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**Chemistry.** — "*Catalysis. (Part VI). Temperature coefficients of heterogeneous reactions.*" By NIL RATAN DHAR. (Communicated by Prof. ERNST COHEN).

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In foregoing papers<sup>1)</sup>, the temperature coefficients of catalysed and uncatalysed reactions in a homogeneous medium have been studied. It has been shown that a positive catalyst produces a lowering in the value of the temperature coefficient of the reaction, the reverse is the case with a negative catalyst. It was also proved that the higher the order of a reaction, the smaller is the temperature coefficient.

The object of this paper is to discuss the experimental researches and find, if possible, similar relations in the domain of heterogeneous reactions.

In order to make clear the question of the temperature coefficients of heterogeneous reactions, it is necessary to indicate briefly their characteristics.

In a reaction between a liquid and a solid, according to the diffusion theory of reaction velocity a thin layer of liquid adhering to the solid remains unaffected by stirring and the reaction is maintained by the transport of dissolved substances across this layer of diffusion. Moreover, it is assumed that at the boundary surface between two phases, the velocity of the chemical reaction is extremely high. When the diffusion is sufficiently slow compared with the other stages of the reaction the velocity of the whole reaction will be determined by the rate of diffusion alone.

This theory was first proposed by NOYES and WHITNEY<sup>2)</sup> for some special cases, but its general applicability to various types of heterogeneous reactions was indicated by NERNST and BRUNNER<sup>3)</sup>, and has since been accepted by several investigators as giving the best explanation of facts in heterogeneous systems.

On the other hand, the general applicability of the diffusion theory

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<sup>1)</sup> Jour. chem. soc. 1917, **111**, 707; Annales de chimie, 1919.

<sup>2)</sup> Zeit. Phys. Chem. 1897, **23**, 689.

<sup>3)</sup> ibid. 1904, **47**, 52, 56.

was contested by ERICSON-AUREN and PALMAER <sup>1)</sup>, TAMMANN <sup>2)</sup>, MARC <sup>3)</sup>, SENTER <sup>4)</sup>, WILDERMANN <sup>5)</sup> etc.

Since, according to the diffusion theory, in chemical reactions which occur merely at the boundary between two phases, the phenomenon is essentially one of diffusion, it is useless to try and determine the order of reactions from the rate at which they proceed; this method of argument is only applicable, according to kinetic considerations to the probability of collisions in homogeneous systems and loses its significance when applied to heterogeneous systems. Moreover, if the velocity is controlled by a diffusion process, one will get a coefficient of the velocity similar to that for a uni-molecular reaction and the coefficient will be independent of the actual order of the more rapid chemical reaction, which accompanies the process. Consequently it is impossible to establish a relation between the order of a reaction and its temperature coefficient in heterogeneous systems.

(a) *Temperature coefficients of uncatalysed reactions.*

Another consequence of the diffusion theory is that the temperature coefficient for an elevation of 10° should be of the order 1.3 i.e. of the same order of magnitude as the temperature coefficient of diffusion (compare OHÖLM <sup>6)</sup>). We shall now see if experimental results confirm this inference from the diffusion theory. The following is the summary of results. (See table 1 next page).

These results support the diffusion theory of reaction velocity in heterogeneous medium. In this connection it is interesting to observe that elevation of temperature up to a certain limit is found to be without influence on the decomposition of some alcoholic compounds by sodium amalgam (LÖWENHERZ, Zeit. Phys. Chem. 1900, **32**, 480; 1902, **40**, 400) and on the velocity of dissolution of Casein in alkalies (ROBERTSON, Jour. Phys. chem. 1910, **14**, 377).

On the other hand, the following summary of results shows that the conclusion as to the effect of temperature, is not corroborated in these cases. (See table 2 next page).

It has already been pointed out that velocities of diffusion only determine the rate of reaction when no other processes interfere and specially when no slow processes, taking place in the homogen-

1) Zeit. Phys. Chem. 1906, **56**, 689.

2) ibid. 1910, **69**, 257.

3) ibid. 1908, **61**, 385; 1909, **67**, 470.

4) Jour. Phys. Chem. 1905, **9**, 311.

5) Zeit. Phys. Chem. 1909, **66**, 445.

6) ibid. 1905, **50**, 309; 1910, **70**, 385.

TABLE 1.

