inside the crystal. Since the Q-value of the reaction is 4·785 MeV., it appears that the efficiency of this crystal is somewhat reduced for heavily ionizing particles.

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Measurement of Activated Diffusion of Adsorbed Molecules

IN continuation of a previous study[1] on the contribution of 'surface diffusion' to the transport of adsorbed molecules within porous adsorbents, rates of adsorption of n-butane have been measured.

For this purpose, a small metal beam balance was constructed which could be operated under high vacuum conditions. The weighing was performed with movable riders manipulated by means of external controls through ground joints in the enclosing glass tube. The beam was 5 cm. long and fitted with agate knife edges. A sensitivity of $\tan\alpha = 0{\cdot}022$ per 1 mgm. was achieved. The pan carrying the adsorbent was hung on a thin glass rod 30 cm. below the balance and was surrounded by a glass tube inserted in a temperature bath. In the present investigation, an electronically controlled low-temperature thermostat[2] was used with 'dry ice' as refrigerant. Any given temperature in the range from room temperature to − 80° C. could be maintained within ± 0·1° C. for any desired period.

In order to simplify the mathematical treatment of the diffusion problem, rates of adsorption were measured at constant pressures. These were maintained by adsorbing a certain quantity of butane at a convenient temperature, say, 0° C., on an amount of silica gel 100–500 times greater than that of the adsorbent under investigation on the balance.

After proper degassing, the adsorbent was cooled to the desired temperature and the balance system then connected to the constant-pressure device. The increase in weight of the adsorbent (4–125 mgm.) was followed with time, until equilibrium was reached. At − 14° C. this occurred in about three hours, while at the lowest temperature (− 79·5° C.) experimental periods were as long as 30 hr. From a plot of w_τ/w_∞ versus time (w_τ and w_∞ are weight increases at time τ and at equilibrium), overall diffusion coefficients could be evaluated using a solution of the general differential equation of diffusion for a system of finite length and for the particular boundary conditions. The range $w_\tau/w_\infty = 0{\cdot}4$ to $0{\cdot}6$ was chosen to give representative values for the diffusion coefficient.

Rates of adsorption of n-butane in porous silica plugs were measured at various temperatures (− 14° to − 80° C.), porosities ($\varepsilon = 0{\cdot}72$ to $0{\cdot}53$) and surface coverages ($y/y_m = 0{\cdot}37$ to $6{\cdot}9$, where y_m is monolayer capacity in millimoles/gm.). The plugs (0·3 gm.) were formed by compressing Linde silica (300 m.²/gm.) into small steel cylinders, thus allowing adsorption to occur only through one plane.

In order to demonstrate the feasibility of the above method and to indicate the bearing of surface diffusion on molecular transport in porous media, some of the results obtained may be quoted. For a plug of porosity 0·53 and a surface coverage of $y/y_m = 0{\cdot}9$, the following overall diffusion coefficients were obtained: $7{\cdot}20$, $2{\cdot}33$ and $0{\cdot}64 \times 10^{-5}$ cm.²/sec. at − 14·4°, − 44·2° and − 79·5° respectively. Following Barrer's[3] calculations for the transient state of gas flow into a porous system, these coefficients are corrected for Knudsen streaming. In this way, the corresponding surface diffusion coefficients are obtained: $5{\cdot}04$, $1{\cdot}87$ and $0{\cdot}60 \times 10^{-5}$ cm.²/sec. This indicates that, under the above conditions, 70, 80 and 94 per cent of the total transport is due to the mobility of adsorbed molecules along the surface. From these diffusion coefficients an activation energy of 3,000 cal./mole results, corresponding to 47 per cent of the adsorption energy.

At the lower temperatures, diffusion coefficients vary only slightly with the porosity of the adsorbent, whereas at higher temperatures there is a considerable increase with porosity. In this range the activation energy is also somewhat greater. Diffusion coefficients depend markedly on the surface coverage. For example, at a coverage $y/y_m = 0{\cdot}37$, $\varepsilon = 0{\cdot}72$ and $t = -\,44{\cdot}5°$ C., an overall diffusion coefficient of $4{\cdot}08 \times 10^{-5}$ cm.²/sec. was obtained. This increased steadily with greater coverage and reached a maximum value of $8{\cdot}56 \times 10^{-5}$ cm.²/sec. in the multilayer region at $y/y_m = 3{\cdot}0$, whereafter it decreased.

As a whole, these results are in agreement with those obtained in experiments based on a steady-state flow method, as recently reported by Carman[4].

