Dependence of the Exchange Reaction Rate in Catalyst Bed upon the Rate of Feed Gases and the Length of the Bed

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In a recent paper¹⁾ we published a preliminary report of this article. In the present paper other series of experiments concerning chromic oxide catalyst are included and the reexamination of the relation under consideration is made.

Many papers concerning the kinetics of gaseous reactions in flow systems have appeared since the time of Bodenstein²⁾. A brief summary of these papers is made by Harris³⁾. In addition to these kinetic studies of chemical reactions, transport phenomena occurring in the flow systems have been treated from an engineering standpoint. Colburn and Chilton⁴⁾ discussed the mass- and heat-transfer phenomena at the gas-liquid

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1) S. Sakata and N. Morita, *Chem, Eng.* (*Japan*), **19**, 64 (1955).

2) M. Bodenstein and K. Wolgast, *Z. physik. Chem.*, **61**, 422 (1908).

3) G.M. Harris, *J. Phys. & Colloid Chem.*, **51**, 505 (1947).

4) A.P. Colburn, *Ind. Eng. Chem.*, **22**, 967 (1930); **23**, 910 (1931); T.H. Chilton and A.P. Colburn, ibid., **23**, 913 (1931); A.P. Colburn and W.J. King, ibid., **23**, 919 (1931); T.H. Chilton and A.P. Colburn, ibid., **26**, 1183 (1934); **27**, 255 (1935).

and the gas-solid boundaries, and introduced the concept of the height of a transfer unit, H. T. U. Hurt[5] applied this concept to catalytic reaction and introduced concepts of the height of a reaction unit, H. R. U., and the height of a catalytic unit, H. C. U. For an unpoisoned catalyst surface and for reaction with no volume change, the relation: H. R. U. = H. T. U. + H. C. U., is established. H. T. U. is independent of the nature of catalyst and is slightly influenced by the change of temperature and pressure; it can be calculated by the condition of gas flow. The method of the calculation of this quantity, or the film resistance, and the degree of contribution to H. R. U., or the over-all resistance, have been considered by Hougen[6], and the minimizing methods of film resistance due to transfer of mass have been indicated.

Contrary to the general complexity of kinetics of reactions conducted in flow systems, exchange reaction has very simple properties even when the reaction is conducted in a flow system. The most prominent property of exchange reaction is that during the course of the reaction the chemical concentrations of all components of the system do not change and, therefore, the reaction rate is independent of the progress of the reaction and can be defined only by the mechanism of the reaction. Consider an *exchange reaction*:

$$AX+BX' \longrightarrow AX'+BX, \qquad (1)$$

where X and X' are the same chemical species (atom or atomic group) and differ only in the fact that X is originally combined with a chemical species A, and X' is combined with another species B. Assume that for the detection of this exchange reaction, we used, as usual, an isotope of X, i. e. X*, then the *isotopic exchange reaction*:

$$AX+BX^* \longrightarrow AX^*+BX, \qquad (2)$$

is a fraction of the reaction (1), and the fractional percentage is easily seen from a probability calculation, in so far as the isotopic effect is negligible. Now we denote the rate of reaction (1) by R, number of exchange per sec. per cc. of reactor. Then this exchange reaction rate, R, which is differential in its nature but which can be measured by integral conversion of the isotopic exchange reaction (2), is independent not only of the duration of the reaction, but also of the volume or the shape of the catalyst bed so long as the over-all resistance of the reaction remains constant. In other words, when R changes with any one of the following variations: the feed rate F cc. (S. C.)/sec., reactor diameter D cm., height of the bed Z cm., and the volume of the catalyst $(1/4)\pi D^2 Z$, while the temperature remains constant, then the change shows that any one of the steps of the reaction has been influenced by that variation. When the reaction is catalytic, then so long as the intrinsic catalytic activity remains constant, the change in R indicates some change in mass-transfer steps.

