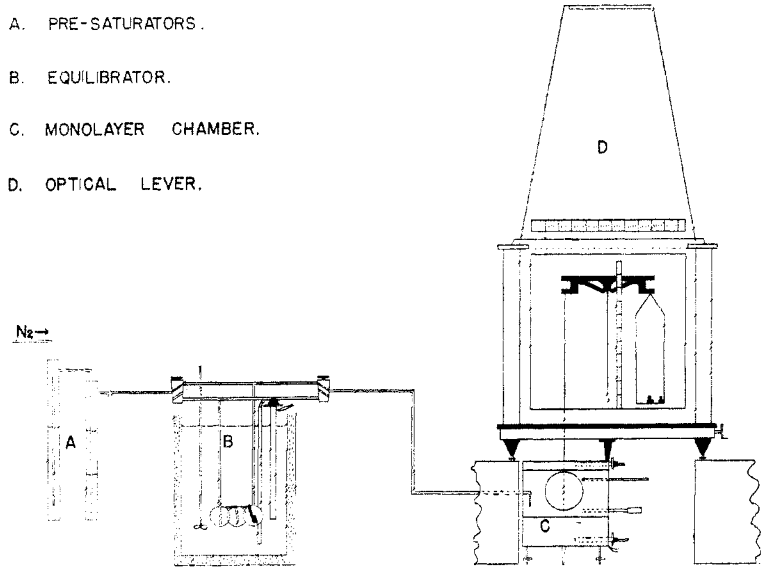

Fig. 2.—Complete assembly of adsorption apparatus.

passes through holes in the floor of the balance and the top casting. The position of the plate and the balance arm is read on a folded optical lever mounted above the balance. Light from a straight filament is reflected from a small mirror on the beam and focused on a translucent scale just above the balance case. A 1-mm. vertical movement of the plate displaces the image of the filament by 10 mm. Figure 2 shows a photograph of the complete assembly.

Hexane or other organic vapor is passed through the monolayer box in a stream of nitrogen that has been saturated with liquid hexane at a temperature corresponding to the desired vapor pressure as read from published tables. Water-pumped nitrogen flows at about 150 ml. per minute through a wash bottle full of water before going to the equilibrator. Two three-way stopcocks lubricated with an aqueous grease allow the equilibrator to be by-passed when necessary. The vapor line from the equilibrator to the monolayer chamber is wound with resistance wire so that it may be heated to prevent condensation of hexane in the line when operating at high relative vapor pressures. The stream of nitrogen and vapor is directed into the gutter surrounding the monolayer. Excess gas escapes through several holes in the box.

The trough is cleaned by rinsing it with acetone and then steaming it out over a specially constructed boiler that fits into the gutter of the inverted base. The barrier is also cleaned and wiped with acetone on a paper towel and rinsed with distilled water. The platinum slide is flamed before each run.

The trough is filled with subphase (0.01 *N* H_3PO_4) to a level 3 or 4 mm. above the edge and the surface is sucked off. This procedure is repeated several times and the liquid is finally adjusted to a level 1 to 2 mm. above the edge. The gutter is partially filled with distilled water and the wall casting, including the barrier mechanism, is put on. The platinum slide and chain are placed in the box and the chain is fished through the holes and hung on the balance hook when the box is assembled.

The optical indicator is brought to a convenient position by adjusting the balance chain. When the box comes up to temperature nitrogen gas is started and a true zero is recorded when equilibrium is reached. The surface is tested for cleanliness by advancing the barrier as far as possible. A clean surface will show no change in surface pressure on compression.

Stearic acid in benzene solution is delivered onto the surface of the trough from a micrometer-driven syringe with a long hollow needle which is inserted through a small hole in the front of the box. Evaporation of the benzene and spreading of the monolayer is observed through the window. The contact angle with the plate is also checked at this time. Since it is essential that this angle be zero, measurements can only be made under conditions such that the surface pressure rises as equilibrium is approached. Changes in surface pressure are recorded as changes in the position of the optical indicator on the scale. When the surface pressure under nitrogen has been recorded, the gas stream is directed through the equilibrator to saturate it with hexane and surface pressure is again recorded when the light spot stops moving.

