NOTE

The Free Energy Change in the Reaction between Nitrogen Peroxide and Solid Potassium Chloride

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The free energy change in the reaction

$$KCl(s) + 2NO_2(g) = KNO_3(s) + NOCl(g) \qquad (1)$$

was calculated in a previous publication[1] to be −5623 calories at 298.1°K. Owing to lack of data which would permit the direct calculation of the free energy of formation of solid potassium nitrate it was necessary to arrive at a value for (1) by an involved procedure using freezing point data and activity. It was necessary also to calculate the free energy of formation of solid potassium chloride by means of the value for sodium chloride.

Recently Southard and Nelson[2] have determined the molal heat capacities of $KCl(s)$ and $KNO_3(s)$ from 15 to 285°K. and by means of these data and the entropy of potassium obtained by Kelly,[3] the entropies of oxygen, chlorine and nitrogen given by Giauque and co-workers[4] and the heats of formation given in the "I. C. T.," Vol. V, have calculated the free energy of formation of $KCl(s)$ to be −97,700 cal. at 298.16°K. and that of $KNO_3(s)$ to be −95,000 calories.

Giauque and Clayton[5] have also very recently obtained new data from which they calculate an improved value of 20,650 calories for the free energy of formation of $NO(g)$ at 298.1°K.

The free energy change in (1) at 298.1°K. may now be evaluated by direct combination of free energy equations using the improved values mentioned above and those formerly used for the reactions between nitric oxide and oxygen to give nitrogen dioxide and for the reaction between nitric oxide and chlorine to give nitrosyl chloride. The value so obtained is −6042 calories, or if N_2O_4 is used instead of NO_2 −4915 calories. If Dixon's[6] recent value of −4300 calories for the formation of nitrosyl chloride from nitric oxide and chlorine is used, these values become, respectively, −5502 and −4375 calories.

Since the larger quantities in this calculation are now known with considerable certainty, all reasonable doubt as to the magnitude or sign of the free energy change in (1) has been removed.

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[1] Whittaker, Lundstrom and Merz, *Ind. Eng. Chem.*, **23**, 1410 (1931).

[2] Southard and Nelson, THIS JOURNAL, **55**, 4865 (1933).

[3] Kelly, Bureau of Mines Bulletin 350 (1932).

[4] Giauque and Johnston, THIS JOURNAL, **51**, 2300 (1929); Giauque and Overstreet, *ibid.*, **54**, 1731 (1932); Clayton and Giauque, *ibid.*, **54**, 2610 (1932).

[5] Giauque and Clayton, *ibid.*, **55**, 4875 (1933).

[6] Dixon, *Z. physik. Chem.*, Bodenstein Festband, 679 (1931).

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WASHINGTON, D. C.

RECEIVED MARCH 20, 1934

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF OREGON STATE COLLEGE]

The Effect of Non-Electrolytes upon Diffusion in Gelatin Gels

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In an earlier investigation[1] it was observed that the presence of a non-electrolyte in a gelatin gel in which urea was diffusing would affect the diffusion velocity of the urea. The gels had been prepared to contain 1.5% of the non-electrolyte and urea was permitted to diffuse from a solution containing a like concentration of the same non-electrolyte into the gel. Of the ten non-electrolytes used, four caused a decrease in the diffusion velocity of urea and six caused an increase. The greatest decrease was 11.9% produced by methanol and the greatest increase was 32.7% by sucrose. The present investigation was undertaken to determine the reasons for the changes in the diffusion velocity of urea brought about by the presence of the non-electrolytes in the gels.

Experimental Procedure

Gels were prepared of electrodialyzed calf-skin gelatin to contain 3% of gelatin and varying amounts of the non-electrolytes, methanol, urea, glycerol, glucose and sucrose. The diffusion velocity of urea from a 3% solution, also containing an equilibrium amount of the non-electrolyte being studied, was determined by the method of Friedman and Kraemer.[2] All experiments were performed at 5°.