In addition to this prominent feature of exchange reaction, isotopic exchange reaction has two other characteristics. The one is that the heat of reaction is nearly zero, and the other is that the integral rate is expressed by the first order equation. These characteristics are amenable to the kinetic study of chemical reaction.

Anticipating these characteristics, we have studied the catalytic exchange reaction of oxygen atoms between gaseous oxygen and water vapor by use of heavy oxygen. By using chromic oxide catalyst, values of R were measured at varying temperatures by varying the feed rate of reacting gases and the length of the catalyst bed.

Rate Equation

One of the authors in an earlier paper[7] introduced a mathematical relation between the percentage exchange and the gas flow rate, as concerned with the catalytic exchange reaction of oxygen atoms between gaseous oxygen and water vapor on the surface of solid catalyst. There it was ascertained that the exchange reaction rate was related by a simple probability relation to the rate of isotopic exchange reaction regardless of which step of the reaction (viz. adsorption, desorption, surface reaction, or any mass-transfer process) was rate controlling, so long as isotopic effect was negligible, and the following relation was obtained,

$$R'=\{N_A N_B/(N_A+N_B)\}(1/t)\{-\ln(1-x)\} \qquad (3)$$

Here, N_A and N_B are the total numbers of molecules of chemical species AX+AX* and BX+BX* in a unit volume of feed gases at S. C. and remain constant during the exchange reaction, x is the conversion represented by the net fraction of isotopic exchange to equilibrium, and t is the contact time in sec. R' denotes the rate of the exchange reaction concerning per unit volume of the reacting gases at S. C. and is related

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[5] D. M. Hurt, ibid., 35, 522 (1943).

[6] B. W. Gamson, G. Thodos and O. A. Hougen, *Trans. Am. Inst. Chem. Eng.*, 39, 1 (1943); O. A. Hougen and K. M. Watson, *Ind. Eng. Chem.*, 35, 529 (1943); K. H. Young and O. A. Hougen, *Chem. Eng. Progr.*, 46, 146 (1950); O. A. Hougen, *Z. Electrochem.*, 59, 479 (1953).

[7] N. Morita, This Bulletin, 15, 166 (1940).

with R by the relation: $R=R'F_e(273/T)\ (p/760)$, where F_e is the void fraction of the catalyst bed and T and p are the temperatures in °K and pressure in mmHg. The time of contact can be expressed by: $t=(\pi D^2ZF_e/4F)\ (237/T)\ (p/760)$, and therefore Eq. (3) becomes:

$$R=(4F/\pi D^2Z)\{N_AN_B/(N_A+N_B)\}\{-\ln(1-x)\}. \tag{4}$$

Norris[8] contemplated the rate equation deduced by Duffield and Calvin[9] as identical with Eq. (3), and set forth his opinion concerning the application of the equation for heterogeneous reactions. Harris[10] also introduced the same kind of equation for isotopic exchange reactions and deduced equations dealing with the kinetic implication of isotopic effect. For oxygen isotopes, isotopic effect is not large and we will not consider it in this paper.

In addition to the rate equation deduced above, we can point out the following interesting relation:

$$\text{N. R. U.}=\int_{u_A}^{u_{Ao}}\frac{du_A}{u_A-u_{Ae}}=\ln\left(\frac{u_{Ao}-u_{Ae}}{u_A-u_{Ae}}\right)$$
$$=-\ln(1-x) \tag{5}$$

$$\text{or,}\quad \text{H. R. U.}=Z/(\text{N. R. U})=Z/\{-\ln(1-x)\}, \tag{6}$$

where u_A is the fraction of AX^* in N_A, and u_{Ao} and u_{Ae} denote the original and equilibrium values of u_A, respectively. By this relation we can calculate H. R. U. from the conversion x. H. T. U. can be calculated from the conditions of the flow of reacting gases in the reactor by Hougen's method or introduced others, and then we can find the percentage contribution of mass-transfer process for the over-all reaction velocity.

