TABLE II

Cholinesterase activity in plasma and RBC of control and streptozotocin-treated rats

Values are averages of six rats and standard deviations

Enzyme activity*		Control rats	Test rats
Plasma	AchE	44·8 ± 7·4	57·6 ± 6·5′
	BChE	23·1 ± 4·1	32·5 ± 7·0′
RBC	AChE	452 ± 21	558 ± 28″
	BChE	22·8 ± 7·2	38·4 ± 9·8″

* Expressed as micromoles of substrate utilized/ml-hour.

AChE, acetylcholinesterase; BChE, Butyrylcholinesterase; ′p < 0·05 and ″p < 0·01—Student's '*t*' test.

zotocin were noted to last only for 48 to 72 hrs after the injection, which indicated that a different mechanism might be operating to account for elevated plasma and RBC ChE activities in the case of these rats unlike the alloxan diabetic rats. It is interesting to note that Keply[13] reported alteration in ChE activity of RBC of human subjects with protein caloric malnutrition. In order to check whether any such mechanism is operative in streptozotocin-treated rats, further studies are in progress.

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KNUDSEN DIFFUSION AND NEGATIVE ACTIVATION ENERGY OF ADSORPTION

NEGATIVE activation energy in chemisorption of gases on solids has been observed by many workers like Sastri and Ramanathan[1], Taylor and Liang[2], Kubokawa and Taylor[3], Low and Taylor[4] and by Decrue and Susz[5]. In most cases, surface heterogeneity effects have been proposed to account for this. In our case we observed also the occurrence of negative activation energy in the temperature range 31°–253° C for oxygen adsorption on copper vanadate pretreated with hydrogen at 40 mm pressure and 130° C and we propose a Knudsen diffusion model to account for this behaviour.

In 1953, Sutherland and Winfield[6] have developed a mathematical model for Knudsen diffusion for rapid gas adsorption on porous solids and in 1965, Peers[7] has shown that such a model gives rise to an Elovich rate equation in a constant volume system. However no further work has been carried out in this aspect.

The conditions for the Knudsen diffusion being the rate-controlling step (according to these authors) are:

1. Pressure should be less than 2 atm.
2. Pore radius should be < 100 Å.
3. Rapid uptake of gas.
4. Rapid establishment of equilibrium between the pore wall and the gas molecules.
5. Adsorption taking place in a constant volume system.

For such conditions, Sutherland and Winfield[6] have deduced

$$-\frac{dp}{dt} = \frac{p_0 Y}{\pi^{1/2} t} \qquad (1)$$

where,

p_0 = initial pressure,

$$Y = \frac{D_k \pi b r^2 t^{1/2}}{V D^{1/2}} \qquad (2)$$

b = No. of cylindrical pores, each of length 1,

V = Volume of system,

r = Average pore radius,

D_k = Knudsen diffusion constant

$$\approx 1\cdot 33\, r \left(\frac{2RT}{\pi M}\right)^{1/2}$$

$$D_k/D^{1/2} = 1\cdot 94\, k_e^{1/2} (RT)^{3/4} (\pi M)^{-1/4} \qquad (3)$$

k_e = Intrinsic adsorption coeff.

Now,

$$\frac{d \ln K_p}{dT} = \frac{\Delta H}{RT^2}$$

Let $\Delta H = -Q$ where Q is the heat of adsorption (it is negative since the adsorption is exothermic).

So,

$$\frac{d \ln k_e}{dT} = \frac{-Q}{RT^2}$$

or,

$$k_e = A \cdot e^{Q/RT},$$

where A = const.

So,

$$k_e^{1/2} = A \cdot e^{Q/2RT} \quad (4)$$

By combining eqns. (1)-(4), we get,

$$-\frac{dp}{dt} = K \cdot \frac{T^{3/4} e^{Q/2RT}}{t^{1/2}} \quad (5)$$

This equation explains the occurrence of −ve activation energy, because at a certain range of temperature, the variation of $T^{3/4}$ is negligible in comparison with the variation of the exponential term; and as T increases, $-dp/dt$ decreases. Hence the rate has a −ve temp. coeff. and appears to have a −ve activation energy of magnitude Q/2. The following calculation will show the predominance of the $e^{Q/2RT}$ term over $T^{3/4}$ term.

For constant t and K, and Q = 4 kcal/mole:

$T^{\circ K}$	$T^{3/4}$	$e^{Q/2RT}$	$-dp/dt$ (For $t = 1, K = 1$)	
300	70·5	30·5	2000	$-dp/dt$ decreases
400	88·9	12	1068	as the temp.
500	102·5	7·6	820	increases.

In our case[8], all the above conditions have been observed:

1. Initial pressure for adsorption is 12·32 cm.
2. Surface area of the sample is only 11 m²/g, hence pore radius should be small.
3. Rapid equilibrium—it is established within 2-3 hrs.
4. Heat of adsorption is very small, only 1-2 kcal/mole.
5. Expt. has been conducted in a constant volume apparatus.

Figure 1 gives the plot of $-dp/dt$ vs. $1/t^{1/2}$ for our sample at 98° C, 167° C, 253° C.

