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ISOTOPIC EXCHANGE BETWEEN GASEOUS DEUTERIUM AND AQUEOUS ALKALINE SOLUTION

By

Chao-Feang LIN^{*)}

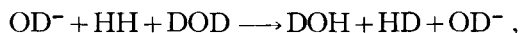
(Received December 12, 1967)

Abstract

The isotopic exchange reaction between gaseous deuterium and aqueous potassium hydroxide solution was investigated at various concentrations of hydroxyl ion ranging from 0.01 to 1 gram ion per liter and at 100°C. The reaction was confirmed to be homogeneous, with the rate proportional to the partial pressure of deuterium gas and to the concentration of hydroxyl ion. "Impurities" in the potassium hydroxide alleged to catalyze the exchange in a previous work was disproved. The hydroxyl-ion concentration of the solution after the reaction in a glass vessel was determined by means of pH meter; the pH decreased rapidly as the volume of the solution was smaller. It was concluded that the exchange reaction is catalyzed by hydroxyl-ion and that the decay of catalytic activity of the solution is caused by the decrease in hydroxyl-ion concentration through a reaction of alkali with glass of the reaction vessel.

Introduction

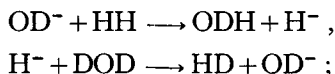
The isotopic exchange between gaseous hydrogen and heavy water in alkaline solution at 100°C was reported by WIRTZ and BONHOEFFER (1936).¹⁾ The exchange was unappreciable in neutral or acid solution. The authors attributed the reaction to the acid-base catalysis,



in which a deuteron transfers from DOD to HH as a proton migrates simultaneously from the latter to OD⁻.

The reaction was further investigated by ABE (1941),²⁾ who questioned the above mechanism on the ground that the proposed mechanism implied that not only base but also acid would accelerate the exchange in contrast to the observation. He rejected the alternative mechanism that the deuteron and the proton transfer separately in two consecutive acts as,

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on the ground that the intermediate H^- was of too high an energy to proceed the first step practically. After seeking some other mechanism from various observations, he arrived at conclusions that the reaction was catalyzed by impurities, which might be colloidal iron caused by a concentrating process of alkali in an iron pot; and that the catalyst was destroyed by precipitating in flakes of ferrous hydroxide when it was digested at 100°C with aqueous alkaline solution.

The conclusions were objected by WILMARTH, DAYTON and FLOURNOY (1953).³⁾

The present work is devoted to clarify the situation.

Experimental**Materials**

Deuterium gas: Heavy hydrogen gas of more than 99.5% of deuterium content from Stuart Oxygen Co., San Francisco was purified by passage through a Pd-thimble heated at about 300°C.

Distilled water: The middle fractions of distillate from alkaline permanganate solution were slightly acidified with sulfuric acid and redistilled to collect the middle fractions of distillate, which were stored in a reservoir with a soda-lime tube against atmospheric carbon dioxide.

Potassium hydroxide solutions: Approximately 2N potassium hydroxide solution was prepared from "extra pure grade" potassium hydroxide from Kanto Chemical Co., Tokyo, immediately after the pellets were rinsed with distilled water in order to remove carbonate on their surface. Protected against atmospheric carbon dioxide, the solution was stored in a polyethylene bottle connected with a soda-lime tube and with a buret, by which the solution was standardized against 2N hydrochloric acid and measured off for experiments. Standard potassium hydroxide solution was prepared by diluting a portion of stock potassium hydroxide solution with distilled water before use. "Control" potassium hydroxide solution was prepared by mixing proper portions of stock potassium hydroxide solution, 2N hydrochloric acid, and distilled water: impurities, if any, contained in the original portion of stock potassium hydroxide solution remained in the control solution, whereas the hydroxyl ion reduced the amount by the neutralized part. "Diffused" potassium hydroxide solution was prepared from the potassium hydroxide passed through a dialyzing colloid bag, which was checked for the absence of pinhole leaks or tears with

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about 3-cm level difference between the inner and outer liquids maintained for weeks; the "diffused" potassium hydroxide solution was concentrated by vacuum evaporation.

Glass: Two kinds of glass were used; one is Hario glass, a sort of Pyrex glass, purchased from Sibata Glass Works Co., Tokyo, and the other is Anti-alkali glass purchased from Corning Glass Works Co., Corning, N. Y. Hario glass will be meant by glass in what follows unless otherwise stated.