Experimental Procedure

Four kinds of quartz tubes were used as the reactor, of which two were vertical and two were horizontal. We call these tubes V–I, V–II, H–I and H–II, respectively, whose dimensions are shown in Tables I–IV. Centered in thereact or is a thin tube of quartz for thermocouple. Pelleted catalyst is poured into the reactor to a fixed height and both ends are filled with granular quartz. The reactor is heated in a properly fitted electrical oven.

Oxygen in cylinder is used as the reacting gaseous oxygen; the content in heavy oxygen was analyzed in advance. The oxygen passes through pressure regulator, flow rate regulator, flow meter, and preheater, and then flows into mixer with water vapor. Heavy oxygen water prepared by fractional distillation of water is placed in a glass cylinder with graduation and pressed with the same pressure used for gaseous oxygen. The water flows at a known speed through the flow rate regulator and flows into evaporator. The evaporator is made of quartz and heated by three small gas burners. The vapor mixes with gaseous oxygen, passes through another preheator, and flows into the reactor. The gaseous mixture from the reactor is passed through condenser. The condensed water is refined as usual[11] and its heavy oxygen content is determined from its excess density as compared with normal water. Comparing the heavy oxygen content with original concentration the conver sion x is determined.

Chromium oxide is prepared from recrystallized chromium alum. The precipitated hydroxide of chromium with ammonia is repeatedly washed with water until no sulphuric acid ion is detectable. The hydroxide is dried in an electrical air oven and then powdered. One part of this powder is throughly mixed with three parts of the "Naegi" kaolin and a small quantity of water is added. The paste is pressed out of a press made of brass, having several pores of 2 mm. dia. in the bottom, and then cut into 2 mm. lengths. The pellete are first air-dried and then placed in an electrical oven at 110°C, and finally dried at 500°C for 7 hr. under oxygen gas stream. Before each experiment, a reacting gas mixture is passed through the catalyst for several ten-minute periods after which we can expect the steady state of the exchange reaction.

Results obtained

Tables I–IV show the results obtained under various conditions of experiments. In these tables A is the cross sectional area of the reactor and α is the volume ratio of gaseous oxygen to water vapor. Experimental number show the order of experiments. Throughout all the experiments the

TABLE I

DATA OBTAINED BY V–I (RUN 600)

$D=1.6$ cm., $A=2.01$ cm², $Z=24.0$ cm. (No. 1–19): 23.5 cm. (No. 29–36); 23.8 cm. (No. 37–51)

Exp. No.	Temp. °C	F/A $\frac{\text{cc.}}{\text{sec.}\cdot\text{cm}^2}$	α	x	$R\times10^{-18}$ $\frac{\text{atoms}}{\text{sec.}\cdot\text{cc.}}$	H. R. U. cm.
632	542	16.5	2.28	.789	7.34	15.1
611	538	15.0	2.14	.823	7.49	13.9
636	522	16.4	2.38	.605	4.10	25.3
629	501	17.3	2.06	.432	2.96	41.5
602	489	15.2	2.05	.405	2.32	46.3
633	488	17.1	2.07	.375	2.42	50.0
631	541	23.0	2.19	.652	7.13	22.3
613	540	22.3	2.18	.729	8.35	18.3
635	522	22.8	2.18	.490	4.51	34.9
630	500	23.6	2.01	.312	2.70	62.9
614	492	22.6	2.11	.321	2.54	62.1
634	487	23.8	1.99	.233	1.93	88.8
645	563	32.0	2.08	.895	21.29	10.6

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[8] T.H. Norris, *J. Phys. & Colloid Chem.*, 54, 777 (1950).

[9] R.B. Duffield and M. Calvin, *J. Am., Chem. Soc.*, 68, 557 (1946).

[10] G.M. Harris, *Trans. Faraday Soc.*, 57, 716 (1951).

[11] T. Titani and N. Morita, This Bulletin, 13, 409 (1938).

