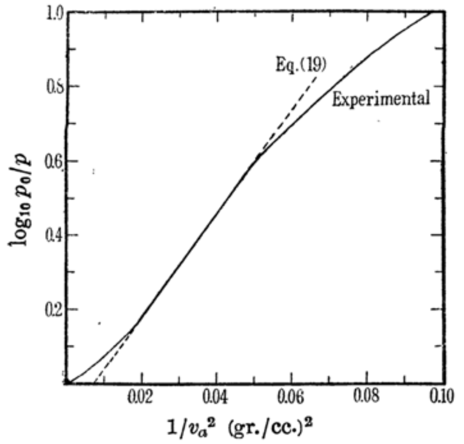


Fig. 3.—The Adsorption Isotherm of H_2O on Anatase Plotted According to H. J.

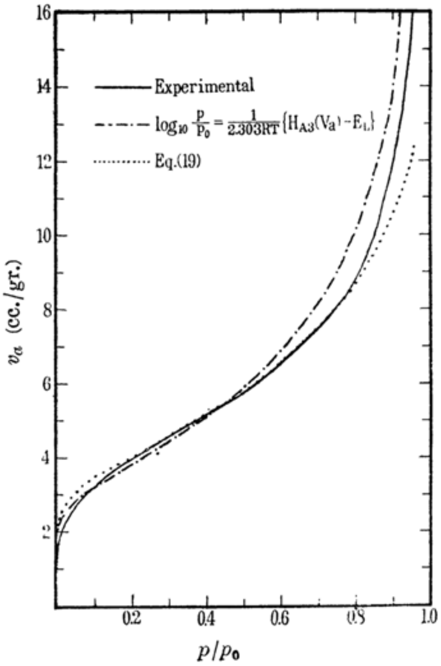


Fig. 4.—Adsorption Isotherm of Water on Anatatse at 25°C.

shown in Fig. 2 and column 3 of Table 2. In Fig. 2, curve I represents $H_{A1}(v_a)$, curve II $H_{A2}(v_a)$ and curve III $H_{A3}(v_a)$, respectively. It is to be noted that Eq. (13) is very similar to the empirical formula suggested by Lamb and Coolidge⁽⁵⁾ on the integral heats of adsorption of various organic vapors on charcoal. As v_a is increased, $-H_{A1}(v_a)$ decreases slowly towards E_L, whereas $-H_{A2}(v_a)$ and $-H_{A3}(v_a)$ rapidly decrease and asymptotically approach E_L.

It seems that $H_{A1}(v_a)$ represents the change of H_A in the process of packing the first layer, $H_{A3}(v_a)$ in the formation of the higher layers and $H_{A2}(v_a)$ in the intermediate state. In Fig. 2 the full line gives the variation of H_A through the whole region in a smooth curve.

In Fig. 3 are presented the adsorption data⁽⁶⁾ of water vapor on one gram of the anatase sample at 25°C. plotted according to the original authors. The straight line is obtained in the relative pressure range 0.3—0.7 (v_a varies in this region from 4.7 to 7.4 cc./gr.). We obtain as the H. J. isotherm in this case,

$$\log_{10}\frac{p}{p_0}=0.070-\frac{12.9}{v_a^2} \qquad (19)$$

while, inserting $H_{A3}(v_a)$ of (18) to (9), we get

$$\ln\frac{p}{p_0}=-\frac{\bar{S}(v_a)}{R}-\frac{1}{RT}\cdot\frac{14200}{v_a^2}$$

or

$$\log_{10}\frac{p}{p_0}=-\frac{\bar{S}(v_a)}{4.58}-\frac{10.4}{v_a^2} \qquad (20)$$

By comparing (19) and (20), it may be concluded that the general tendency of the adsorption is mainly determined by the enthalpy part of the isotherm in the medium region of relative pressure. That the function $H_{A3}(v_a)$ is adopted instead of $H_{A1}(v_a)$ and $H_{A2}(v_a)$, is because it not only represents the actual enthalpy change in the medium the higher

---

(5) A. B. Lamb and A. S. Coolidge, *J. Am. Chem. Soc.*, **42**, 1146 (1920).

(6) W. D. Harkins and G. Jura, *J. Am. Chem. Soc.*, **66**, 1356 (1944).

pressure regions but also reflects the outline of the whole isothermal variation as shown in Fig. 4.

IV. The Harkins—Jura's Theory and the Constants in Their Isotherm

In the case of the water vapor—anatase system, it has been found that $H_A - E_L$ is inversely proportional to v_a^2 in the later stage of adsorption, and that it determines the outline of the isotherm. If it is admitted that these conclusions generally apply to the H. J. type isotherms, a reasonable solution to the questions raised at the beginning of this paper is obtained.

(i) Multimolecular Adsorption and H_A (v_a).—We have in general

$$\log_{10}\frac{p}{p_0} = -\frac{\bar{S}(v_a)}{2.303R} + \frac{1}{2.303RT}\{H_A(v_a) - E_L\} \qquad (21)$$

According to the above viewpoint, we put

$$H_A(v_a) - E_L = -K_n/v_a^2 \qquad (22)$$

where K_n is a constant.

Provided that the first term of the right-hand side of (21) is neglected, the fact that the H. J. isotherm contains the inverse square term of v_a is necessarily ascribed to the form of H_A (v_a) given by (22).