Apparatus

Reaction vessel: Fig. 1 shows a reaction vessel. The vessel was a glass tube of 20 to 80 ml capacity provided with constrictions S_1, \dots and with breakable joints B_1, \dots , which enable us to conduct consecutive experiments with one

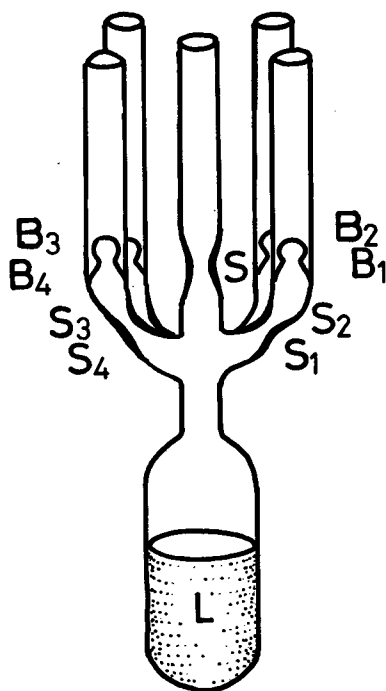


Fig. 1. Reaction vessel.

B_1, B_2, B_3 and B_4 : Breakable joint

S_1, S_2, S_3 and S_4 : Constriction

L: Solution to be studied

and the same solution only renewing gas by vacuum manipulation without contaminating the contents with air or stopcock-grease vapour.

Vacuum line: Vacuum line contained deuterium-storage bulb, mercury

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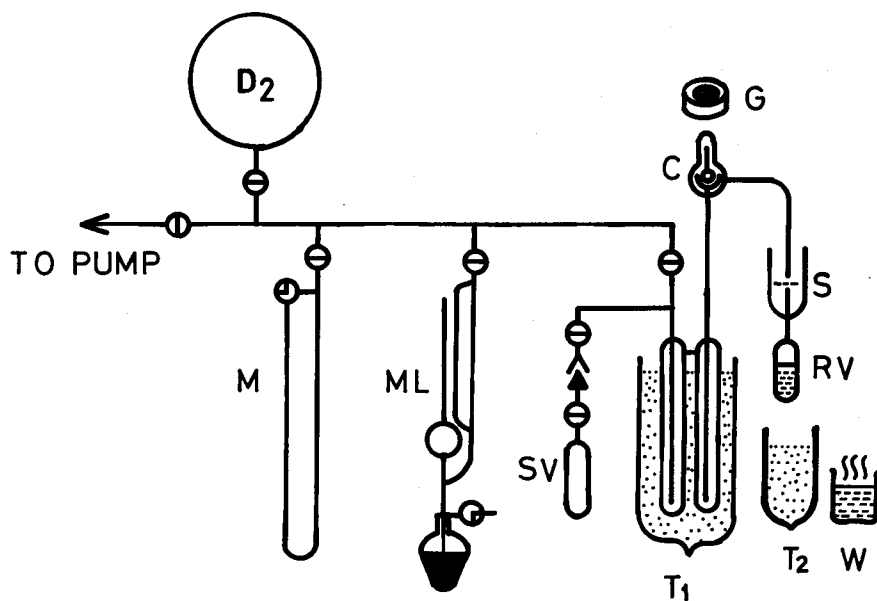


Fig. 2. Vacuum sampling system.

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|--|---------------------------------------|
| D ₂ : Reservoir of D ₂ gas | C : Greaseless stopcock |
| M : Hg manometer | RV : Reaction vessel |
| ML : McLeod gauge | T ₂ : Liquid nitrogen bath |
| SV : Gas-sampling vessel | W : Boiling water bath |
| T ₁ : Liquid nitrogen trap | G : Magnet |
| S : Constriction | |

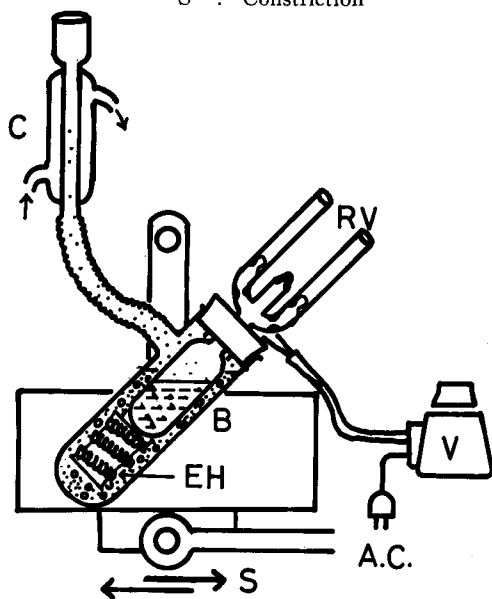


Fig. 3. Boiling water bath with shaker.

- | |
|-------------------------------|
| B : Boiling water bath |
| EH : Immersed electric heater |
| C : Condenser |
| V : Voltage adjuster |
| RV : Reaction vessel |
| S : Shaker |

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manometer, MacLeod gauge, gas-sampling vessel, liquid nitrogen trap, and greaseless stopcock, as shown in Fig. 2.

