ported to and from the reaction cell. The apparatus used to continuously circulate a batch of actinometer fluid through the reaction cell is shown schematically by Ragonese and Williams (1971). This arrangement allows light to pass through the 25 mm quartz tube, except for the small reaction cell, and be reflected off the surrounding elliptical-reflector surface. The incident intensity measured at the reaction cell wall approximates the intensity which would prevail under the limiting case of a transparent reaction system.

The 25 mm quartz tube was then wrapped with black paper, except for the reaction cell surface, and the incident wall intensity was redetermined. This case corresponds to the use of an extremely high optical density (opaque) reaction system since light can not penetrate the 25 mm quartz reactor tube.

RESULTS AND CONCLUSIONS

The wall intensity was 3.00×10^{-7} keinsteins $m^{-2}s^{-1}$ in the case of the transparent reactor and 2.58×10^{-7} keinsteins $m^{-2}s^{-1}$ in the case of the opaque reactor. These numbers are the averaged values for duplicate determinations in which the conversion of the actinometer was held to less than 1% for any given determination of the incident wall intensity. This result approximates the maximum attainable difference in incident wall intensity for this particular elliptical-reflector reactor and might be approached in practice if a high optical density liquid actinometer were used in conjunction with a low optical density gas phase reaction system.

This difference in incident wall intensity is solely attributable to that portion of the lamp output which passed through the transparent section of the 25 mm tube and was reflected onto the reaction cell wall. This difference will diminish as the optical density of the reaction system approaches that of the actinometer. For example, if the optical density of the reaction system was only 1.0 then approximately 63% of the light would be absorbed in passing through the reactor diameter according to the Beer-Lambert absorption equation. Therefore, as an approximation, the difference in incident wall intensity would be reduced 63% from the difference reported here. While the results obtained are limited to the specific elliptical reflector-reactor geometry used, they are of some value in estimating the expected effect in other reactors. For example, if the reactor tube diameter were decreased with respect to the lamp diameter in a geometrically similar reflector, the maximum difference in wall intensity would also be expected to decrease relative to the result reported here since a smaller fraction of the source output would be intercepted by the reactor.

This result should serve to alert workers in this field to the magnitude of the potential error possible in determining the incident wall intensity when the optical density of the actinometer and reaction system are different and to provide an experimental method by which the error can be determined.

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The Possible Role of Diffusion in Metabolism

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When considering most chemical reactions, it is the usual chemical engineering practice to examine the overall process of diffusion of reactants to the zone where the chemical reaction occurs in order to determine if the diffusion step or the reaction step is the rate-controlling one. However, in the biological sciences it is more common to look at only the reaction step when considering metabolic reactions, thus overlooking the possibility that diffusion might be the rate-limiting factor. In addition, people involved in studying the metabolic conversion of various reactants to products also very frequently assume that the reactions are first order and calculate their data using this assumption, which may be quite valid. However, since first-order kinetics and diffusion-controlled reactions result in mathematical equations having the same concentration dependency, it is possible that mass transfer control of the metabolic reactions could also be read into their results.

In order to determine if diffusion is the controlling mechanism in a chemical reaction it is usual to do one of three types of experiments: (1) vary the temperature and examine the magnitude of the activation energy, (2) vary the distance for mass transport and see if that affects the reaction rate, and (3) vary the diffusivity and look at that effect on the reaction rate, or combinations of these three experiments. However, when the reactions to be studied occur in a living animal, it is not possible to do experiments (1) and (2). The usual mammalian temperature is 37°C and is relatively constant, and the distances of reaction obviously cannot be varied. Thus, it would appear that variations in the diffusivity provide the best experiment for this purpose.

Let us now examine a simplified reaction scheme for glucose metabolism in the body shown in Figure 1. Various intermediates of the reaction sequence are left out of this diagram, and the complete mechanism can be found in any standard biochemistry test; however, the more important features are shown. Pyruvate and lactate intermediates are frequently measured as an indication of metabolism. For example, if there is an oxygen

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deficiency, there will obviously be a shift of pyruvate toward the lactate product. The lactate/pyruvate ratio is thus a standard clinical measure of oxidation rates. If, however, one varied the diffusivity of both of the reactants, glucose and oxygen, and measured the concentration of the *intermediate* products, pyruvate and lactate, one might be able to determine if mass transfer is a controlling factor.

We have previously found (Navari et al., 1971) that changes in the plasma protein levels will affect the diffusivity of various substances as they pass through the blood plasma on their way to the tissue. In addition, we have also shown that the diffusivities of all substances are affected by the same relative amount by variations of protein levels. In this case, if we altered the albumin level, it would presumably change the diffusivities of glucose and oxygen by the same ratio. Then, if mass transfer were a controlling factor in the metabolism of glucose, the levels of pyruvate and lactate should vary as the diffusivity, but the pyruvate/lactate ratio should remain a constant.

EXPERIMENT

We used 40 Dutch-belted rabbits for a period of six months. These were divided into two groups; one on a normal diet and one on a 1% cholesterol diet, in order to include the effect of different diets. Each group was then divided into two equal sub-groups: (1) elevated plasma albumin levels and (2) normal plasma albumin levels. The rabbit albumin was injected intramuscularly every 10 to 14 days in an amount calculated to increase the concentration to the normal upper physiological level. Thus, the plasma albumin level in all of the rabbits was in the usual physiological range.

