

exchanger (and also the sulphonic acid anion).

A complete description of the sorption rate might necessarily involve the interaction energy for the process considered as an activation energy for the diffusion coefficient. If so, a larger ion would exhibit a smaller activation energy and hence a larger sorption rate (or diffusion coefficient). The results of Fig. 2 could then be reasonably connected with the periodicity of the atomic volumes. As for the latter, the ion charge must also be taken into account. Among the alkalis, the sorption rate increases with increasing (crystallographic) ion volume in accordance with the above picture. Unfortunately, the result for  $Z > 45$ , was obtained with a different batch of Dowex 50 and so no conclusions can be drawn from the result for cesium. The complete description might also contain entropy factors. These are apparently not known for the systems studied here. Following the picture given above it is reasonable that, under wetter conditions, the sorbing water molecules would mainly interact with water already sorbed, thus roughly explaining why the individuality of the counter ions disappears in such a case.

A more complete study of these phenomena would seem to be of interest. The temperature dependence of the sorption rate might give a clue for the interpretation of the interaction mechanism suggested.

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3. *Handbook of Physics and Chemistry*, 41st Ed. 1959-60, Chemical Rubber Publishing Co, p. 2499 ff.
4. Boyd, G. E., Adamson, A. W. and Myers, L. S. *J. Am. Chem. Soc.* **69** (1947) 2836.
5. Barrer, R. M. *Diffusion in and through solids*. Cambridge University Press 1941, Ch. 1.
6. Cf. e.g. Moelwyn-Huges, E. A. *Physical Chemistry*, Cambridge University Press 1947, p. 233, Fig. 1.
7. Gluechauf, E. *Endeavour*, **10** (1951) No. 37.

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## Sheet Ion Exchangers as Resistance Gauges for Moisture in Gases

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The sulphonation of sheets, rods, tubes or any shape of solid polystyrene yields a thin layer of polystyrene sulphonic acid<sup>1</sup>, a well-known cation exchange material. Many other ways of forming a sheet ion exchanger are possible<sup>1</sup> or conceivable.

It has been found that the electrical resistance of this material is a good measure of the relative humidity in air. The ion exchange groups may be saturated by Na<sup>+</sup>-ions for instance, so that the moisture detector is less likely to be affected by materials sorbed from the gas which may cause precipitation *etc.* The ion exchange layer of course is a hydrophilic substance, the moisture content of which is a function of the water partial pressure in the surrounding gas if equilibrium prevails. The conductance of the sheet ion exchanger will increase with increasing moisture content and so the resistance of an exchanger unit will be an appropriate measure of the moisture content. At constant temperature, it will after calibration with standard salt solutions<sup>2</sup> be a good moisture detector. Changing the temperature of course changes both the equilibrium conditions and conductance and must be corrected for by recalibration.

Practical exchanger units can be made by simply clamping two platinum electrodes on a sulphonated piece of polystyrene or better by winding a double spiral on a sulphonated (sodium ion-saturated) rod or hole cylinder using two wires of platinum (stainless steel was found to corrode in the long run), the wires being separated by about 0.5 mm or so. The wires should be long in order to reduce the resistance.

A typical calibration curve is given in Fig. 1. At decreasing humidities, the resistance increases steadily; at very low figures, the resistance may be impractically high. The resistance is preferably measured at 1 000 Hz to avoid polarization phenomena at the electrodes. Such effects were often obtained when DC was used. Any of the common electrical circuits can be used

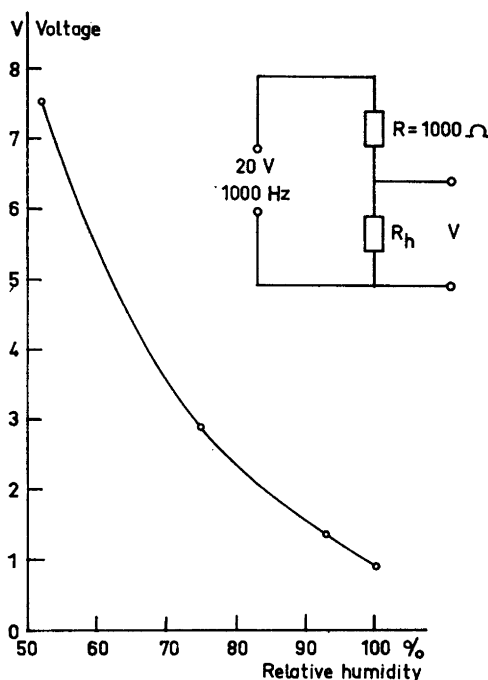


Fig. 1. Typical calibration curve of sheet ion exchanger resistance hygrometer. The voltage,  $V$ , is measured (at equilibrium) across the variable hygrometer resistance,  $R_h$ , with an electronic voltmeter in the circuit as indicated. The hygrometer is placed in a closed glass vessel, the relative humidity of which is varied by using standard salt solutions. The temperature was  $25^\circ \pm 0.1$ .

including AC bridges, simple volt-ampère coupling, or cross-coil instruments.