I wish to thank Dr. P. C. Carman, who made the permeability data necessary for the calculation of the Knudsen streaming available to me. This communication is published with the permission of the South African Council for Scientific and Industrial Research, Pretoria.

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Activity Data and the Association of Hydrogen Chloride in Concentrated Solutions

IN some experiments in which concentrated solutions of hydrochloric acid were employed it was necessary to consider the part played by associated hydrogen chloride in determining its properties. Examination of data on the activity of hydrogen chloride[1] showed that the curve relating mean activity (a) to concentration (c) was continuous throughout, although its slope increased markedly at about 2 N.

Up to 4 N the activity coefficient γ is given with reasonable accuracy by the semi-empirical relationship:

$$\log\gamma = \frac{-Ac}{1+Bc} + Dc + Ec^2 - \log(1 + 0{\cdot}036m) \quad (1)$$

c (N)	0° C.				20° C.			50° C.		
	log γ obsv.	$'c$	$10^3 \times K$	$10^2 \times K^1$	log γ obsv.	$'c$	$10^2 \times K^1$	log γ obsv.	$'c$	$10^2 \times K^1$
5	0·44	4·5	3·20	2·5	0·39	4·4	3·1	0·30	4·4	3·2
6	0·59	5·4	1·38	2·1	0·52	5·2	3·0	0·42	5·3	3·0
7	0·74	6·1	0·79	2·4	0·66	5·9	3·2	0·53	6·0	2·8
8	0·89	6·8	0·44	2·6	0·79	6·6	3·2	0·65	6·7	3·0
9	1·03	7·4	0·15	2·9	0·93	7·3	3·2	0·76	7·2	3·5
10	1·17	8·0	0·14	3·1	1·05	8·0	3·1	0·87	7·8	3·6
Mean K^1				2·6			3·1			3·2

where $c/m = a_1 - b_1m$, and A, B, D, E, a_1 and b_1 are constants that have been evaluated by Harned and Owen[2].

Above 4 N the observed values of γ are less than would be expected from the above relationship. If deviations are due to association into an ion pair or a truly associated type, the values of the concentration interpolated from the curve relating calculated log γ and c, using log $\gamma_{\text{obsv.}}$, might be assumed to be the actual concentrations of the free ions.

Fig. 1 shows the curves for log γ against c calculated from the above relationship for $c = 4 - 10\,N$ at 0°, 20° and 50° C. The experimental values of log γ were then interpolated from these curves to give values of $'c$ corresponding to the free ion concentration (see table).

Consider now the equilibrium :

$$H^+ + Cl^- = HCl$$

$$K = \frac{c - 'c}{'c^2} \cdot \frac{\gamma_{HCl}}{\gamma_{Cl^-} \cdot \gamma_{H^+}} = \frac{c - 'c}{'c^2} \cdot \frac{\gamma_{HCl}}{\gamma^2{}_{\pm HCl}}, \qquad (2)$$

where c is the total hydrogen chloride concentration.

If this association were of the normal type as understood in the case of acetic acid, then $\gamma_{HCl} \sim$ constant $= 1$ at $c = 0$. However, this assumption leads to values of K that are not constant (see table). Making the further assumption that, as for acetic acid in dilute solution, either $\gamma_{H^+} = \gamma_{Cl^-} = \gamma_{HCl} = 1$, or $\gamma_{HCl} = \gamma^2{}_{\pm HCl}$, a constant $K^1 = \frac{c - c^1}{'c^2}$ (see table) is obtained. The values of K^1 are remarkably constant and show little variation with temperature, indicating that $\Delta S_{\text{ass.HCl}} \approx 0$ and $\Delta F_{\text{ass.HCl}} = \Delta H_{\text{ass.HCl}} = 2 \cdot 1$ k.cal./mole.

According to equation (2), K/γ_{HCl} can be calculated from the data in the table ; extrapolation to $c = 0$ gives K. Theory[3] and experiment[4] demonstrate a linear relationship between log γ and c in dilute solutions. The extrapolation was therefore carried out as shown in Fig. 2 [5].

Values of K thus obtained were, within extrapolation error, independent of temperature and had a value $K_{c=0} = 0 \cdot 056$, being in reasonable agreement with the value of K^1 ; the corresponding value of $\Delta H_{\text{ass.HCl}} = 1 \cdot 7$ k.cal.

