

## ``Vapor Snake" Phenomenon and ``Plastic Crystals"

Syûzô Seki

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- <sup>1</sup> K. Hirota, Bull. Chem. Soc. Japan 16, 232 (1941).  
<sup>2</sup> L. J. Gillespie and S. Breck, J. Chem. Phys. 9, 370 (1941).  
<sup>3</sup> K. Hirota, J. Chem. Soc. Japan (printed in Japanese) 64, 16 and 112 (1943); cf. Chem. Abst. 41, 3346 (1947).  
<sup>4</sup> Guthrie, Wilson, and Schomaker, J. Chem. Phys. 17, 310 (1949).  
<sup>5</sup> The specification of the apparatus used: equidistant annular space 1.5 mm, its length 94 cm, volume of reservoirs 23 cc, higher temperature 76°C and lower temperature 25°C. Cf. Bull. Chem. Soc. Japan 16, 475 (1941).

## Application of Ursell and Mayer's Treatment for Imperfect Gases to Adsorption

SYŌ ONO

*Institute of Applied Science, Faculty of Engineering,  
Kyushu University, Fukuoka, Japan*

December 28, 1949

MANY attempts to derive the adsorption isotherm from a knowledge of the intermolecular forces have been made, based upon the idea of lattices. It seems, however, to be doubtful that the lattice theories of adsorption lead to really satisfactory results. To make further progress the author made the general development of the Gibbs phase integral for a system consisting of adsorbate molecules and an adsorbent according to Ursell<sup>1</sup> and Mayer's<sup>2</sup> method for treating imperfect gases.

We will denote the potential energy of the system containing  $n$  adsorbate molecules alone by the symbol  $U_n(\{\mathbf{n}\}, 0)$  and the potential energy of the system containing  $n$  adsorbate molecules and an adsorbent by  $U_n(\{\mathbf{n}\}, 1)$ , where the boldface symbol  $\{\mathbf{n}\}$  indicates the coordinates of  $n$  molecules. We define  $F_n(\{\mathbf{n}\}, \epsilon)$  by

$$F_n(\{\mathbf{n}\}, \epsilon) = \exp\left(-\frac{U_n(\{\mathbf{n}\}, \epsilon)}{kT}\right), \quad (1)$$

where  $\epsilon$  assumes the value 1. According to the result proved by Mayer and Montroll,<sup>3</sup> we may write the expansion of  $F_M(\{\mathbf{M}\}, \epsilon)$  in the form

$$F_M(\{\mathbf{M}\}, \epsilon) = \sum \{k\{\mathbf{m}_i\}_M\}_u \prod_{i=1}^k [g_m\{\mathbf{m}_i\}_M + \epsilon h_m\{\mathbf{m}_i\}_M], \quad (2)$$

where  $\sum \{k\{\mathbf{m}_i\}_M\}_u$  is used to indicate summation over all unconnected sets of subsets. The inverses of (2) are

$$g_m\{\mathbf{m}\} = \sum \{l\{\mathbf{M}_j\}_m\}_u (-)^{l-1}(l-1)! \prod_{j=1}^l F_M(\{\mathbf{M}_j\}_m, 0), \quad (3)$$

and

$$h_m\{\mathbf{m}\} = \sum \{l\{\mathbf{M}_j\}_m\}_u (-)^{l-1}(l-1)! \times \left[ \prod_{j=1}^l F_M(\{\mathbf{M}_j\}_m, 1) - \prod_{j=1}^l F_M(\{\mathbf{M}_j\}_m, 0) \right]. \quad (4)$$

The grand partition function of the system at the fugacity  $z$  is given by

$$\Xi(T, z, \epsilon) = \sum_{n=0}^{\infty} \frac{z^n}{n!} \int \cdots \int F_n(\{\mathbf{n}\}, \epsilon) d\{\mathbf{n}\}, \quad (5)$$