The unit responds quickly to changes in humidity. The rate is probably governed by the diffusion of water in the layer and thus the latter should be thin (a few microns). Units responding in a few seconds can be produced.

A special point for the possible use of this method for meteorological purposes is that pure water can be condensed or poured on the unit and the calibration will still be valid after evaporation and subsequent equilibration. This property is hardly provided by such hygrometers that are based on the impregnation of glass with lithium salts or phosphoric acid.

The units can be made very small and might be applicable in cavities difficult to reach with other hygrometers.

Obviously, the calibration curve will change if another cation is used. The study of the resistance properties and water diffusion kinetics would themselves be an interesting field of study.

A draw-back of the method is that some hysteresis effects have been detected when travelling along a resistance-humidity curve. The effect was not found to exceed what corresponds to 2% RH. Another draw-back is that, if thicker layers of sheet ion exchangers are wanted, they are difficult to prepare from commercial polystyrene apparently due to the very low, or quite absent, cross-linkage and to mechanical cracking of the hydrophilic material formed on the polymer blocks or sheets. It seems that this disadvantage could now be overcome by a moderate dose of ionizing radiation (e.g. by  $^{60}\text{Co}$   $\gamma$ -rays) which is known to introduce cross-linking<sup>3</sup>. This would be expected to improve the mechanical stability but might at the same time decrease the swelling of the ion-exchanger and hence somewhat decrease the sensitivity of the hygrometer.

This hygrometer is an example of the application of ion exchangers for quite a different use than the usual one. There is a commercial unit which has properties very similar to the present unit (which has been used since 1953 in this laboratory) but, from the pamphlets<sup>4</sup> supplied, it was not possible to see whether the ideas and the materials are the same or not. The applications should comprise a lot of cases of interest in the laboratory and elsewhere. A special case is the dry-boxes used for radioactive or moisture-sensitive materials. We have not attempted any extended systematic studies of the design of this hygrometer. It is therefore likely that anyone interested can find useful modifications and improvements of the description given above.

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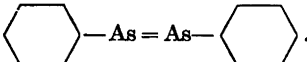
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## The Structure of Arsenobenzene

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Arsenobenzene is generally formulated as: . Double

bonds, however, are rarely formed between atoms heavier than oxygen.

Lyon and Mann<sup>1</sup> have previously cast some doubt upon the validity of the classical formula on the basis of molecular weight determinations but no satisfactory structure of the molecule has so far been proposed.

In order to obtain a satisfactory molecular formula we are investigating the crystal structure of arsenobenzene. The compound was obtained by the reduction of phenyl arsonic acid. Two different kinds of crystals can be recognised under the polarizing microscope. One kind forms transparent needle shaped crystals which exhibit parallel extinction and are optically biaxial. The other kind of crystals are a little opaque and show oblique extinction. The transparent ones become opaque between 182°C and 192°C and melt at 196°C. The

opaque crystals melt at 196°C. We have not yet proved that the transparent crystals are changed to the opaque form by heating but it appears to be likely. Chemical analysis on the mixture give the following results: C 47.60; H 3.37; calc. for  $(AsC_6H_5)_n$ : C 47.40; H 3.32.

Weissenberg and precession photographs proved the transparent crystals to be monoclinic. Filtered Cu-radiation was employed. The unit cell has the following dimensions, unique axis *b*, the needle axis:

$$\begin{aligned} a &= 24.04 \text{ \AA} \\ b &= 6.20 \text{ \AA} \\ c &= 12.22 \text{ \AA} \\ \beta &= 111.2^\circ \end{aligned}$$

The following extinctions were found:  $h0l$  for  $h = 2n + 1$  and  $0k0$  for  $k = 2n + 1$ . Hence the space group is  $P2_1/a$ . The density of the crystal is 1.73. Consequently there are 12  $As-C_6H_5$  groups in the unit cell. As the general point is four fold the  $As-C_6H_5$  groups must be linked together in groups of three or of six.

The Patterson projection along the *b*-axis indicated very strongly that the molecular unit contains six arsenic atoms forming a non planar ring with a centre of symmetry. A Fourier projection based upon the As-coordinates reveals the whereabouts of the benzene rings.

On this basis we propose that arsenobenzene is  $(AsC_6H_5)_6$ . Each As-atom forms two single As-As bonds (approximately 2.4 Å) with its neighbours in the ring and a third As-C bond. Isomers of different conformations are possible. The opaque crystals are triclinic. They will be investigated in more detail later.

A refinement of the structure of the monoclinic crystals is in progress.

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