Reaction.	Reference.	$\frac{k_t + 10}{k_t}$
(1) $\text{CaCO}_3 + \text{HCl}$	SPRING (Zeit. Phys. Chem., 1887, 1, 209)	1.5
(2) Metals + acids	VELEY (Journ. chem. soc. 1889, 55, 361)	1.21
(3) "	ERICSON-AUREN (Zeit. anorg. Chem. 1901, 27, 209)	1.1
(4) Solution of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in water	BRUNER and TOLLOCZKO (Zeit. Phys. Chem. 1900, 35, 283)	1.5
(5) Various reactions	BRUNNER (Zeit. Phys. Chem. 1904, 47, 56)	1.3
(6) Evaporation of water	JABLZYNSKI (Jour. chim. Phys. 1912, 10, 241)	1.1
(7) Cu and $\text{NH}_4\text{OH}$	YAMASAKI (7 <sup>th</sup> Inter. Cong. App. Chem. 1909, Sec. X, 172)	1.15
(8) $\text{O}_2$ and pyrogallates $\text{O}_2$ and haemoglobin CO and "	BOSELLI (J. Chim. Phys. 1911, 9, 689; 1912, 10, 1)	1.1
(9) Halogens and metals Chromic acid and metals Ferric salts and metals	VAN NAME and his associates (Amer. J. Science 1910 [4], 237; 1916 [4], 42, 301; 1917 [4] 43, 449)	1.28
(10) Quinol and $\text{O}_2$	EULER and BOLIN (Zeit. Physiol. Chem. 1908, 57, 80)	1.2
(11) Dissolution of various salts in water	WAGNER (Zeit. Phys. Chem. 1910, 71, 401)	about 1.2
(12) Dissolution of $\text{CO}_2$ and $\text{O}_2$ in water	CARLSON (Medd. K. Nobel Inst. bd 2, No. 5, 1910).	1.4
(13) Mg and HCl	BONSDORFF (ibid bd. 3, No. 8, 1915)	1.44

TABLE 2.

Reaction.	Reference.	$\frac{k_t + 10}{k_t}$
(1) Dissolution of benzoic acid in water	BRUNER and TOLLOCZKO (loc. cit.) WILDERMANN (loc. cit.)	1.8
(2) Ni and CO	MITTASCH (Zeit. Phys. Chem. 1902, 40, 1)	1.53
(3) Development of photographic plates	SHEPPARD and MEES (Proc. Roy. Soc. 1905, 76, 217)	2.
(4) Precipitation of AgCl, AgBr etc.	JABLZYNSKI (Zeit. Phys. Chem. 1913, 82, 115)	2
(5) Slow oxidation of S	BODENSTEIN and KARO (ibid. 1911, 75, 30)	1.87
(6) $\text{H}_2$ and $\text{KMnO}_4$ CO and $\text{KMnO}_4$	JUST and KAUKO (ibid. 1911, 76, 601; 1913, 82, 71)	2.
(7) Velocity of absorption reversal of (a) HgS (b) S	FREUNDLICH and associates (ibid. 1913, 85, 660; 1915, 89, 147)	(a) 4 (b) 5
(8) Ferrous salts and oxygen	MC. BAIN (Journ. Phys. Chem. 1901, 5, 623) BOSELLI (loc. cit.)	2.2

eous phase is connected with the progress of the reaction. It seems probable, that in the examples of reactions cited in Table 2, the changes concerned are *real* chemical reactions rather than diffusion processes. For these reactions it would be interesting to find out a relation between their orders and their temperature coefficients, but unfortunately no experimental work in this direction is available.

(b) *Temperature coefficients of catalysed reactions.*

We shall now consider the temperature coefficients of reactions catalysed heterogeneously. The following is the summary of important reactions investigated up till now:

TABLE 3

Reaction.	Reference.	$\frac{k_t + 10}{k_t}$
(1) Decomposition of $H_2O_2$ by catalase (blood)	SENER, Zeit. Phys. Chem. 1903, 44, 257	1.7
(2) Decomposition of $H_2O_2$ by colloidal Au, Pt, Ir etc.	BREDIG and his pupils, <i>ibid</i> 1899, 31, 258, 320; 1901, 37, 1, 323; 1901, 38, 122; 1909, 66, 175	1.6
(3) Decomposition of $H_2O_2$ by colloidal Ag	MC. INTOSH, Jour. Phys. Chem. 1902, 6, 15	5
(4) Decomposition of $H_2O_2$ by colloidal $MnO_2$	MARK. DISSERT. Heidelberg, 1907	2
(5) Hydrogenation in presence of colloidal Pd	ZALKIND and PITCHTSCHIKOFF, J. Russ. Phys. Chem. Soc. 1914, 46, 1527	1.75
(6) Oxydation of $NaH_2PO_2$ by colloidal Pd or Pd black	SIEVERTS and PETERS, Zeit. Phys. Chem. 1916, 91, 199	2
(7) Reduction of methylene blue by $HCOOH$ in presence of colloidal metals	BREDIG and SOMMER, <i>ibid</i> 1910, 70, 34	2
(8) Decomposition of (a) $HCOOH$ and (b) $HCOONa$ in presence of colloidal Rh	BLACKADDER, <i>ibid</i> 1913, 81, 385	(a) 2 (b) 2.5
(9) Oxydation of phenyl thiocarbamide in presence of blood charcoal	FREUNDLICH and BJERCKE, <i>ibid</i> 1916, 91, 1	2.3
(10) Oxydation of oxalic acid in presence of blood charcoal	WARBURG, Pflüg. Arch. 1914, 155, 547	2.1
(11) Enzyme actions	Generally higher than	2

The following table shows the summary of results obtained with catalysts in the solid state:

TABLE 4.