$d\{\mathbf{n}\}$  being the configuration element of  $n$  molecules, where  $\epsilon$  assumes 0 or 1 according as the system contains the adsorbent or not. Using the expression (2) we obtain

$$\Xi(T, z, \epsilon) = \exp\left[\sum_{l=1}^{\infty} V b_l z^l + \sum_{l=1}^{\infty} a_l \gamma_l z^l\right], \quad (6)$$

in which  $V$  is the volume of the system and  $a$  is the area of the surface of the adsorbent. Here  $b_l$  and  $\gamma_l$  are the cluster integrals respectively defined as

$$b_l = \frac{1}{V l!} \int \cdots \int g_l\{\mathbf{l}\} d\{\mathbf{l}\}, \quad (7)$$

and

$$\gamma_l = \frac{1}{a l!} \int \cdots \int h_l\{\mathbf{l}\} d\{\mathbf{l}\}, \quad (8)$$

the integration being extended over a region bounded by the volume of the container. From (6) we at once have the expression for the average number of the molecules contained in the system. And the increase in the number of molecules per unit area of the surface of the adsorbent due to insertion of the adsorbent will be expressed by

$$\theta = \sum_{l=1}^{\infty} l \gamma_l z^l, \quad (9)$$

which gives the equilibrium number of adsorbed molecules as a function of the fugacity. The pressure can be expressed as a function of the fugacity by means of Mayer's equation:

$$p = kT \sum_{l=1}^{\infty} b_l z^l. \quad (10)$$

From (9) and (10) we can, in principle, calculate the adsorption isotherm.

The details of the theory will appear in the Memoirs of Faculty of Engineering, Kyushu University 12, No. 1.

<sup>1</sup> H. D. Ursell, Proc. Camb. Phil. Soc. 23, 685 (1927).

<sup>2</sup> J. E. Mayer, J. Chem. Phys. 5, 67 (1937).

<sup>3</sup> J. E. Mayer and E. W. Montroll, J. Chem. Phys. 9, 2 (1941).

## "Vapor Snake" Phenomenon and "Plastic Crystals"

SYŌZŌ SEKI

*Department of Chemistry, University of Osaka, Osaka, Japan*  
January 19, 1950

IN a recent communication, M. K. Phibbs and H. I. Shiff have reported the "vapor snake" phenomenon in cyclohexane.<sup>1</sup> They concluded from their experiments that this phenomenon was attributed to the high vapor pressures of cyclohexane (35 mm Hg at the melting point). However, judging from their description, one may receive an impression that they do not necessarily regard this condition as the decisive one. Indeed, they suggest also that this phenomenon is due to the highly symmetrical molecular structure of this substance. This latter condition, probably, may be rather essential in such a sense as will be given.

Quite independently, we have found just the same phenomenon in cyclohexanol and carbon tetrachloride during the course of fractional distillation in high vacuum and have already reported the results as well as some explanation in a Japanese scientific journal in 1948.<sup>2</sup> As this was written in Japanese and discussed in a somewhat different way from the above authors, we should like to explain the results and interpretation briefly in the present letter.

According to Timmermanns,<sup>3</sup> the so-called plastic crystals are generally composed of molecules of spherical shape and they form solid solutions with each other in wide range of concentrations regardless of the difference of chemical properties of component molecules. He pointed out, furthermore, the fact that the entropy change at the melting point is much smaller than that at the transition point between this plastic crystalline and ordinary crystalline phases and that the remarkable plastic property is characteristic of this phase. Plastic crystals are thus in an intermediate state between the solid and the liquid states.

In our Laboratory, under the direction of Professor Nitta, we have been studying the structure and properties of this sort of crystal for several years. The substances investigated with x-rays are pentaerythritol,<sup>4</sup> tetranitromethane,<sup>5</sup> cyclohexanol,<sup>6</sup> cyclohexane,<sup>7</sup> and berylliumoxyacetate.<sup>8</sup> The analysis of the Laue effect and the diffuse scattering of x-rays of these crystals have revealed that, whereas the centers of mass of molecule are truly so arranged as to form an ordinary crystal lattice, a part or the whole of the molecule is no longer fixed and undergoes violent thermal motions.

This fact stands in contrast to the liquid crystal—the well-known intermediate phase between the solid and the liquid—in which the molecules have ordinarily rod-like shape and stack themselves together to form swarms, but do not constitute an ordinary crystalline lattice.

The vapor pressures of cyclohexanol and carbon tetrachloride measured by the present author at their melting points are only 0.7 mm Hg and 7 mm Hg, respectively.<sup>5,9</sup> They are much lower in comparison with that of cyclohexane; nevertheless they show this vapor snake phenomenon. In our opinion, therefore, the high vapor pressure of the crystal is not the necessary condition for the occurrence of this anomalous phenomenon, but the state of plastic crystal (not of the super-cooled liquid!) is a more essential factor. An ordinary liquid, when solidified, going to the polycrystalline phase, forms cracks in every direction. We can obtain this polycrystalline state of these substances without observing any vapor snake phenomenon, if we solidify them rapidly down below their transition points by immersing into the liquid air. Accordingly, the violent thermal motion of the molecules in the crystalline lattice seems to play an important rôle in this phenomenon. Thus, it is to be expected that the crystal of  $C(SCH_3)_4$ , of which the crystal structure has been determined recently and is known that the molecules are in violent thermal motion,<sup>10</sup> will also show this vapor snake phenomenon.