Exp. No.	Temp. °C	F/A $\frac{\text{cc.}}{\text{sec.}\cdot\text{cm}^2}$	α	x	$R\times10^{-18}$ $\frac{\text{atoms}}{\text{sec.}\cdot\text{cc.}}$	H. R. U. cm.
640	542	32.1	2.02	.717	12.15	18.9
610	537	35.2	2.21	.653	10.60	22.7
651	522	33.7	1.81	.381	5.09	49.7
648	501	32.0	2.33	.339	3.69	57.5
601	494	34.7	2.20	.366	4.49	52.9
642	561	37.7	2.61	.844	18.39	12.8
646	560	40.7	2.21	.856	22.62	12.3
639	539	39.2	2.18	.590	10.08	26.7
650	533	42.6	2.00	.506	9.03	33.8
643	523	38.7	2.37	.581	9.31	27.3
638	503	38.1	2.42	.286	3.51	70.7
604	598	64.8	2.49	.931	46.53	8.9
617	580	47.5	2.28	.890	29.36	10.9
619	556	49.4	2.03	.634	14.72	23.9
612	554	60.7	2.08	.558	14.51	29.4
616	500	48.9	2.22	.227	3.57	93.5
603	492	67.7	2.30	.183	3.81	119

TABLE II

DATA OBTAINED BY V–II (RUN 700)

$D=2.5$ cm., $A=4.9$ cm², $Z=6.0$ cm.

Exp. No.	Temp. °C	F/A $\frac{\text{cc.}}{\text{sec.}\cdot\text{cm}^2}$	α	x	$R\times10^{-18}$ $\frac{\text{atoms}}{\text{sec.}\cdot\text{cc.}}$	H. R. U. cm.
702	475	0.43	2.00	.652	0.539	5.7
704	425	〃	〃	.197	.112	27.4
703	400	〃	〃	.145	.080	38.2
712	475	0.46	2.00	.555	0.444	7.4
707	450	〃	〃	.450	.328	10.0
714	425	〃	〃	.210	.129	25.5
713	400	〃	〃	.161	.096	34.3
710	500	1.50	2.00	.524	1.327	8.1
708	475	〃	〃	.278	0.581	18.5
716	475	〃	〃	.231	.470	22.9
715	450	〃	〃	.111	.210	51.3

TABLE III

DATA OBTAINED BY H–I (RUNS 100–500)

$D=1.6$ cm., $A=2.01$ cm², $Z=30.0$ cm.

Exp. No.	Temp. °C	F/A $\frac{\text{cc.}}{\text{sec.}\cdot\text{cm}^2}$	α	x	$R\times10^{-18}$ $\frac{\text{atoms}}{\text{sec.}\cdot\text{cc.}}$	H. R. U. cm.
107	590	34.7	2.27	.894	17.61	13.3
503	580	43.9	1.92	.945	31.00	10.3
105	540	44.2	2.06	.670	11.54	27.1
210	535	33.4	2.57	.729	9.09	23.0
109	520	35.8	2.21	.404	4.25	57.9
405	520	42.1	2.10	.442	5.73	51.5
207	495	44.1	2.03	.374	4.89	64.2
110	480	35.4	2.11	.185	1.69	141
301	470	34.9	1.92	.196	1.86	137
111	445	35.7	2.05	.085	0.76	333
205	438	44.6	1.94	.099	1.12	289
103	580	62.0	1.95	.924	38.50	11.6
106	580	47.8	1.82	.845	22.21	16.1
504	570	57.0	2.23	.959	41.34	9.4
502	530	52.5	2.79	.643	10.68	29.2
108	520	49.5	1.56	.596	11.90	33.1
208	506	63.0	1.81	.409	8.26	57.1
508	505	55.2	2.40	.460	7.37	48.6
507	500	45.3	1.72	.398	5.85	59.1
201	480	52.2	3.06	.189	4.32	69.0
505	450	57.8	2.06	.261	8.36	50.0

TABLE IV

DATA OBTAINED BY H–II (RUN 000)