The above calculations seem to indicate the validity of the assumption that $\gamma_{HCl} = 1$ and the alternative relationships $\gamma_{Cl^-} = \gamma_{H^+} = \gamma_{HCl}$, or $\gamma^2{}_{\pm HCl} = \gamma_{HCl}$.

The figures for K and K^1 are in accord with that found for nitric acid by light absorption experiments[5], namely, $K_{c=0} = (5 \pm 1) \times 10^{-2}$. The agreement is to be expected, for these two acids have similar strengths.

Available thermochemical data[6] reveal a considerable fall in the heat of formation of solutions of hydrogen chloride at about 2 N, becoming much more marked at 5 N onwards. The data for sodium chloride and sodium hydroxide do not show a similar fall until higher concentrations are reached, indicating that at 5 N the association in solutions of these substances is relatively small. It is possible to calculate $\Delta H_{\text{ass.HCl}}$ in an approximate manner from the equations : $Na^+(5\,N) + H_2O + Cl^-(5\,N) = Na^+(5\,N) + OH^-(5\,N) + HCl(H^+,Cl^-, + HCl_{\text{ass.}} = 5\,N) + 15 \cdot 7$ k.cal., and $H_2O = H^+ + OH^- + 13 \cdot 7$ k.cal.

If there were no association of the hydrogen chloride, the heats of these reactions should be identical. The difference $\Delta H_{\text{ass.HCl}} = 2 \cdot 0$ k.cal. is in good agreement with the above.

I should like to express my thanks to Sir Eric Rideal for his help and advice. The above forms a part of a research pro-

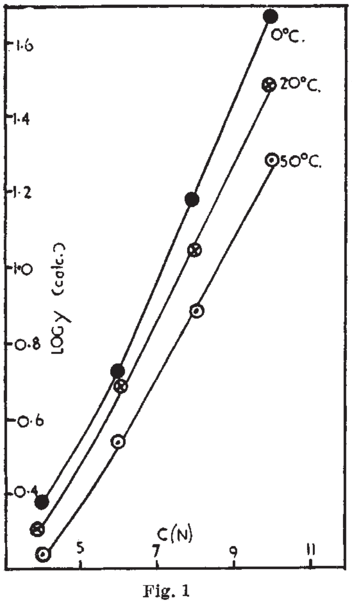

Fig. 1

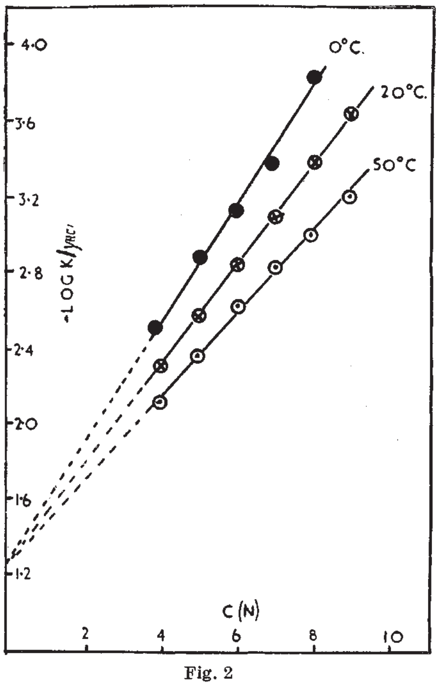

Fig. 2

Fig. 1. log $\gamma_{\text{calc.}}$ plotted against the HCl normality. ●, 0° C. ; ⊗, 20° C. ; ⊙, 50° C.

Fig. 2. $-\log K/\gamma_{HCl}$ plotted against the HCl normality. ●, 0° C. ; ⊗, 20° C. ; ⊙, 50° C.

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Reaction Kinetics of the Cytochrome System

In living wheat roots three cytochromes co-operate, the prosthetic groups of which correspond spectroscopically to the types *a* (= cytochrome oxidase), *c* and *b* of animal preparations. Succinoxidase is the main dehydrogenase system[1]. A factor *X*, characterized by a strong band at 570–575 mμ, is probably linked between succindehydrogenase and cytochrome *b* [1,2]. Studies of the time-course of oxidation, performed by means of a new automatic spectrophotometric technique[1], show a direct electron transference in the sequence succindehydrogenase ⇀ *X* ⇀ *b* ⇀ *c* ⇀ *a* ⇀ oxygen. The process of oxidation of the reduced cytochromes is a first-order reaction in accordance with the overall formula $Fe^{2+} \rightarrow Fe^{3+} + e$. The molar velocity of oxidation, calculated as $V_e = \frac{1}{\frac{1}{2}t} \cdot c$ ($\frac{1}{2}t$ is time in seconds for the half-way point of oxidation, *c* is relative molar concentration), shows very similar values for all cytochromes (see table), a fact compatible with a uniform electron transference between the reacting cytochromes, these probably being located in a fairly compact structural unit near the surface of the cells (cf. ref. 1).

