

LETTERS TO THE EDITOR

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On Waring's Problem

LET $G(k)$ denote the least integer s such that the Diophantine equation

$$N = x_1^k + \dots + x_s^k$$

is solvable for all sufficiently large positive integer N , where n, x_1, \dots, x_s denote positive integers.

The upper limits for $G(5)$ have been given by various writers ranging from Hardy and Littlewood to L. K. Hera. The best result known hitherto is $G(5) \leq 28$, due to Hera. The author of this note has been able to improve this to

Theorem $G(5) \leq 25$.

The author has been able to arrive at this result by improving, among other things, a theorem of Davenport on 'admissible exponents', viz., lemma 1. Suppose that $\lambda_1, \dots, \lambda_s$ are admissible exponents and that $1 - \frac{1}{k} < \lambda_i < 1$. Then $1, \lambda_1, \dots, \lambda_s$ are admissible exponents, provided that there exists an integer l satisfying

$$1 \leq l \leq k_{2-},$$

$$k\lambda_1 - (k-1) \leq \frac{1}{2}l$$

$(2^l - 1)[k\lambda_1 - (k-1)] + \sigma \leq l + 1$ ($\sigma = \lambda_1 + \dots + \lambda_s$).

This theorem is not powerful enough for

$k > 3$ since it does not lead to an admissible

set $1, x_1, \dots, \lambda_s$ such that $1 + \sigma > k - 1 + \frac{1}{2^{k-2}}$

But this can be improved by the

lemma 2. Suppose that $1, \lambda_1, \dots, \lambda_s$ are admissible exponents.

Then $1, \theta, \lambda_1\theta, \dots, \lambda_s\theta$ are admissible exponents

where $\theta = 1 - \frac{1}{k}$.

Other consequences of lemma 2 are

$$G(6) \leq 40 \text{ and } G(7) \leq 56.$$

These are also improvements on the previous results.

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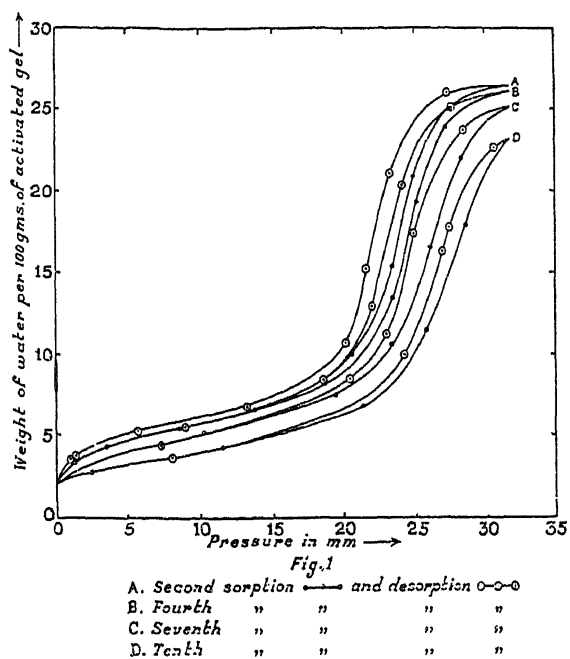
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October 23, 1939.

Drift of the Hysteresis Loop in Sorption

THAT "Hysteresis in Sorption" is real^{1,2,3,4,8} and is perfectly reproducible¹⁰ a large number of times in some cases and that the concept of cavities⁶ having narrow necks, is a general cause¹⁰ of the hysteresis effect, have already been established. For the non-existence or the disappearance of the hysteresis loop, however,

one of the causes has been shown to be the elasticity of the cavity wall.⁹ In the present investigation, a series of sorptions and desorptions of water vapour at 30° C. have been conducted on ferric oxide gel¹¹ activated at 200° C. and degassed in vacuum ($2 \cdot 10^{-4}$ mm.), for five hours, with the aid of a quartz fibre spring balance. Some of the results are shown in Fig. 1. The results indicate a unique behaviour as seen from the following striking



characteristics. With progressive sorptions and desorptions, (a) The sorptive capacity of the gel at the saturation pressure diminishes, (b) The hysteresis loop becomes smaller, (c) The hysteresis loop drifts away from the axis other than that of pressure, (d) The tail-end of the hysteresis loop which extends up to zero pressure in the second cycle of sorption and desorption tapers away from zero pressure in the subsequent cycles, (e) The gel retains some amount of water irreversibly at the end of first cycle of sorption and desorption which remains practically unaltered in the subsequent cycles.

The sorption isotherm as in the case of titania gel-water system¹⁰ shows an inflection beyond which there is a rapid rise in the sorptive capacity of the gel. Such an inflection clearly indicates, as in copper oxide-water system,⁷ a change in the nature of the process, i.e., a

change from monomolecular adsorption to capillary condensation. In the porous ferric oxide gel, some of the capillaries are open pores and some are cavities having narrow necks, the latter being responsible for the hysteresis effect. The decrease in the sorptive capacity of the gel at saturation pressure, indicates a decrease in the total capillary volume. If there were no cavities in the gel, there would be no hysteresis loop and the sorption and the desorption curves would be coincident. Assuming that the area of the hysteresis loop is a measure of the total cavity volume, the fact that the hysteresis loop becomes smaller, with progressive sorption and desorption, shows that the total cavity volume decreases. The continuous drift of the hysteresis loop and the tail-end of the hysteresis loop terminating away from zero pressure suggest that the diameters of the cavities and their necks are continuously increasing. The tendency of the sorption and desorption curves to come close to each other indicates a decrease in the disparity between the diameters of the cavities and their necks. So each cycle of sorption and desorption results in the widening of the cavities and their necks and the diminution in the total cavity volume. All these changes indicate that in ferric oxide gel-water system, with progressive sorptions and desorptions, the colloidal particles coalesce with the production of bigger particles. In fact, the above changes simulate those taking place in a definite mass of a system of closely packed spherical particles, as progressive increase in the size of the particles proceeds.