$D=1.7$ cm., $A=2.27$ cm², $Z=3.0$ cm. (No. 002–013); 2.1 cm. (No. 0.17–021)

Exp. No.	Temp. °C	F/A $\frac{\text{cc.}}{\text{sec.}\cdot\text{cm}^2}$	α	x	$R\times10^{-13}$ $\frac{\text{atoms}}{\text{sec.}\cdot\text{cc.}}$	H. R. T. cm.
013	500	0.44	2.00	.791	1.649	1.9
004	475	〃	〃	.535	0.807	3.9
003	450	〃	〃	.346	0.446	7.1
005	425	〃	〃	.271	0.332	9.5
002	400	〃	〃	.113	0.126	25.0
021	724	46.1	1.68	.624	166.1	1.5
020	693	46.5	1.64	.446	111.8	2.0
018	653	45.9	1.70	.234	57.7	3.9
017	598	45.9	1.70	.068	20.1	13.5

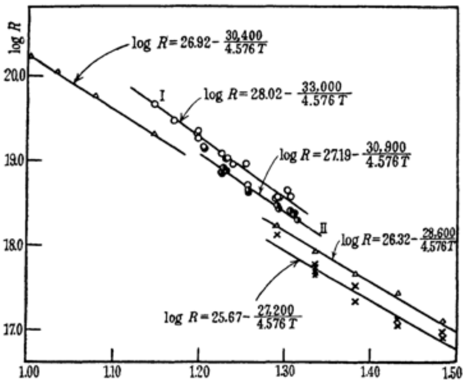

Fig. 1. Exchange reactions of oxygen atoms.

△ Run 000
◑ Run 600 $F/A\leq23.8$ cc.(s.c.)/sec.·cm².
○ 〃 〃 ≥32.0
× Run 700

same catalyst was used repeatedly, having been only treated with oxygen gas at 500°C before each run. During these runs the catalytic activity had remained almost constant, as will be shown later.

In Fig. 1 the points indicated by circles are the relations of $\log R$ vs. $1/T$ obtained by run 600. The fluctuation of each experimental point is rather large and the effect of the differences in linear velocity of reacting gas mixture F/A on the rate R can not be confirmed point-by-point. But, generally speaking, these points show a tendency toward a smaller R with decreasing gas velocity. When, for convenience, we classify these points into two groups, one with a feed rate larger than 32.0 and the other with one smaller than 23.8 cc. (S. C.)/sec.·cm², then we can draw the two lines I and II in Fig. 1. The ratio in R for the two lines ranges from 1.3 to 1.5. These differences can be attributed only to the differences in the flow velocities of reacting gases. The mean value of α is 2.18, most of the values deviating not more than ±5%, although the maximum deviation is about 20%. The effect of α on R was examined in an other run of experiments not included in this paper, and it was ascertained that these deviations in α had no effect on the rate R.

The results obtained by runs 000 and 700 are represented by triangles and crosses, resp. (Fig. 1), where the shorter catalyst beds and smaller feed rates were applied. The decreases in R are more conspicuous than those in line-II, and at run 700 the values of R are about one-fourth the values in line-I.

The runs 100–500 are conducted in a horizontal reactor and differ slightly from run 600 in the length of the catalyst bed. Deviation from linearity of the experimental results (not shown in Fig. 1) is more marked than in run 600. As runs 100–500 were the preliminary experiments done at high feed rates, and, in addition, as the reactor was horizontal and channeling was conceivable, thus a larger experimental error may have resulted. Taking this fact into consideration, the coincidence with run 600 is considerable, indicating that during all the runs the catalytic activity remained almost constant.

Discussion

As noted in Fig. 1, the activation energy of the exchange reaction ranges from 33.3 to 27.2 kcal./equiv. These high values of activation energy indicate that the mass-transfer processes can not be the main controlling factor of the reaction. The values of the frequency factor also show that the internal surface of the catalyst plays a dominant role. The value ranges from 1×10^{28} to 5×10^{25}. The outer-surface area a_v of the catalyst pellets is 21.6 cm^2/cc. and the collision frequency of the water molecules on this surface is 1.26×10^{24} molecules/sec.·cc. under the operating conditions of 500°C and 1/3.2 atm. The frequency factor is about 8,000–40 times greater than this collision frequency.

