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XXXI. *General Curves for the Velocity of Complete Homogeneous Reactions between Two Substances at Constant Volume.* By GEORGE W. TODD, D.Sc.(Birm.), B.A. (Camb.)*.

[Plate IX.]

WHEN m molecules of a substance A react with n molecules of a substance B to give one or more resultants, there being no back reaction, the velocity of the reaction is given by

$$\frac{dx}{dt} = k \cdot C_A^m \cdot C_B^n,$$

where x is the change in the concentration C in time t and k is the velocity constant. If k is known, the changes in concentration for various initial concentrations of the reacting substances can be worked out by integrating the above equation, but the integration often absorbs valuable time. By choosing suitable quantities it is possible to plot curves which will apply generally to all reactions of a similar type. The author has worked out some of these, and puts them on record hoping that they may save much time and labour.

Bi-molecular Reaction.

If the reaction is bi-molecular of the type $A + B \rightarrow 1$ or more resultants, the reaction velocity is given by

$$\frac{dx}{dt} = k(a-x)(b-x),$$

where a, b are the initial concentrations of A, B respectively. The equation may be written

$$\frac{dx}{dt} = ka^2 \left(1 - \frac{x}{a}\right) \left(\frac{b}{a} - \frac{x}{a}\right).$$

Putting $\frac{x}{a} = X$, where X = fraction changed,

$$\frac{dX}{dt} = K(1-X)(p-X),$$

where $K = ka$ and $p = \frac{b}{a}$.

Take (i.) initial concentrations equal, i. e. $a = b$ or $p = 1$, then

$$Kt = \int_0^X \frac{dX}{(1-X)^2} = \frac{X}{1-X}.$$

* Communicated by the Author.

The maximum value of $X=1$. Giving X values up to 1 we get

X	0	·1	·2	·3	·4	·5	·6	·7	·8	·9	1·0
Kt.....	0	·111	·250	·428	·666	1·00	1·50	2·33	4·00	9·00	∞

These are plotted on fig. 1 ($p=1$), and the curve will apply to any bi-molecular reaction in which the initial concentrations are equal.

Take (ii.) one of the substances in excess, say $\frac{b}{a}=p$, where $p>1$. Then we have

$$Kt = \frac{1}{1-p} \left\{ \log_e \frac{p(1-X)}{p-X} \right\}.$$

$p=1·5.$

X ...	0	·1	·2	·3	·4	·5	·6	·7	·8	·9	·95	1·0
Kt ...	0	·071	·159	·267	·401	·572	·808	1·15	1·69	2·77	8·66	∞

$p=2.$

X ...	0	·1	·2	·3	·4	·5	·6	·7	·8	·9	·95	1·0
Kt ...	0	·054	·117	·194	·288	·405	·559	·771	1·10	1·70	2·32	∞

$p=3.$

X ...	0	·1	·2	·3	·4	·5	·6	·7	·8	·9	·94	·97	1·0
Kt ...	0	·036	·077	·126	·183	·255	·344	·386	·549	·851	1·09	1·42	∞

These are plotted on fig. 1 (Pl. IX.), and the curves will apply to any bi-molecular reaction of the type $A+B \rightarrow 1$ or more resultants.

Ter-molecular Reaction.

Let the reaction be represented by $2A+B \rightarrow 1$ or more resultants, then the velocity of reaction is given by

$$\begin{aligned} \frac{dx}{dt} &= k(a-x)^2(b-x) \\ &= ka^3 \left(1 - \frac{x}{a}\right)^2 \left(\frac{b}{a} - \frac{x}{a}\right). \end{aligned}$$

Bringing to the same notation as before gives

$$Kt = \int_0^X \frac{dX}{(1-X)^2(p-X)},$$

where $K=ka^2$.

Take (i.) equal initial concentrations, *i. e.* $p=1$, then

$$Kt = \int_0^X \frac{dX}{(1-X)^3} = \frac{1}{2} \frac{(2-X)X}{(1-X)^2},$$

which gives

X	0	·1	·2	·3	·4	·5	·6	·7	·8	·9	1·0
Kt.....	0	·117	·281	·520	·889	1·50	2·63	5·06	12·0	50	∞

These are plotted on figs. 2 and 3, and the curve applies to any ter-molecular reaction in which the initial concentrations are equal.

Take (ii.) B in excess, *i. e.* $p = \frac{b}{a} > 1$. We have

$$Kt = \int_0^x \frac{dX}{(1-X)^2(p-X)} = \frac{1}{(1-p)^2} \left\{ \log_e \frac{p(1-X)}{p-X} - \frac{X(1-p)}{1-X} \right\},$$

$p=1.5$.