After six months of such a regimen, blood analyses of the rabbits were performed to determine the levels of two intermediates of the catabolism of glucose, pyruvate, and lactate. In addition, electrophoretic and total protein analyses provided the data for the levels of protein fractions in the blood. The analyses were performed using typical, standard tests which are available from a number of companies specializing in clinical chemistry.

RESULTS AND DISCUSSION

The change in the plasma diffusivity for each rabbit caused by the changes in protein level was calculated using an equation described previously (Chisolm et al., 1971). The values for each group were then averaged and plotted versus the average lactate and pyruvate levels; these plots are shown as Figures 2 and 3. In those figures, the ratio D_{AS}/D_{AB} is the diffusion coefficient of the metabolites (glucose and oxygen) divided by their diffusion rate through water. As can be seen, a semi-logarithmic relationship does appear to exist between the diffusivity ratio and the concentration of the reaction intermediates, indicating that the reactions are mass transport controlled. In addition, the slopes of the lines in the two figures are equal, denoting a constant lactate/pyruvate ratio, and further confirming the accuracy of the data.

These data support the hypothesis that diffusion may sometimes be the rate-controlling step in metabolism. This observation merits further studies as it may possibly provide a mechanism for the control of metabolic disorder, for example, altering the diffusivity.

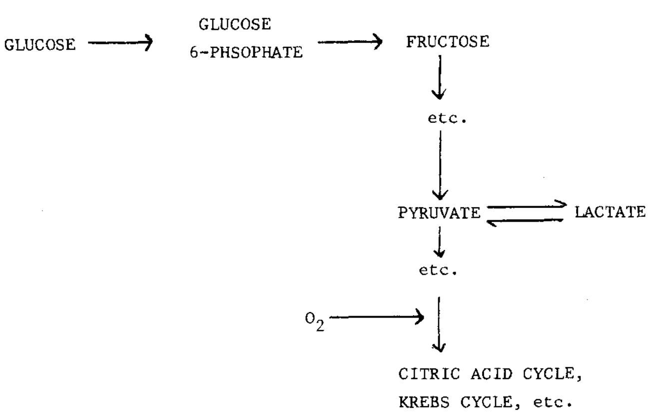

Fig. 1. Simplified glucose metabolism.

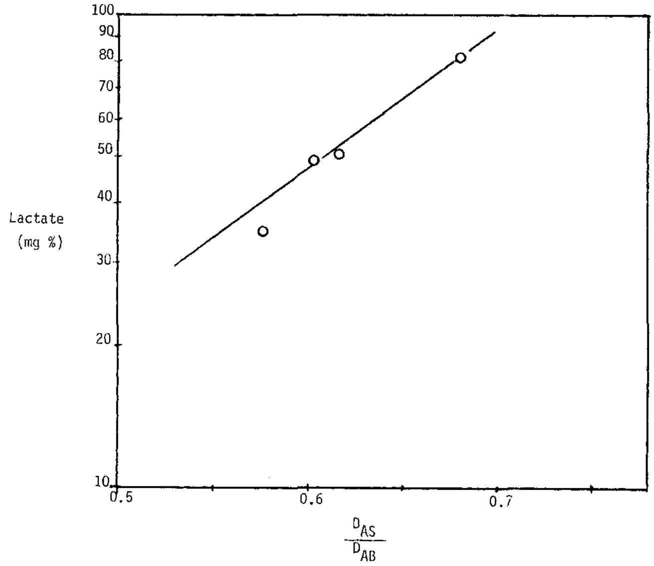

Fig. 2. Lactate concentration.

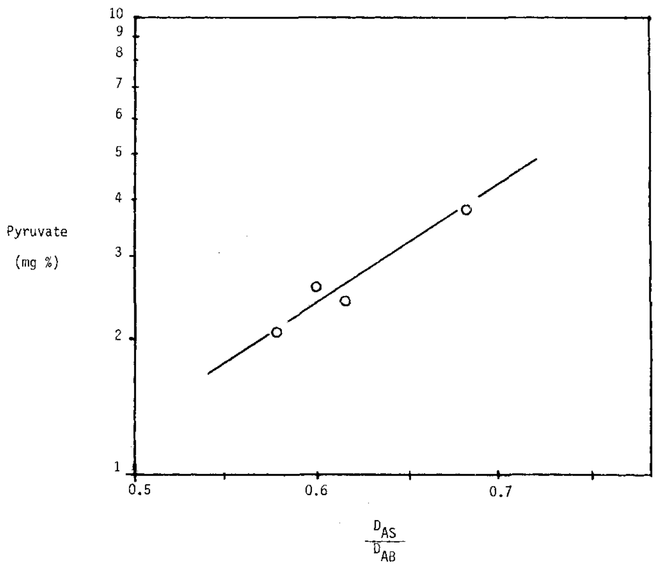

Fig. 3. Pyruvate concentration.

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