Although the mass-transter can not be the rate-controlling step, the decrease in linear velocity of reacting gas mixture and the shortening of the bed length retard the over-all rate R to a significant extent. Decrease in R accompanies the decrease in both activation energy and frequency factor. This fact clearly indicates that the mass-transfer processes have influence on the over-all rate to some extent.

The relative importance of film resistance to the rate R can be seen by calculating H. T. U. From the observed values of the pellet density of the catalyst 1.02 g./cc. and the bulk density of the catalyst bed 0.735 g./cc., and from the data cited in preceeding sections, we have calculated H. T. U. by Hougen's method. In Table V, the mass velocity G, mean diffusivity D_m and mean viscosity μ_m are calculated from the temperature, volume velocity and mixing ratio of the gas mixture. From these values the j_d factors are calculated by $j_d=1.82(D_pG/\mu_m)^{-0.51}$, and then H. T. U. by H. T. U.$=(1/a_vj_d)(\mu_m/\rho D_m)^{2/3}$, where D_p is the effective diameter of the catalyst pellet and is equal to $0.2\sqrt{1.5}=0.245$ cm., and ρ is the density of the reacting gas mixture. From Table V it can be seen that even at the highest temperature in the experiments H. T. U. is 10% of H. R. U., in most cases only one percent or a fraction. The correctness of these calculations is not certified for such flow systems with small Reynolds numbers, but film resistance seems insufficient to explain the retardation of the rate caused by the slowing down of the gas flow.

TABLE V

CONTRIBUTION OF MASS-TRANSFER

Exp. No.	Temp. °C	$G\times10^2$ $\frac{\text{g.}}{\text{sec.}\cdot\text{cm}^2}$	$\mu_m\times10^4$ $\frac{\text{g.}}{\text{sec.}\cdot\text{cm.}}$	D_m $\frac{\text{cm}^2}{\text{sec.}}$	H. T. U. cm.	$\frac{\text{H. T. U.}}{\text{H. R. U.}}$ ×100
021	724	5.51	4.28	1.265	.151	10.33
017	598	5.49	3.83	1.033	.155	1.15
013	500	0.054	3.61	0.864	.015	0.79
002	400	0.054	3.27	0.702	.015	0.06
103	580	7.54	3.87	1.000	.182	1.57
210	535	4.18	3.73	0.922	.134	0.58
507	500	5.43	3.56	0.864	.158	0.27
604	598	8.11	4.00	1.032	.185	2.07
645	563	3.93	3.84	0.972	.131	1.24
632	542	2.04	3.80	0.933	.094	0.62
648	501	3.97	3.67	0.864	.133	0.23
603	492	8.39	3.63	0.850	.194	0.16
710	500	0.183	3.61	0.864	.028	0.34
702	475	0.052	3.51	0.820	.015	0.24
715	450	0.183	3.43	0.780	.028	0.05
703	400	0.052	3.27	0.702	.015	0.04

As long as the intrinsic catalytic activity remains constant, uniform packing of catalyst and piston-like flow of reacting gases will give the largest value of R and any deviation from these conditions always reduces the rate R. Thus non-uniform gas flow, channeling, local eddy motion, convective circulation, longitudinal diffusion of isotopic components, and other disturbances always have retarding effects on R. If we assume that the reaction was conducted under complete mixing of the reacting gases as if it were in a tank reactor, then the observed rate R for high conversion and small flow rate would be as small as one-third compared with the rate when the reaction was conducted under piston flow.