X	0	.1	.2	.3	.4	.5	.6	.7	.8	.9	1.0
Kt	0	.077	.180	.323	.440	.548	1.38	2.37	4.62	12.48	∞

$p=2$.

X	0	.1	.2	.3	.4	.5	.6	.7	.8	.9	1.0
Kt	0	.046	.133	.234	.379	.595	.941	1.56	2.90	7.5	∞

$p=3$.

X	0	.1	.2	.3	.4	.5	.6	.7	.8	.9	1.0
Kt	0	.038	.086	.151	.247	.373	.577	.932	1.68	4.01	∞

$p=4$.

X	0	.1	.2	.3	.4	.5	.6	.7	.8	.9	1.0
Kt	0	.028	.064	.111	.177	.274	.416	.665	1.07	2.7	∞

These figures and the graphs plotted from them (fig. 2) will apply to any ter-molecular reaction of the type $2A + B \rightarrow 1$ or more resultants, B being in excess.

Take (iii.) A in excess, and let $\frac{a}{b} = p > 1$, then we have

$$Kt = \int_0^x \frac{dX}{(p-X)^2(1-X)} = \frac{1}{(p-1)^2} \left\{ \log_e \frac{p-X}{p(1-X)} - \frac{X(p-1)}{p(p-X)} \right\},$$

where $K = kb^2$.

$p=1\frac{1}{2}$.

X	0	.4	.7	.8	.9	1.0
Kt	0	.576	2.05	3.69	8.24	∞

$p=1\frac{3}{2}$.

X	0	.1	.2	.5	.7	.8	.9	.94	1.0
Kt	0	.050	.114	.482	1.13	1.85	3.54	6.02	∞

$p=2$.

X	0	1	.2	.3	.4	.5	.7	.9	.95	.97	1.0
Kt	0	.027	.062	.110	.162	.239	.503	1.29	1.87	2.37	∞

$p=3$.

X	0	.1	.5	.7	.9	.95	.98	1.0
Kt	0	.012	.093	.224	.531	.575	.797	∞

These figures and the corresponding graphs (fig. 3) apply to any ter-molecular reaction of the type $2A + B \rightarrow 1$ or more resultants, A being in excess.

Quadri-molecular Reaction.

Let the reaction be of the type $3A + B \rightarrow 1$ or more resultants, and let the initial concentrations be equal. The general equation is

$$\frac{dx}{dt} = (a-x)^3(b-x)$$

$$= ka^4 \left(1 - \frac{x}{a}\right)^3 \left(\frac{b}{a} - \frac{x}{a}\right),$$

when $\frac{b}{a} = 1$

$$Kt = \int_0^x \frac{dX}{(1-X)^4} = \frac{1}{3} \left\{ \frac{1}{(1-X)^3} - 1 \right\},$$

and $K = ka^3$.

X.....	0	·1	·2	·3	·4	·5	·6	·65	·7	1·0
Kt	0	·123	·32	·64	1·21	2·33	4·87	7·43	12·0	∞

Now take B in excess, putting $\frac{b}{a} = p > 1$. The equation becomes

$$Kt = \int_0^x \frac{dX}{(1-X)^3(p-X)}$$

$$= -A \log_e(1-X) + B \frac{X}{1-X} + \frac{C}{2} \left\{ \frac{1}{(1-X)^2} - 1 \right\} + D \log_e \frac{p}{p-X},$$

where A, B, C, D are constants depending on the value of p .

$p=2$. Then $A=1$. $B=-1$. $C=1$. $D=-1$.

X	0	·2	·4	·6	·7	·8	1·0
Kt	0	·149	·501	1·68	3·49	9·09	∞

$p=3$. Then $A=\frac{1}{8}$. $B=-\frac{1}{4}$. $C=\frac{1}{2}$. $D=-\frac{1}{8}$.

X	0	·3	·5	·7	·8	·9	1·0
Kt	0	·184	·564	2·06	5·16	22·7	∞

$p=6$. Then $A=\frac{1}{125}$. $B=-\frac{1}{25}$. $C=\frac{1}{5}$. $D=-\frac{1}{125}$.

X	0	·5	·7	·8	·9	1·0
Kt	0	·265	·925	2·25	9·52	∞

These figures give the graphs (fig. 4) for a quadri-molecular reaction of the type $3A + B \rightarrow$, the substance B being in excess.