We have been able to reproduce surface-pressure measurements to 0.05 dyne and surface concentrations to 0.1 Gibb ($= 0.1 \times 10^{-10}$ moles/cm.^{2}).[10] Equilibrium is usually reached in one-half hour at 30° using stearic acid and hexane vapor. Equilibrium values of surface pressures have been observed unchanged for 24 hours.

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(10) R. B. Dean, *J. Phys. Colloid Chem.*, **55**, in press (1951).

EUGENE, OREGON RECEIVED APRIL 23, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF OREGON]

The Sorption of Vapors by Monolayers. IV. Calculation of the Amount of Hexane Adsorbed on a Stearic Acid Monolayer[1]

BY KENNETH E. HAYES AND ROBERT B. DEAN[2]

A thermodynamic method for the calculation of the amount of organic vapor adsorbed on a long chain monolayer is presented, and the method applied to the system stearic acid-*n*-hexane. The thermodynamic standard state used in this computation is chosen as the surface concentration of stearic acid given by the spreading pressure of stearic acid under hexane vapor. The adsorption of hexane follows a type III isotherm at low stearic acid concentrations, but at high acid concentrations goes over to a type V with a limiting ratio of one molecule of hexane to one of stearic acid.

Stearic acid monolayers in the presence of organic vapors behave like expanded films of myristic acid. The amount of vapor adsorbed may be found by making use of the Gibbs adsorption equation.

Application of the Gibbs equation to the system: stearic acid, hexane, nitrogen and phosphoric acid solution (used as the liquid phase) leads to the result

$$-d\gamma = d\pi = S dT + \Gamma_1 d\mu_1 + \Gamma_2 d\mu_2 + \Gamma_N d\mu_N + \Gamma_A d\mu_A + \Gamma_W d\mu_W \quad (1)$$

where the subscripts 1, 2, N, A and W indicate, respectively, hexane, stearic acid, nitrogen, phosphoric acid and water. *S* denotes the surface density of the entropy, γ the surface tension and π the surface pressure. As we are dealing with a five-component system we need five independent

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(1) Presented by Dr. Myer G. Horowitz, at the 119th Meeting of the American Chemical Society, Colloid Division, Symposium on Surface Tension of Solutions, Boston, Mass., April, 1951.

(2) The work was supported by a grant from the Frederick Cottrell fund of the Research Corporation.

intensive variables in order to describe the system completely; these variables are: (1) the temperature T. (2) The total pressure of the system P_0 (P_0 equals one atmosphere). (3) The relative partial pressure of hexane P. (4) The molality of the phosphoric acid m. (5) The surface concentration of the stearic acid Γ_2. As all measurements are carried out at fixed and constant values of T, P_0 and m it is seen that equation 1 reduces to

$$d\pi = \Gamma_1 d\mu_1 + \Gamma_2 d\mu_2 + \Gamma_N d\mu_N \qquad (2)$$

and by fixing the location of the Gibbs surface by setting $\Gamma_N = 0$, equation 2 then reduces to

$$d\pi = \Gamma_1 d\mu_1 + \Gamma_2 d\mu_2 \qquad (3)$$

For a fixed value of Γ_2, we may write from equation 3

$$(\partial\pi/\partial P) = \Gamma_1(\partial\mu_1/\partial P) + \Gamma_2(\partial\mu_2/\partial P) \qquad (4)$$

and if we assume that the hexane in a gaseous mixture with nitrogen and water vapor behaves as a perfect gas we may replace $(\partial\mu_1/\partial P)$ of eq. 4 by RT/P, giving

$$(\partial\pi/\partial P) = \Gamma_1 RT/P + \Gamma_2(\partial\mu_2/\partial P) \qquad (5)$$

It is at once evident that when we are dealing with a clean liquid surface, *i.e.*, when $\Gamma_2 = 0$ we can evaluate Γ_1 immediately, as has been done by Micheli[3] and Cassel and Formstecher.[4] In a previous paper in this series[5] Dean and Li have used equation 5 to calculate Γ_1 by making the assumption that the term $\Gamma_2(\partial\mu_2/\partial P)$ is small in relation to $(\partial\pi/\partial P)$. Koenig[6] has recently shown how the function $(\partial\mu_2/\partial P)$ may be obtained.