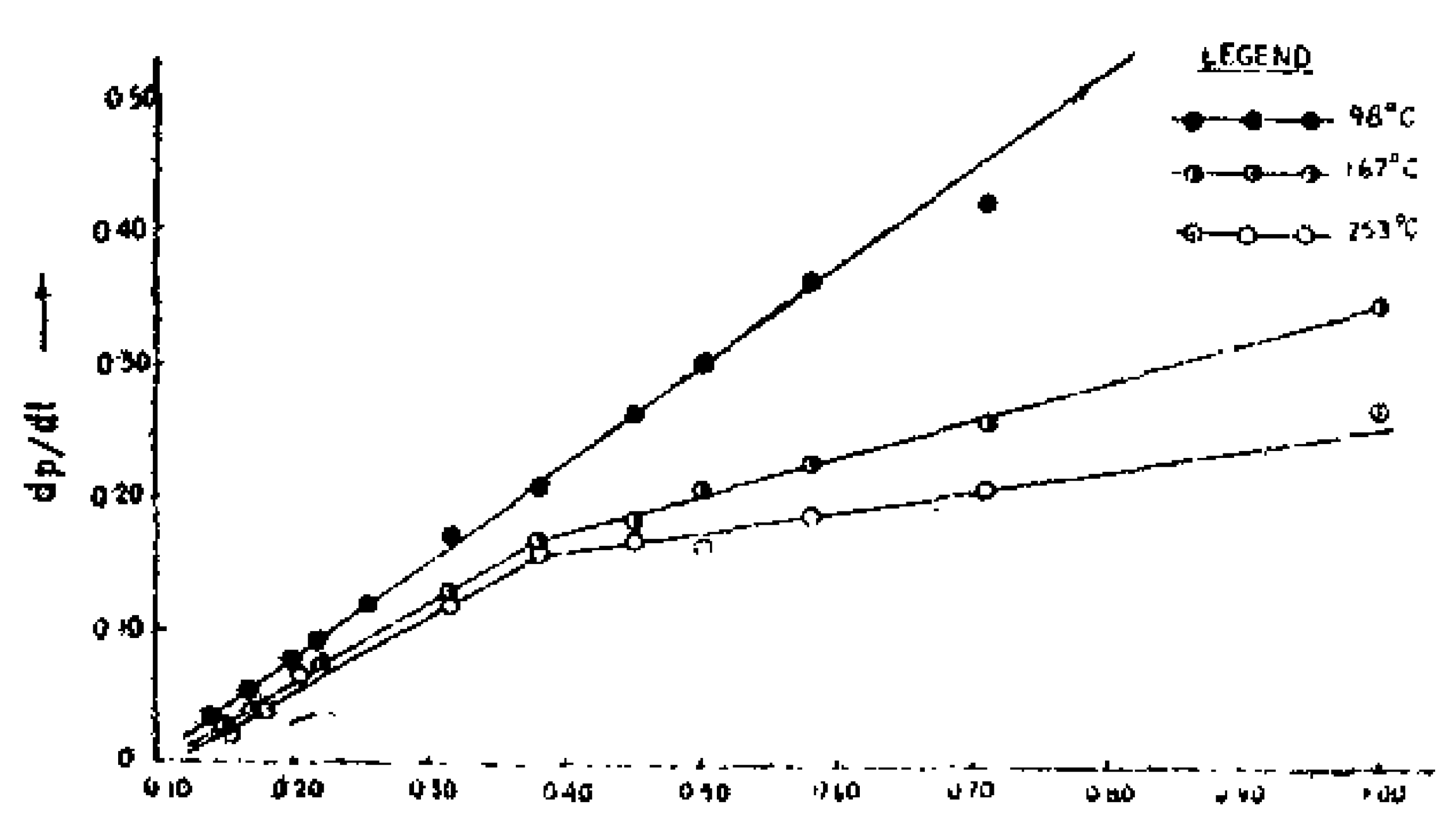

Fig. 1

In view of the graphical evaluation of $-dp/dt$ values, the agreement can be described as fair. As is expected, the slope of the plots (const. × $e^{Q/2RT}$) increases as temperature decreases. But at higher temperatures the plots have one break, the slope of the 2nd stage being smaller than that of the first. Moreover, the break in the plots appears in the region where the corresponding Elovich plots[8] show discontinuities. The change in slope is evidently due to change in Q, other factors remaining constant. The heat of adsorption in the 2nd stage (Q_2) is not only greater than Q_1 (slope is higher) but also $Q_2 \gg RT$ and the change in T has little influence in changing the slope in the 2nd stage at different temperatures.

Hence, this equation[5] may be used to test whether the Knudsen diffusion is rate-controlling or not, and if the pore radius of the sample is known, this may be used as an indirect method for the evaluation of heat of adsorption, Q, from the slope of $-dp/dt$ vs. $1/t^{1/2}$ plots.

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CYCLIC CHANGES IN PERIPHERAL PLASMA PROGESTERONE IN BUFFALO HEIFERS

In cow with silent heat Dobrowolski and coworkers[1] observed significantly lower levels of blood progesterone at all stages of the oestrous cycle. No such study has been reported in buffalo. The investigation was undertaken to determine the peripheral plasma progesterone levels in buffalo heifers during the various phases of oestrous cycle as incidence of silent heat in this species is quite high during summer[2-4].

The study was carried out during June-July, 1976 with 9 Murrah buffalo heifers 3-4 years of age and average weight 325 ± 25 kg. The animals were checked or heat twice daily at 8 A.M. and 4 P.M. using vasectomized bull. Jugular venous blood was collected in heparinised tubes, which were immediately centrifuged and plasma stored at − 15° C. Progesterone was determined by the competitive protein binding assay as described by Murphy[5]. The efficiency value of the method was 82%.

All the buffalo heifers were in 'silent' heat with no apparent symptoms of oestrus. On rectal palpation of the genitalia, mucus discharge invariably came out. Corpus luteum (CL) could only be detected in 6 animals at 10th and 15th day of the service; 5 heifers