Now let the substance A be in excess, so that $\frac{a}{b}=p>1$. We have

$$Kt = \int_0^x \frac{dX}{(p-X)^3(1-X)},$$

where $K=kb^3$.

The solution is

$$Kt = -A \log_e \frac{p-X}{p} + B \frac{X}{p(p-X)} + \frac{C}{2} \left\{ \frac{1}{(p-X)^2} - \frac{1}{p^2} \right\} - D \log_e (1-X),$$

A, B, C, D being constants depending on p .

$p=1\frac{1}{2}$. Then $A=-64$. $B=-16$. $C=-4$. $D=64$.

X	0	·2	·4	·6	·7	·8	1·0
Kt	0	·15	·47	1·51	3·01	11·49	∞

$p=1\frac{1}{2}$. Then $A=-8$. $B=-4$. $C=-2$. $D=8$.

X	0	·2	·5	·6	·7	·8	·9	1·0
Kt	0	·082	·411	·602	1·15	2·15	4·76	∞

$p=2$. Then $A=-1$. $B=-1$. $C=-1$. $D=1$.

X	0	·3	·6	·8	·9	·95	·97	1·0
Kt	0	·065	·216	·575	1·01	1·58	2·02	∞

The graphs for these are shown in fig. 5.

There is yet the quadri-molecular reaction of the type $2A+2B \rightarrow 1$ or more resultants. In this case we have

$$Kt = \int_0^x \frac{dX}{(1-X)^2(p-X)^2},$$

where $K=ka^3$ and $p=\frac{b}{a}>1$.

The solution is

$$Kt = \frac{2}{(p-1)^3} \log_e \frac{p(1-X)}{p-X} + \frac{1}{(p-1)^2} \left\{ \frac{p+1-2X}{(1-X)(p-X)} - \frac{p+1}{p} \right\}.$$

$p=1\frac{1}{2}$.

X	0	·2	·4	·6	·7	·8	1·0
Kt	0	·21	·70	2·2	4·7	11·7	∞

$p=2$.

X	0	·1	·3	·5	·75	·85	·9	1·0
Kt	0	·03	·129	·36	1·465	3·33	6·00	∞

$p=3$.

X	0	·5	·8	·9	·95	1·0
Kt	0	·141	·707	1·80	4·14	∞

The general curves for this type of quadri-molecular reaction are shown in fig. 6.

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Application of the Curves.

(i.) To find the velocity coefficient k .

When the order of the reaction and the initial concentrations are known we have only to measure the fraction (X) changed in a given time t in order to find Kt from the curve and therefore k .

(ii.) To find the fraction (X) changed in a given time t .

This requires a knowledge of k , the order of the reaction, and the initial concentrations. Then X for a given t can be read straight from the curve.

(iii.) To find the Order of a reaction.

Two or more determinations of X and t are needed together with a knowledge of the initial concentrations. The particular curve on which the points (X, t) best lie, determines the order of the reaction.

London,
December 1917.

XXXII. *On the Coefficients of Potential of Two Conducting Spheres.* By Prof. A. ANDERSON *.

IT may be of interest to show how the coefficients of potential of two conducting spheres may be obtained directly without a previous determination of the coefficients of capacity and induction, and without making use of electric images. For this purpose the following elementary proposition, which is easily seen to be true, may be used.

If a conducting sphere whose radius is a have a charge E , and if other charged bodies be brought into the field, the potential V of the charge E at an external point P whose distance from the centre of the sphere is r will be given by the equation

$$rV = E + a(U - U'),$$

where U is the potential at the centre of the sphere of the introduced charges, and U' their potential at P' , the inverse point of P in the sphere.

Let A and B be the centres of two spheres whose radii are a and b , the distance AB being c . Let I_1 be the inverse point of A in the sphere B , I_2 the inverse of I_1 in A , I_3 the inverse of I_2 in B , and so on. Also, let J_1 be the inverse of B in the sphere A , J_2 the inverse of J_1 in B , J_3 the inverse of J_2 in A , and so on.

Let U be the potential of the sphere A at B , U_1 , U_2 , U_3 , &c. its potentials at I_1 , I_2 , I_3 , &c., and U'_1 , U'_2 , U'_3 , &c. its potentials at J_1 , J_2 , J_3 , &c. Also, let V be the potential of the sphere B at A , V_1 , V_2 , V_3 , &c. its potentials at I_1 , I_2 , I_3 ,

* Communicated by the Author.