Hitherto we did not consider the effect of pressure drop through the reactor. Eq. (4) does not contain pressure p. This is due to the fact that the calculations of N_A+N_B and of F are made at the same pressure (i. e. 1 atm). However, the change in pressure will affect the state of adsorption, collision frequency and other stages, and may ultimately affect the intrinsic catalytic activity or other factors governing the rate. Though this is the case, yet the highest value of the pressure drop is about 120 mmHg and the mean pressure throughout the reactor, 760+60 mmHg, is only 8% greater than the normal value. This small deviation will not cause any serious error in the results.

For comparison with our results, we have calculated the rate of exchange reaction between hydrogen and deuterium catalyzed by zins oxide by using Holm and Blue's data[12]. In this case R can be calculated by the equation, again neglecting isotopic effect: $R=(N/2)(S.V.)\cdot\{-\ln(1-x)\}$, where N is the total number of molecules of hydrogen and deuterium in a unit volume. Applying this equation to the data of Table V of Holm and Blue's paper, we have obtained the relation of $\log R$ vs. $1/T$ as shown in Fig. 2.

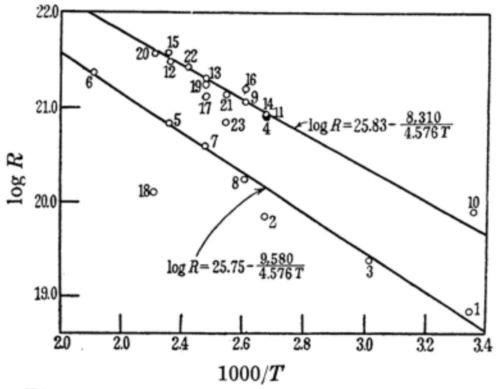

Fig. 2. Exchange reaction of hydrogen atoms (Holm, Blue).

Here the numbers affixed to the experimental points are the order of their data in the mentioned Table. From Fig. 2 we can observe that all the points except Nos. 4, 9, 18 and 23 are almost in linear relation with $1/T$ and that there is no speciality as indicated by the signs b and c in their table. The fact that the points can be divided in two groups: one with lower $S.V.$ and the other with higher $S.V.$ is in qualitative coincidence with our results. But the difference in R in their two groups is about ten and this difference is greater than ours. For hydrogen, isotopic effect may contribute a large effect on the velocity of isotopic exchange reaction and the calculated values of R may be incorrect in absolute value, but the error will not change greatly the mutual relation of these values. As they used a very small quantity of catalyst, the turbulence of reacting gases at the inlet and outlet may have contributed a considerable percentage. In addition, it is not certain to what extent the intrinsic catalytic activity remains constant during the run. These facts make any quantitative comparison difficult.

Summary

(1) Exchange reaction has the prominent feature that the rate does not change with the progress of the reaction and can be determined only by the mechanism of the reaction. Therefore we can immediately detect the effect of variation in any one of the reacting conditions by the observed conversion of the isotopic exchange reaction.

(2) The relation between exchange reaction and isotopic exchange reaction is considered and an equation which gives the exchange reaction rate (R) using the integral conversion of the isotopic exchange reaction (x) is introduced.

(3) The method is applied to the exchange reaction of oxygen atoms between gaseous oxygen and water vapor catalyzed by chromic oxide, and examination is made of the effect of the variation in the rate of feed gases and in the length of the catalyst bed.

(4) At feed rates higher than 32.0 cc. (S. C.)/sec. cm^2 the value R remains almost constant, but by the lowering of the feed rate more than this and by the shortening of the bed length, R is decreased. This decrease accompanied decreases both in activation energy and in frequency factor.

(5) The results are explained by the effects of mass-transfer through the gas film, of eddy or diffusional mixing of the reacting gases and of other kinds of disturbances. Mass-transfer resistance of the gas film is a small fraction of the retardation. Mixing of the reacting gases may contribute a higher percent.

(6) The results are compared with the rate of exchange between hydrogen and deuterium measured by Holm and Blue.

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[12] V.C.F. Holm and R.W. Blue, *Ind. Eng. Chem.*, **44**, 107 (1952).