

in such inhibitions. This previously unappreciated danger will also be present whenever a buffer is used which can form five membered chelate rings.

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Received April 3, 1967.

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## Diffusion in Gels and Polymeric Solutions

IN a recent communication, Metzner<sup>1</sup> directed attention to some experiments in which abnormally high rates of diffusion were found for the transfer of solutes of low molecular weight in certain polymer solutions and colloidal suspensions. On the basis of these results he speculated on a molecular explanation of how the rate of ordinary diffusion in a liquid may be increased appreciably by using macromolecules or colloidal particles.

Metzner's article appeared just after a study had been completed in this laboratory in which the diffusion coefficients of carbon dioxide and sulphur dioxide in aqueous solutions of carboxymethylcellulose (CMC) had been measured<sup>2,3</sup>. Unlike Metzner, we found no anomalous diffusion rates in the CMC solutions; in fact, our calculated diffusion coefficients were in all cases less than, or at best equal to, the corresponding values in pure water. We afterwards repeated these determinations and extended our measurements to other polymeric solutions. The present communication lists our results and compares them with comparable values in the literature.

In brief, our experimental method of determining liquid phase diffusivities involves measuring the transient rate of absorption of a soluble gas into a quiescent liquid substrate<sup>3</sup>. The precision of our technique has been demonstrated by measuring the diffusion coefficient of carbon dioxide in pure water—the numerical value of which is known accurately from a variety of different experimental determinations<sup>4</sup>. Our results are shown in Table I together with some representative values of diffusion coefficients in aqueous polymer solutions which we have obtained from the literature<sup>5-11</sup>. In no case do the diffusion coefficients in the polymer solutions exceed those in the pure solvent.

The results listed by Metzner are from three sources, the major source being the work of Astarita<sup>12</sup>. In the latter study diffusion coefficients were measured with a laminar liquid jet. To deduce diffusivity values from absorption rates in laminar liquid jets calls for detailed knowledge of the fluid mechanical behaviour of the jet<sup>13</sup>, in this case a non-Newtonian jet. We cannot, however, suggest any ready explanation of why Astarita's results are significantly greater than those of Table 1. Of the other two sources the results of Hopper<sup>14</sup> appear to scatter, that is, for benzoic acid diffusing in solutions of cyclohexane, the addition of 2 per cent polyisobutylene gives a diffusivity greater than that in the pure solvent, whereas the addition of 4 per cent gives a value smaller than the pure solvent.

To sum up, we have measured the diffusion coefficients of soluble gases in gels and polymeric solutions and we have found in all cases that the diffusion coefficient in the solution is smaller than that in the pure solvent. A search of the literature on diffusion in gels and polymer solutions supports our findings. We have not attempted

Table 1. DIFFUSIVITY RATIOS

Diffusing solute	Medium	$\frac{D_{\text{solution}}^*}{D_{\text{pure solvent}}}$	Reference
Carbon dioxide	0.5 per cent CMC† in water	0.97	3
Carbon dioxide	2.0 per cent CMC in water	0.92	3
Carbon dioxide	4.0 per cent PEG 400‡ in amyl acetate	0.93	5
Sulphur dioxide	0.5 and 2.0 per cent CMC§ in water	1.0 (actually $\frac{D_{2.0}}{D_{0.5}}$ )	5
Water	8 per cent CMC in water	0.87	6, 7
HPO <sub>4</sub> (Na <sub>2</sub> HPO <sub>4</sub> )	2.5 and 20 per cent gelatine in water	0.42 ( $\frac{D_{20}}{D_{2.5}}$ )	8
I <sup>-</sup> (NaI)	1.5 per cent agar-agar in water	0.90	9
β-Naphthol	1.0 per cent CMC in water	0.74	10
Benzoic acid	20 per cent kaolinite clay aqueous slurry	0.92	10
Sucrose	PVP¶ solutions in water	As low as 0.25	11

\* Ratio of diffusion coefficient in solution to that in the pure solvent.

† Carboxymethylcellulose.

‡ Polyethylene glycol (average molecular weight, 400).

§ These values have not been referred to the pure solvent because of imprecision in the determination of the diffusivity of sulphur dioxide in pure water. This imprecision resulted from large convective effects which were, however, suppressed by the CMC gels<sup>5</sup>.

¶ Polyvinylpyrrolidone.

to be exhaustive in our study, but we have not encountered a significant body of results, other than the work of Astarita, to support the notion that diffusion rates may be augmented by adding non-interacting macromolecules. Metzner's speculations may indeed be valid, but it is obvious that much experimental work is needed before a quantitative description of transport in structured fluids can be formulated.

This work was supported in part by a grant from the US Public Health Service.

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Received January 19, 1967.

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## PHYSIOLOGY

### Effect of Physical Training on Cardiac Catecholamine Concentrations

HUMAN beings who exercise intensely for long periods develop a symptomatology usually referred to as the athletic heart. It has been shown that the athletic heart is also present in animals. For example, enlarged heart and bradycardia were found in the hare when compared with the domesticated rabbit<sup>1</sup>. Recently, Tipton was able to produce an experimental bradycardia and cardiac hypertrophy in chronically exercised albino rats<sup>2</sup>.

Different hypotheses have been put forward to explain the bradycardia in athletes. According to Raab, the dominating vagus tone would result from an initial decrease in the sympathetic activity of the heart<sup>3</sup>. On the other hand, Tipton and Taylor have advanced the view that the decrease in the heart rate is a consequence of an increase in the amount of a non-neural cholinergic substance bound to the myocardium<sup>4</sup>. Because the mechanism of bradycardia in the athletic heart is still not