For a fixed value of P we may write from equation 3

$$(\partial\pi/\partial\Gamma_2) = \Gamma_1(\partial\mu_1/\partial\Gamma_2) + \Gamma_2(\partial\mu_2/\partial\Gamma_2) \qquad (6)$$

As the partial pressure of the hexane vapor is arbitrarily controlled independently of Γ_2 we may set $(\partial\mu_1/\partial\Gamma_2)$ equal to zero; equation 6 then becomes

$$(\partial\pi/\partial\Gamma_2) = \Gamma_2(\partial\mu_2/\partial\Gamma_2) \qquad (7)$$

and therefore

$$\mu_2^0 - \mu_2 = \int_{\Gamma_2}^{\Gamma_2^0} (\partial\pi/\partial\Gamma_2)\, d\Gamma_2/\Gamma_2 \qquad (8)$$

where μ_2^0 is the chemical potential of the stearic acid in the monolayer in some arbitrary standard state given by Γ_2^0.

In general $\mu_2^0 - \mu_2$ may be found from a plot of $(\partial\pi/\partial\Gamma_2)1/\Gamma_2$ *vs.* Γ_2. If μ_2^0 is known from independent measurements a plot of the chemical potential against the relative partial pressure of hexane, at specified values of the surface concentration of stearic acid, enables a calculation of the function $(\partial\mu_2/\partial P)$ to be made. Substitution of these values, along with the values of the function $(\partial\pi/\partial P)$, into equation 5 gives values for the amount of hexane adsorbed directly.

Experimental

Materials.—Benzene was Baker and Adamson "B and A" quality free from thiophene and was twice redistilled, the fraction boiling between 79.5 and 80° being collected.

n-Hexane was of the pure grade Phillips Petroleum Company, this was further purified by repeated shaking with concentrated sulfuric acid until a further amount of added acid remained colorless. The hexane was then twice distilled and the fraction boiling between 68.5 and 69.5° was collected. Stearic acid was from Armour and Company and was a sample from the same lot used by Ralston[7] in his investigations, it was recrystallized from ethanol, m.p. 69.4°.

The hexane and benzene were tested and found to be free from surface active impurities.

Benzene solutions of stearic acid were prepared by weighing the stearic acid and dissolving in the redistilled benzene in a volumetric flask. The concentrations used were 0.0004 and 0.00072 *M*.

Phosphoric acid solutions (0.01 *N*) were prepared from Baker and Adamson Reagent Grade phosphoric acid, and this was used as a liquid phase throughout the entire investigation.

Apparatus and Methods.—The apparatus and *modus operandi* are described in detail elsewhere.[8]

Results and Discussion

Figure 1a shows the surface pressure–surface concentration relationships for stearic acid under hexane vapor, the concentration units being in Gibbs,[9] *i.e.*, moles × 10^{-10} per cm. sq. Figure 1b which is a plot of the same data in the more conventional units, is included to show the expansion of the stearic acid monolayer due to the adsorbed hexane, an effect very similar to the effect of increasing temperature on myristic acid monolayers.[10]

Figure Ia yields the greater portion of the information required to calculate Γ_1, the surface concentration of hexane. It is immediately obvious that for any single isobar, the function $(\partial\pi/\partial\Gamma_2)_P$ is sensibly constant in each of two regions, and zero in the transition region, a fact that greatly facilitates further computation (Table I).

TABLE I

VALUES OF THE FUNCTION $(\partial\pi/\partial\Gamma_1)_P \times 10^{-10}$ GIVEN AT THE VARIOUS EXPERIMENTAL VALUES OF THE RELATIVE PARTIAL PRESSURE OF HEXANE VAPOR

Column A contains values of the function for high values of Γ_2. Column B contains values of the function for low values of Γ_2.

P	*A*	*B*
0.24	1.90	1.38
.32	2.38	1.38
.52	2.67	1.27
.63	3.56	1.22
.80	4.22	1.03
.92	4.92	1.00
1.00	5.28	0.92

From the Γ_2–π graph we have constructed a graph of π *vs.* P and from this have calculated values of the function $(\partial\pi/\partial P)\Gamma_2$ for selected values of Γ_2 (Table II).

In order to calculate $\mu_2^0 - \mu_2$ (Equation 7) it was necessary to have some convenient standard state as a reference line. Koenig[6] has suggested using the surface concentration Γ_2^0 at the spreading

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(3) L. I. A. Micheli, *Phil. Mag.*, **3**, 895 (1927).