Eq. (22) suggests the picture on the potential field in the neighbourhood of the adsorbent surface, namely in the early stage of adsorption the molecules are settled in the deep potential near the surface, while as the adsorption proceeds the packing of the molecules is gradually extended to the place of flattened potential further from the surface and finally those occupying the furthest sites evolve only the heat of condensation. These situations are characteristic of the multimolecular adsorption, and are roughly reflected on the form of H_A (v_a) in Eq. (22). We may hence deduce the conclusion that this form of $H_A(v_a)$ and consequently the H. J. isotherm are peculiar to the multimolecular adsorption.

Generalizing Eq. (2), we have the following isotherm,

$$\log_{10}\frac{p}{p_0} = B - \frac{A}{v_a^n} \qquad (23)$$

where n is a constant.

The second term of the right-hand side of (23) seems to be of an adequate form to represent the variation of the enthalpy part in the later stage of adsorption. On account of this the similar interpretations can be applied to this case.

(ii) The H. J. Constants and the "Relative Method".—As mentioned in Sec. II, the differential enthalpy is essentially the function of θ. Introducing v_m in place of N_0,

$$v_m = V\frac{N_0}{\boldsymbol{N}}$$

Thus (22) is rewritten as

$$H_A(\theta) - E_L = -K_m(v_m/v_a)^2 \qquad (24)$$

where K_m is the constant equal to K_n/v^2_m.

If we recall the preponderance of the enthalpy part in the medium pressure region, we put

$$\frac{A}{v_a^2} \approx \frac{1}{2.303RT}\{-H_A(\theta) + E_L\} \qquad (25)$$

where A is the constant in Eq. (2).

As v_m is given by $V\ N_0/\boldsymbol{N}$ or $V\sum/\boldsymbol{N}\sigma_0$*, (24) and (25) give

$$A \approx \frac{K_m}{2.303RT}\ \frac{V^2 \sum^2}{\boldsymbol{N}^2\sigma_0^2} \qquad (26)$$

Since $\sum$ is naturally common for the same adsorbent, AT is expected to be proportional to K_m/σ_0^2, and $AT\sigma_0^2$ to K_m, provided that (25) is valid. It is seen from column 5 of Table 1 that the order of magnitude in AT is reverse to the size of molecule, i. e., water > nitrogen > n-butane > n-heptane. This is quite natural, so far as AT is inversely proportional to σ_0^2. In column 6 are shown the probable values of σ_0 at the temperatures listed in column 2. Eq. (24) indicates that K_m is the excess molar differential enthalpy at $v_a = v_m$, so that the polyatomic molecules or the molecules having large dipole moment should have great values of K_m. This is the same with $AT\sigma_0^2$, regarded as to be proportional to K_m. The result given in the last column is just as expected; the order in $AT\sigma_0^2$ is water > n-heptane > n-butane > nitrogen.

v_a in Eq. (2) remains definite at $p = p_0$ unless B is zero. In Fig. 4, however, the experimental curve increases towards infinity as p approaches p_0, though B is determined as 0,070 in this case. Hence it is to be noted that B is not always equal to the actual value of A/v_s^2.

---

* σ_0 is the area per molecule at $N_a = N_0$, given by Σ/N_0.

From the above point of view, it is possible to give a support to the "relative method". Provided that "heats of adsorption (of a vapor) seem to be roughly the same whether the adsorbent is charcoal, a metal or an oxide⁽⁷⁾", K_m is a peculiar constant to the vapor and independent of adsorbents, so that, roughly speaking, the constant k of (4) depends solely on the kind of vapors at a definite temperature. This is consistent with the original authors' viewpoint.

(iii) The Two-Dimensional Equation of State.—If the contributions of the entropy term to the free energy of the film is ignored according to the results in (i) and (ii), the work required to evaporate N_a adsorbed molecules into the vapor phase can be approximated by the energy of desorption of the film, q_a, in the medium pressure region.

From (24), we have

$$H_A(\theta)-E_L=-K_m(v_m/v_a)^2$$
$$=-K_m(N_0/N_A)^2$$

The corresponding h_2, which has the integrated form of H_A, is written as

$$-h_a=\frac{N_A}{\boldsymbol{N}}E_L+k_2-k_1\frac{N_0^2}{N_A} \qquad (27)$$

where k_2 and k_1 are constants.

Thus q_a is given by

$$-q_a=\frac{N_A}{\boldsymbol{N}}Q_L+k_2-k_1\frac{N_0^2}{N_A} \qquad (28)$$

where Q_L is the molar heat of condensation. Provided that the right-hand side of (27) or (28) is composed of a power series of N_0^n/N_A^{n-1}, we can put

$$k_2=k_3N_0$$

where k_3 is a constant.

Hence we obtain

$$-F_a\approx\frac{Q_L}{\boldsymbol{N}}N_A+k_3N_0-k_1\frac{N_0^2}{N_A} \qquad (29)$$

Substituting (29) into (12), we reach the equation of state from which Harkins and Jura started,

$$\pi\approx b-a\sigma$$

with

$$b=k_3/\sigma_0$$
$$a=2k_1/\sigma_0^2.$$

V. Acknowledgement

The author is grateful to Prof. Isamu Sano of this Institute for his interest and encouragement. He is also indebted to Dr. Yutaka Miyahara of this Instisute, to Dr. Keizo Suzuki of Gifu University, and to Dr. Yuzuru Ôshika of Kobayashi Institute of Physical Research, for their helpful advice. The cost of this research has been defrayed from the Scientific Research Grant of the Ministry of Education.

Chemical Institute, Faculty of Science,
Nagoya University, Chikusa,
Nagoya, Japan

---

(7) S. Brunauer, "The adsorption of Gases and Vapors", Vol. I, p 240, Princeton University Press, Princeton, N. J. (1945).