At normal anion respiration and 19° C., the cytochromes are predominantly oxidized (64–84 per cent; cf. ref. 1). This means that the electron transference only amounts to a small fraction (*c.* 1/10 to 1/30) of the full capacity of a nearly reduced system (0–10 per cent oxidation). This damped activity balances the power of reduction of the succindehydrogenase system. The 'over-dimensioned' capacity of the cytochrome system corroborates earlier experiences as to the low oxygen requirement; wheat roots maintain their full anion respiration at an oxygen tension amounting to only 1/10 to 1/20 of normal aeration (cf. ref. 3).

The re-oxidation of a completely reduced cytochrome system (anaerobical conditions) agrees with $\frac{1}{2}t$ = 10–40 sec. It was found that the diffusion of the oxygen from the medium to the respiring cells is not a limiting factor, whereas the continuous delivery of electrons from succindehydrogenase has a general retarding effect. In absence of succindehydrogenase the re-oxidation would be completed in $\frac{1}{2}$–1 sec.

Relative Velocities of Electron Transference (V_e) in the Cytochrome System of Living Wheat Roots.
Percentage values in brackets. Relative concentration of *a*, 1; *c*, 2; and *b*, 3·5.

Cytochrome	*a*	*c*	*b*
Reduction (from aerobic to anaerobic)	0·090 (100)	0·032 (35)	0·011 (12)
Re-oxidation (from anaerobic to aerobic)	0·100 (100)	0·100 (100)	0·095 (95)

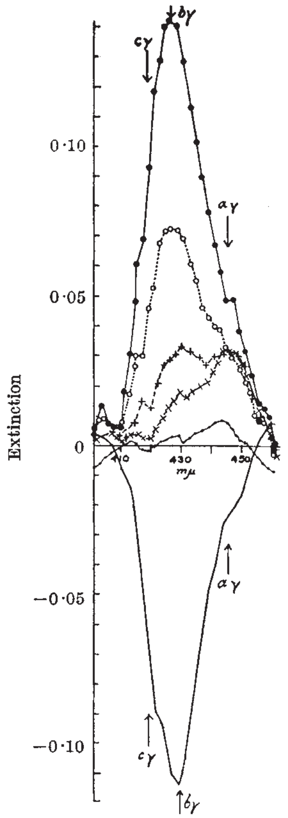

Fig. 1. Oxidation–reduction curves (ε red.–ε ox.; cf. ref. 1) of a 15-mm. thick bundle of wheat roots, exposed to increasing anaerobiosis (oxygen-free succinate) and thereafter re-oxidized. The positive curves illustrate the increasing reduction: ·— after 1 min., ×—× after 4 min., +—+ after 7 min., ○—○ after 13 min., and ●—● after 32 min. The negative curve shows the rapid re-oxidation 1 min. after shifting over to aerated solution. Absorption spectrum automatically recorded in intervals of 2 mμ (cf. ref. 1). The very rapid response of the cytochrome oxidase is clearly shown

After a rapid shift from aerated to complete anaerobiosis, the cytochrome oxidase is reduced with $\frac{1}{2}t$ = 10 sec. (approx.), or about the same as for re-oxidation. The reduction of *c* and *b*, however, is

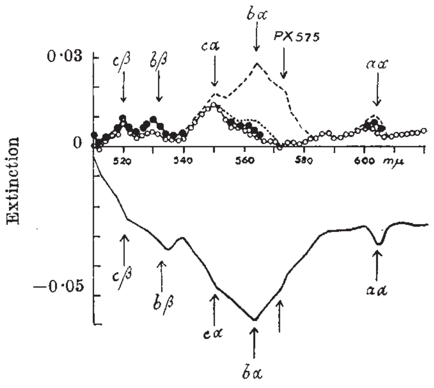

Fig. 2. As in Fig. 1, but comprising the α- and β-bands of the cytochromes. Upper curves, reduction in oxygen-free succinate: ○—○ after 1 min., ●—● after 6 min., - - - - after 16 min., and — — — after 32 min. The time order $a > c > b > PX$ 575 is clearly shown. Lower curve shows the re-oxidation in aerated solution