(4) H. M. Cassel and M. Formstecher, *Kolloid-Z.*, **61**, 18 (1932).

(5) R. B. Dean and Fa-Si Li, THIS JOURNAL, **72**, 3979 (1950).

(6) F. O. Koenig, private communication, ms. in print.

(7) A. W. Ralston, *J. Org. Chem.*, **7**, 546 (1942).

(8) R. B. Dean and K. E. Hayes, Sorption of Vapors on Monolayers. III. Presented at the 119th A. C. S. Meeting, Colloid Division, Symposium on Surface Tension of Solutions, Boston, Mass., 1951; THIS JOURNAL, **73**, 5583 (1951).

(9) R. B. Dean, *J. Phys. Colloid Chem.*, **55**, 611 (1951).

(10) N. K. Adam, *Proc. Roy. Soc.* (*London*), **101A**, 516 (1922).

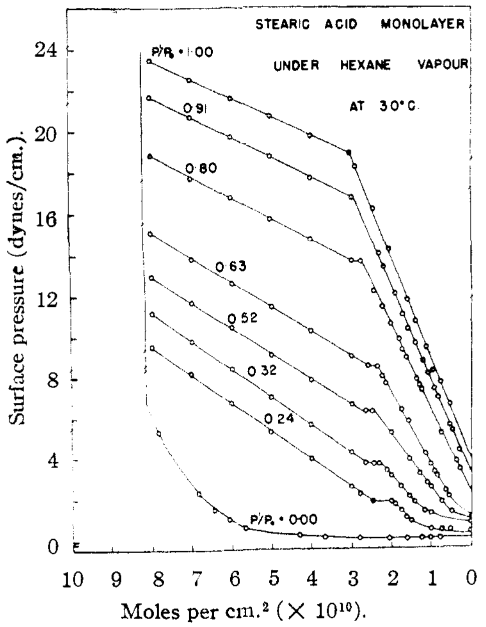

Fig. 1a.—Surface pressure-surface concentration relationships for stearic acid monolayers under *n* hexane vapor at 30°.

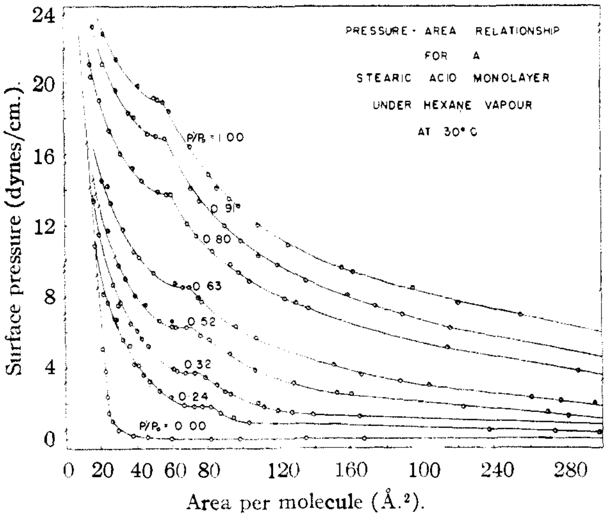

Fig. 1b.—Surface pressure-area relationships for stearic acid monolayers under *n*-hexane vapor at 30°.

TABLE II

VALUES OF THE FUNCTION $(\partial\pi/\partial P)\Gamma_2$ FOR THE SPECIFIED VALUES OF Γ_2 INTERPOLATED TO INTEGRAL VALUES OF THE RELATIVE PARTIAL PRESSURE OF HEXANE

	Γ_2 (Gibbs)				
P	1	1.5	2	4	8
0.1	1.70	3.90	...	12.20	9.20
.2	3.90	6.00	...	13.50	10.00
.3	5.10	8.40	10.70	14.30	11.10
.4	6.60	10.60	13.30	15.70	13.30
.5	8.90	12.60	15.20	18.10	15.20
.6	10.90	13.90	17,00	21.10	18.30
.7	13.50	15.90	18.30	25.00	20.00
.8	15.30	17.00	20.00	29.50	24.60
.9	16.10	18.00	21.00	27.80	22.60
1.0	16.10	18.50	21.00	20.50	22.00

pressure of stearic acid under hexane vapor, π^0 as that standard state; measurements of the spreading pressure of crystalline stearic acid were made under various partial pressures of hexane vapor. Figure 2 shows the linear relationship between log π^0 and P from which the values of Γ_2^0 may be obtained by comparison with Fig. 1a. It is to be noted in passing that the value of the spreading pressure in the absence of hexane is almost identical with that obtained by Cary and Rideal at the same temperature.[11]