Reaction.	Reference.	$\frac{k_t + 10}{k_t}$
(1) Decomposition of ozone	PERMAN and GREAVES (Proc. Roy. Soc 1908, 80 A, 353)	about 1.2
(2) $\text{SO}_2 + \text{O} \rightarrow \text{SO}_3$	BODENSTEIN and his pupils (Zeit. Phys. Chem. 1903, 46, 725; 1905, 53, 166; 1907, 60, 1, 46; 1911, 75, 30; 1912, 80, 148; Zeit. Elektrochem. 1905, 11, 373; Festschrift W. NERNST, 1912, p. 99.	1.36
(3) $\text{CO} + \text{O} \rightarrow \text{CO}_2$		1.40
(4) $\text{SO}_3 \rightarrow \text{SO}_2 + \text{O}$		1.57
(5) $\text{NH}_3 \rightarrow \text{N} + 3\text{H}$		1.10
(6) $\text{H}_2 - \text{O} \rightarrow \text{H}_2\text{O}$		1.18
(7) Decomposition of $\text{H}_2\text{O}_2$	BREDIGAND TELETOFF (Zeit. Elektrochem 1906, 12, 581)	1.28
(8) $\text{Cr}^{++} + \text{H} \cdot \rightarrow \text{Cr}^{+++} + \text{H}$	JABLZYNSKI (Zeit. Phys. Chem. 1908, 64, 748)	1.29
(9) $\text{Ti}^{+++} + \text{H} \cdot \rightarrow \text{Ti}^{++++} + \text{H}$	DENHAM (ibid 1910, 72, 641)	1.29

It will be seen at once on glancing at the two foregoing tables that in the reactions catalysed by solids (with the exception of blood charcoal) the temperature coefficient is about 1.3 i.e. of the same order as that for diffusion; whilst in the case of reactions catalysed by colloidal metals and enzymes the temperature coefficient is about 2 i.e. of the same order as that of an ordinary chemical reaction in homogeneous medium. How is this difference to be explained? With catalysts, which cause reaction between the substances in question to take place with practically infinite velocity, the actual rate of reaction will be determined solely by the velocity with which the reacting substances diffuse to the surface of the catalyst; whether such a catalyst exists, must of course be determined separately for every case.

Adsorption is now considered to be an exceedingly rapid process. If the reacting substances were brought to the surface of the catalyst by capillary forces, the temperature coefficient would correspond to that of the slower process, namely, the chemical change involved. If, on the other hand, the reacting substances are brought to the surface by the slow process of diffusion, then the measured velocity would be that of a diffusion process and the temperature coefficient would be of the order of 1.3, which we have seen in the case when solid catalysts are used. To account for the high temperature coefficient in the case of reactions catalysed by colloidal substances and enzymes, one might suppose that the Brownian movement of these particles acted as very efficient stirring in such a way that the diffusion layer was removed as fast as it was formed, with the

result that the homogeneous chemical reaction in the adsorbed layer is the real process of which we determine the temperature coefficient.

Now it is interesting to observe that BREDIG and TELETOFF (*Zeit. Elektrochem.* 1906, **12**, 583) have calculated the thickness of the diffusion layer from the NERNST diffusion expression (*Zeit. Phys. Chem.* 1888, **2**, 634), utilising the data obtained from the decomposition of hydrogen peroxide in presence of colloidal platinum and found the thickness to be 0.05 mm. i.e. of the same order as BRUNNER found in the case of the dissolution of benzoic acid in water. This seems to show that in spite of the Brownian movement the diffusion layer remains unchanged. If this is true, the above explanation of the high temperature coefficient in the case of colloids and enzymes breaks down. Moreover, on this point of view, the high values of the temperature coefficient obtained in the oxidations of oxalic acid and phenylthiocarbamide in presence of the solid catalyst blood-charcoal, remain entirely unexplained.

Looking at the whole problem, it seems probable that in some cases the slow chemical change affects the velocity of the total reaction, whilst in other cases, diffusion plays the most important role and it is desirable to investigate fully the kinetics of each individual case.

Certainly much light would be thrown on the whole question if we can study the kinetics and temperature coefficients of one and the same reaction without any catalyst and in presence of both homogeneous and heterogeneous catalysts. The velocity of decomposition of hydrogen peroxide, for example, may be investigated at various temperatures (1) without any catalyst and (2) in presence of iodides or any other substance soluble in water (compare BREDIG and WALTON, *Zeit. Phys. Chem.* 1904, **47**, 185) and (3) in presence of colloidal metals,  $MnO_2$ , charcoal, solid metals etc.

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