This is a unique case of a continuous drift with other changes of the hysteresis loop, resulting from progressive sorption and desorption of water vapour and is different from the one predicted by Leonard H. Cohan.⁵ No such drift is noticeable in the sorption of water vapour on gels of titania and silica.¹⁰ Sorption and desorption of carbon tetrachloride at 30° C. on another sample of the same ferric oxide gel have been conducted. There is a hysteresis loop which suffers no such drift. The second and the third hysteresis loops are identical with the first and the sorptive capacity at saturation

pressure remains the same. The permanent and reproducible hysteresis loop has also been scanned as in the case of titania gel-water.¹⁰

It is probable that this interesting colloidal behaviour of ferric oxide gel is connected with its thixotropic property. By virtue of thixotropy, the particles have the facility¹² to coalesce. Whether other thixotropic systems behave in a similar way, is a question to be decided by further investigations which are in progress.

A study of the interesting phenomena *vide infra* accompanying successive sorptions and desorptions of water vapour has thrown much light on the changes in the fine structure of ferric oxide gel. Such a study necessitating the operation of a series of sorptions and desorptions of the vapour on the same sample of the adsorbent in vacuum, has been possible by the excellent advantages of the quartz fibre spring technique.

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November 30, 1939.

¹ Allmand, Hand and Manning, *J. Phys. Chem.*, 1929, **33**, 1694.

² Burrage, *Trans. Faraday Soc.*, 1934, **30**, 317.

³ Foster, *Proc. Roy. Soc. Lond.*, 1934, **146A**, 129.

⁴ Lambert and Foster, *Ibid.*, 1932, **136A**, 363.

⁵ Leonard H. Cohan, *J. Amer. Chem. Soc.*, 1938, **60**, 433.

⁶ McBain, *Ibid.*, 1935, **57**, 699.

⁷ — *Sorption of Gases by Solids*, George Routledge and Sons, Ltd., London, 1932, 443.

⁸ Pidgeon, *Canad. J. Res.*, 1935, **12**, 41; 1934, **10**, 713.

⁹ Rao, K. S., *Curr. Sci.*, 1939, **8**, 256.

¹⁰ —, *Ibid.*, 1939, **8**, 468.

¹¹ —, and Rao, B.S., *Proc. Ind. Acad. Sci.*, 1936, **4**, 562.

¹² Weiser, *The Colloidal Salts*, John Wiley & Sons, Inc., New York, 1933, **3**, 374.

Threshold Potentials and Reactivity under Electrical Discharge

It was observed earlier¹ that time-variations in the electrical quantities such as the magnitude of the ionisation current flowing through,

and the energy consumed in the reaction space were of significance in an analysis of the corresponding reaction-time curves. These studies were carried out in Geissler-, triode-type vessels and in the annular space of the Siemens' ozoniser. For a variety of reasons, especially the possibility of enabling an exposure of a pre-determined mass of a gas to a field which can be calculated with a fair precision on a comparatively simple theory,³ the last type of the vessel is well adapted. A factor which has hitherto been practically entirely ignored by workers in the field of reaction kinetics under electric discharge, has now been observed in the existence of a threshold potential, V_{min} ; this minimum of potential has to be exceeded in order to initiate the change in a given reactant material, which may be (a) pure or (b) a mixture. Almost in every case (the possibility of the explosive reactions constituting a general exception is being investigated) there is a sudden change, usually an increase, in the current through, and the wattage dissipated, in the system, besides the familiar manometric or chemical indication of an insipient reaction, at V_{min} . It is characteristic both of the reaction and nature of the material. The V_{min} values for (a) are identifiable with, or simply related to the corresponding Paschen potentials; work is now in progress on the position in respect of (b).

It has been found that a determination of V_{min} , the threshold potential, serves markedly to throw light on the mechanism of a complex, especially a consecutive chemical reaction. Curves in Fig. 1 illustrate the variation of V_{min} for the reactant material determined at different times during the decomposition of nitric oxide

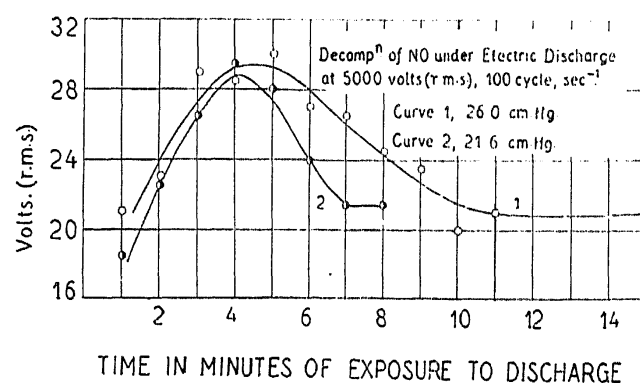


Fig. 1