Boiling-water bath: Fig. 3 shows boiling-water bath B mounted on shaker S for agitating contents of reaction vessel RV at 100°C. Water was boiled by electric heater EH, which connected with power supply through voltage adjuster V; and vapours returned to bath B by condenser C.

Procedure

Fig. 2 and 3 illustrate schematically the procedure. After a known amount of potassium hydroxide solution was pipetted into reaction vessel, RV, through constriction S, the RV was fused to the vacuum line at the same constriction. Contents of reaction vessel were degassed by repeating evacuation to 10^{-6} cmHg with RV immersed in liquid nitrogen trap T_2 followed by fusion of contents by boiling-water bath W with greaseless stopcock C closed. Deuterium gas, whose pressure was read by manometer M, was introduced into the reaction vessel. The reaction vessel was sealed off at constriction S, shaken at 100°C for recorded time t , and the contents were frozen with liquid nitrogen trap T_2 . After the reaction vessel was jointed to the vacuum line at breakable joint B_1 and the interspace was evacuated to 10^{-6} cmHg the gas in reaction vessel was led out, with breakable joint B_1 opened, into gas-sampling vessel SV and analyzed for the isotopic content by means of mass spectrometer RMU-6 of Hitachi Works Ltd., Tokyo. Experiments were thus repeated with one and the same portion of solution several times.

The rate of exchange per unit volume of solution was expressed, after ABE, by $-ADPV_g/V_l t$, where V_g and V_l are the respective volumes of gas and liquid phases in reaction vessel, P is the partial pressure of deuterium gas introduced into the reaction vessel, t the reaction time, and $-AD$ the decrease of deuterium atomic fraction in the gas due to the reaction.

Depression of hydroxyl-ion concentration of 1N potassium hydroxide solution treated in a glass vessel at 100°C was followed by means of pH meter Type K of Horiba Works Ltd., Tokyo and later by means of pH meter Model E of Metrohm Ltd., Switzerland. The electrodes were calibrated against 0.01 M borax and 0.01 M disodium hydrogenphosphate solutions.

Results and Discussion

Table I shows the results of exchange reaction between deuterium gas and 1 N potassium hydroxide solution in glass vessel at 100°C. The second and third columns show the volume, V_l , of 1 N potassium hydroxide solution and the volume, V_g , of the gas phase in the reaction vessel respectively; the fourth column the reaction time, t , for which the reaction vessel was shaken at

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100°C; the fifth column the decrease of deuterium atomic fraction in the gas, $-\Delta D$, caused by the reaction; and the last column the rate of exchange per unit volume of solution, $-\Delta DPV_g/V_l t$. In each run, the partial pressure, P , of deuterium gas initially admitted into the reaction vessel was 15.0 cmHg and the initial deuterium atomic fraction was 0.998.

TABLE I. Rate of Exchange between D₂ and H₂O
in 1 N KOH at 100°C

$P = 15.0$ cmHg, $D_0 = 0.998$

Series-Run No.	V_l [ml]	V_g [ml]	t [hr]	$-\Delta D$	$-\Delta DPV_g/V_l t$ [cmHg/hr]
1-1	40	52.0	2	0.118	1.15
-2	"	50.5	"	0.132	1.25
-3	"	49.0	"	1.128	1.19
-4	"	47.5	"	0.148	1.10
2	"	57.5	5	0.149	1.29
3-1	20	62.0	5	0.114	1.06
-2	"	60.5	"	0.103	0.94
-3	"	59.0	"	0.058	0.51
-4	"	57.5	"	0.049	0.42
4	4	73.0	40	0.036	0.20
5-1	5	56.0	20	0.095	0.80
-2	"	54.5	40	0.006	0.05
6-1	5	85.0	20	0.068	0.87
-2	"	83.0	"	0.006	0.08
-3	"	81.0	"	0.002	0.03

Runs of each of the series 1, 3, 5, and 6 were consecutively conducted with a single portion of solution. In series 5 and 6 each with 5-ml V_l , the rate of exchange per unit volume of solution decreases from run to run pronouncedly in confirmation of ABE's finding. In series 1 with 40-ml V_l , the rate of exchange per unit volume of solution, on the other hand, scarcely decreases at every run.