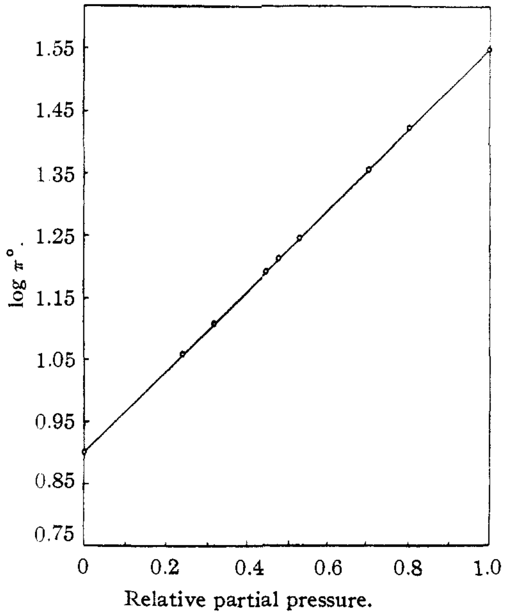

Fig. 2.—Effect of *n*-hexane vapor on the spreading pressure of stearic acid at 30°.

As already stated our data gave values of the function $(\partial\pi/\partial\Gamma_2)_P$ which were constant over several well-defined regions, and hence equation 7 reduces to

$$\mu_2^0 - \mu_2 = \left(\frac{\partial\pi}{\partial\Gamma_2}\right)_p \int_{\Gamma_2}^{\Gamma_2^0} d \ln \Gamma_2 \qquad (8)$$

which may be integrated directly.

Using these values of the chemical potential, values of the function $(\partial\mu_2/\partial P)\Gamma_2$ are easily found from a plot of $\mu_2^0 - \mu_2$ against P (Table III).

TABLE III

VALUES OF THE FUNCTION $(\partial\mu_2/\partial P)\Gamma_2 \times 10^{-10}$, FOR THE SPECIFIED VALUES OF Γ_2, INTERPOLATED TO INTEGRAL VALUES OF THE RELATIVE PRESSURE OF HEXANE

	Γ_2 (Gibbs)				
P	1	1.5	2	4	8
0.1	−1.5	−1.0	−0.4	0.48	0.0
.2	−2.2	−1.2	−0.5	.48	.0
.3	−2.7	−1.7	−0.8	.48	.0
.4	−3.4	−2.0	−1.2	.48	.0
.5	−3.9	−2.4	−1.4	.48	.0
.6	−4.5	−3.1	−1.7	.48	.0
.7	−5.2	−3.3	−2.1	.48	.0
.8	−5.8	−4.0	−2.4	.48	.0
.9	−6.5	−4.4	−2.6	.48	.0
1.0	−7.00	−5.1	−3.0	.48	.0

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[11] A. Cary and E. K. Rideal, *Proc. Roy. Soc.* (*London*), **109A**, 301 (1925).

At high stearic acid concentrations this term is small, and within the limits of our experimental data sensibly constant for any particular value of Γ_2: however, at low concentrations it becomes quite appreciable as the plot of the values of Γ_1 against partial pressure of hexane shows (Fig. 3). The lower curve labeled $\Gamma_2 = 2G$ has been calculated according to Dean and Li[5] assuming the correction term to be negligible.

Figure 3 also includes the curve for $\Gamma_2 = 0$. Values for the adsorption of hexane on a clean water surface are higher than those reported by either Micheli or Cassell and Formstecher.[3,4] It is probable that the drop weight method used by these authors does not permit of sufficient time for the system to reach equilibrium. We find that at least 20 minutes are required to reach this equilibrium.

The maximum adsorption of hexane on a surface almost completely covered by stearic acid gives a limiting ratio of one molecule of hexane to one of stearic acid. It is interesting to note that the adsorption of hexane on stearic acid follows a type III isotherm at low acid concentrations going over to type V at high concentrations. Type V isotherms are usually explained on the basis of capillary condensation, an explanation that is hardly applicable in this case.