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[1] Friedman, THIS JOURNAL, **52**, 1305 (1930)

[2] Friedman and Kraemer, *ibid.*, **52**, 1295 (1930).

Experimental Results

The results obtained are shown in Fig. 1, where the percentage change in the diffusion coefficient of urea has been plotted against the square root of the molar concentration of the non-electrolyte present in the gel. It is to be noted that in every case the presence of a small amount of non-electrolyte caused an increase in the diffusion velocity of urea. With continued increase in the concentration of the non-electrolyte there was further increase in the diffusion velocity of urea until a maximum value was reached. In the case of the five non-electrolytes studied this maximum value was at concentrations between 0.006 and 0.04 molar. With higher concentrations of the non-electrolytes the diffusion velocity was lowered from this maximum value and beyond concentrations ranging from 0.08 to 0.18 molar the diffusion velocity was less than the normal diffusion velocity of urea.

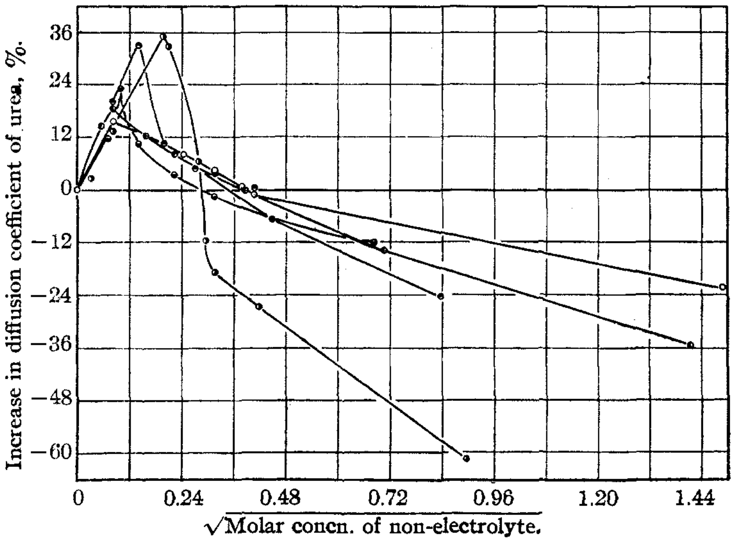

Fig. 1.—Effect of non-electrolytes upon diffusion velocity of urea in gelatin gels: ○, glycerol; ◑, sucrose; ◐, urea; ⊖, methanol; ◓, glucose.

Discussion

The similarity in the behavior of the different non-electrolytes studied eliminates the possibility of any specific action of the non-electrolyte with the gelatin. The change in the diffusion velocity of urea could be due to a change in the viscosity of the diffusion medium within the gel or to a change in hydration of the solid phase of the gel with a resulting change in radius of the pores within the gel. The results obtained would indicate that small amounts of foreign non-electrolyte decrease the hydration of the solid phase, resulting in an increase in the size of the pores within the gel. The subsequent decrease in diffusion velocity must be due to increased viscosity of the diffusion medium in the gel. The shape of the curves obtained is what might be expected when two such factors are influencing diffusion in opposite directions.

Summary

The effect of methanol, urea, glycerol, glucose and sucrose upon the diffusion velocity of urea in gelatin gels has been determined.

These non-electrolytes caused an increase in diffusion velocity at low concentrations up to a maximum at concentrations of 0.006 to 0.04 molar. At higher concentrations there was a lessening of this effect until finally there was a decrease in the velocity of diffusion of urea at concentrations greater than 0.08 to 0.18 molar.

These results have been explained by assuming that non-electrolytes influence diffusion in gels in two ways: (1) by increasing the radii of the pores within the gel due to a decrease in the hydration of the solid phase, and (2) by increasing the viscosity of the medium through which diffusion takes place.

Corvallis, Oregon Received August 30, 1933