<sup>1</sup> M. K. Phibbs and H. I. Schiff, *J. Chem. Phys.* **17**, 843 (1949).

<sup>2</sup> S. Seki, *Kagaku* **18**, 277 (1948).

<sup>3</sup> Timmermanns, *J. Chim. Phys.* **35**, 331 (1938).

<sup>4</sup> I. Nitta and T. Watanabe, *Sci. Papers Inst. Phys. Chem. Research, Tokyo* **34**, 1669 (1938); I. Nitta and T. Watanabe, *Bull. Chem. Soc. Japan* **13**, 28 (1938).

<sup>5</sup> Oda, Iida, and Nitta, *J. Chem. Soc. Japan* **64**, 616 (1943); T. Oda and T. Watanabe, *ibid.* **65**, 154 (1944); S. Seki and I. Nitta, *ibid.* **62**, 907 (1941).

<sup>6</sup> T. Oda, *X-Rays* **5**, 21 (1948).

<sup>7</sup> See reference 6, p. 2; S. Seki and I. Nitta, *J. Chem. Soc. Japan* **69**, 141 (1948).

<sup>8</sup> T. Watanabe and Y. Saito, *Nature* **163**, 225 (1949); Seki, Momotani, and Chihara, *ibid.* **163**, 226 (1949).

<sup>9</sup> I. Nitta and S. Seki, *J. Chem. Soc. Japan* **69**, 85 (1948).

<sup>10</sup> H. J. Backer and W. G. Pedrok, *Rec. trav. Chim.* **62**, 533 (1943).

## Synthetic $SiO_2$ Prism in the Infra-Red

MANSEL DAVIES

Department of Chemistry, University College, Aberystwyth, Wales  
January 20, 1950

THE use of synthetically grown crystals ( $NaCl$ ,  $KBr$ ,  $LiF$ ,  $CaF_2$ , etc.) as prism materials in the infra-red is well known. Lithium fluoride, for instance, is much sought after as it offers good dispersive power in the  $3000\text{ cm}^{-1}$  region of the  $O-H$ ,  $N-H$ , etc. absorption frequencies. It is equally well known that, to the limits of its transmission in this region, quartz provides significantly higher dispersion before its absorption becomes too strong at (or before)  $2800\text{ cm}^{-1}$  ( $3.5\mu$ ). From  $2800$  to  $4000\text{ cm}^{-1}$ , although somewhat less effective than the crystalline material, the dispersive power of fused silica is still about 50 percent greater than that of  $LiF$ .

The purpose of this note is to indicate that transparent fused silica, available in this country from Thermal Syndicate Ltd., Wallsend-on-Tyne, is admirably suited for infra-red work in this region. A prism, height 8 cm, length of face 10 cm, angle  $45^\circ$ , although containing minute air bubbles, transmits adequate radiation for intensity measurements to within a few percent in the Grubb-Parsons single beam instrument down to  $2850\text{ cm}^{-1}$ . The radiation scattered by the prism in this region is not significantly larger than that for clear  $NaCl$ . An approximate indication of the over-all performance in the spectrometer mentioned can be made by stating that the  $2.6\mu$  atmospheric water record approaches in detail Sleator's plot using a grating and slit widths of  $31A$  ( $4.5\text{ cm}^{-1}$ ).<sup>1</sup> With solutions, the details in Fox and Martin's careful grating spectra<sup>2</sup> are recorded, e.g., the  $3111\text{ cm}$  peak in dilute  $CCl_4$  solutions of  $C_6H_5\cdot CH_2OH$ .<sup>3</sup>

To the British purchaser the relative costs of  $LiF$  (without import duties) and  $SiO_2$  prisms of the mentioned size are about 8:1.

<sup>1</sup> Sleator, *Astrophys. J.* **48**, 125 (1918).

<sup>2</sup> Fox and Martin, *Proc. Roy. Soc. A* **162**, 419 (1937).

<sup>3</sup> See reference 2, Fig. 3.