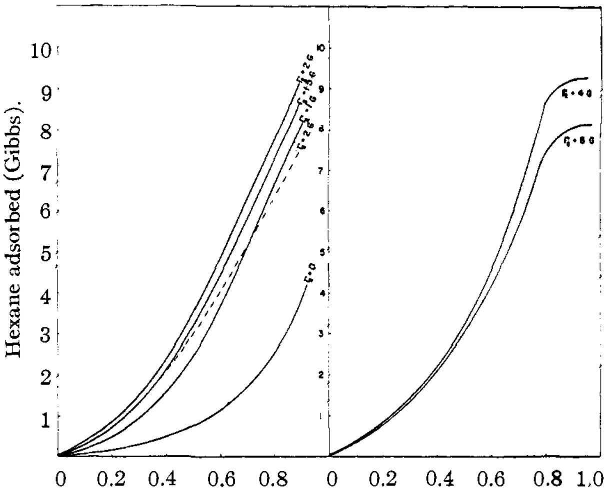

Fig. 3.—Adsorption isotherms for *n*-hexane on stearic acid monolayers at 30°.

EUGENE, OREGON RECEIVED APRIL 23, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

The Crystal Structure of Tetramethylpyrazine

BY DON T. CROMER,[1] AARON J. IHDE AND H. L. RITTER

Tetramethylpyrazine crystallizes from ether at room temperature in the orthorhombic class mmm, space group Pbca ($= D_{2h}^{15}$). Bounded Fourier projections of this crystalline species have been prepared from single-crystal X-ray diffraction data. The disposition of atoms within the unit cell has been determined and the several interatomic distances obtained. The molecule is planar, but the C–N bond length is apparently somewhat shorter than expected while the ring C–C bond appears to be longer.

As a contribution to the literature of crystal structures of simple heterocyclic compounds, we have made a complete structure determination of tetramethylpyrazine. The substance (m.p. 86°) was prepared according to the method of Kipping[2] and crystallized from anhydrous ether. The crystals usually grow in the tabular habit of truncated bipyramids, occasionally modified by a pair of prism faces. The regular octahedra mentioned by Brandes and Stöhr[3] for tetramethylpyrazine were never found in this Laboratory, and may be a polymorphic form. The morphology of our crystals indicates an orthorhombic class, mmm. If the pinacoid bevelments are assigned the form {111}, the axial ratios as determined by single-circle goniometer measurements are 0.902:1:1.104.

Single crystal rotation photographs around the three axes were prepared and the unit translations computed from layer line spacings. The approximate values so obtained were $a_0 = 8.45$, $b_0 = 9.38$, $c_0 = 10.30$ Å. The corresponding axial ratios agree sufficiently well with the goniometric data and these approximate lattice parameters served for the construction of reciprocal lattice nets and the indexing of X-ray reflections. The approximate density of the crystals was determined by displacement in a saturated solution of tetramethylpyrazine in isoamyl ether, as 1.08 g./cc. This gives 3.8 or 4 molecules per unit cell. Oscillation photographs over 10° ranges were taken using the multiple film technique of Robertson.[4] Crystals of 0.4 mm. maximum dimension were used. The very high vapor pressure of tetramethylpyrazine made it necessary to protect the crystals by a thin coat of varnish during exposure. Cu–K_α radiation was used with a Ni filter. All reflections were indexed, and the intensities estimated visually on an arbitrary scale and corrected in the usual way. No correction was made for absorption in the crystal.

More accurate values for the lattice parameters were obtained from selected oscillation photographs. Three of these photographs were found which carried symmetrically placed spots on the zero layer line. The centers of these films could thus be accurately fixed and the positions of the spots accurately measured. For rotation about the *a* axis and on the zero layer line

$$(k/b)^2 + (l/c)^2 = 2(l - \cos x/2\pi r)/\lambda^2$$

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(1) National Lead Company, Titanium Division, South Amboy, N. J.

(2) F. B. Kipping, *J. Chem. Soc.*, 2889 (1929).

(3) P. Brandes and C. Stöhr, *J. prakt. Chem.*, **53**, 510 (1896).

(4) J. M. Robertson, *J. Sci. Instruments*, **20**, 175 (1943).