As shown in the first runs of series 1, 2, and 3 the rate of exchange per unit volume of solution is practically independent of V_l , which indicates that the isotopic exchange reaction takes place in the liquid phase, in conformity with the results of ABE and others.^{1,2,3)}

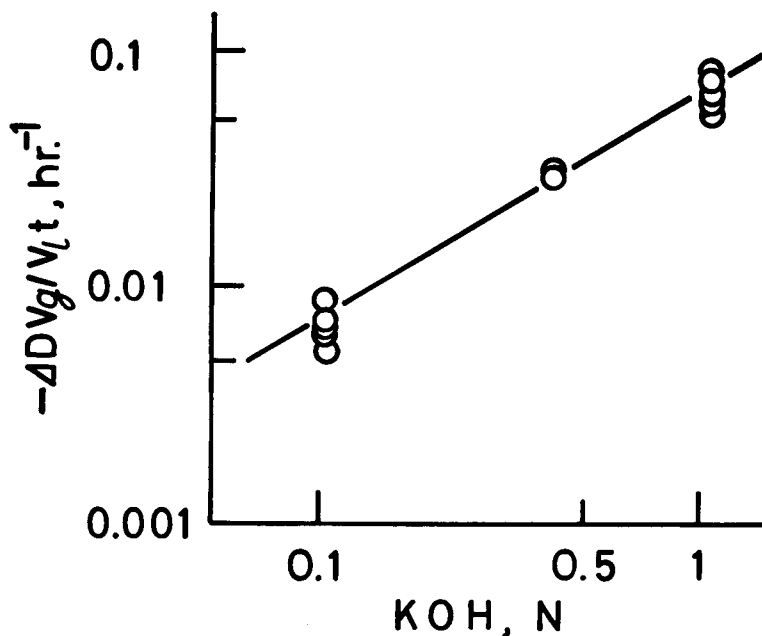
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TABLE II. Dependence of Rate of Exchange on Pressure of D_2

$T = 100^\circ\text{C}$, $t = 2$ hr
 $V_l = 40$ ml, 1 N KOH
 $D_0 = 0.998$

Series No.	V_g [ml]	P [cmHg]	$-\Delta DV_g/V_l t$ [hr $^{-1}$]
1	35.8	10	0.063
2	30.7	18	0.091
3	29.5	37	0.078
4	37.2	53	0.082

Table II shows that the specific rate of exchange, $-\Delta DV_g/V_l t$, is independent of the partial pressure of deuterium gas within experimental errors: the rate of exchange per unit volume of solution is proportional to the partial pressure of deuterium gas.

Fig. 4. Exchange rate of D_2 - HO_2 in KOH solution at 100°C .

The values of $-\Delta DV_g/V_l t$ at 100°C are plotted against the concentration of potassium hydroxide in Fig. 4, which shows that the specific rate of exchange is proportional to the concentration of hydroxyl ion.

Fig. 5 summarizes the final pH values of 1 N potassium hydroxide solution,

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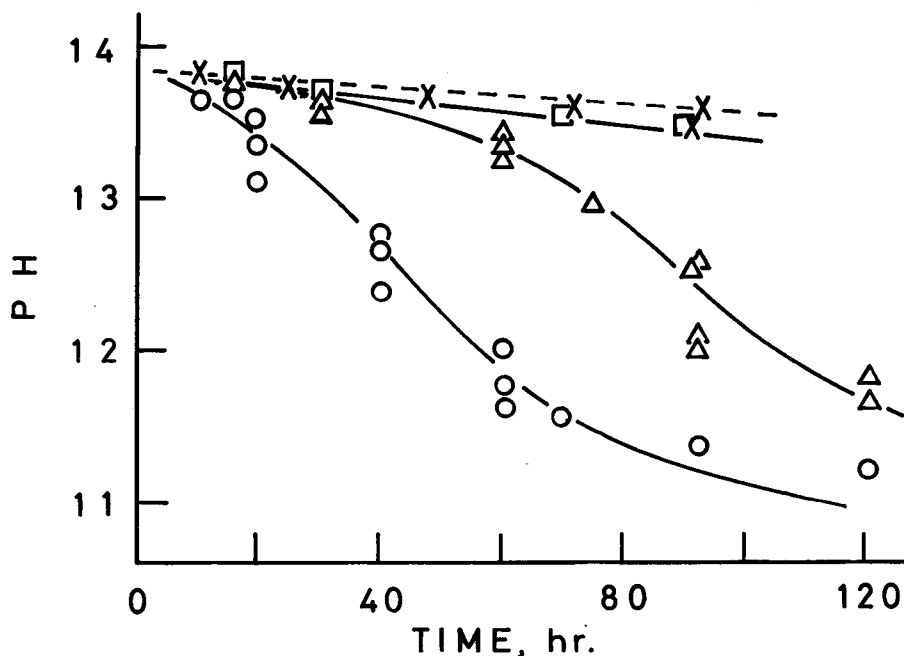


Fig. 5. Changes in pH of 1 N KOH solution shaken in glass vessel at 100°C.

- X-X-- : 5-ml solution in Anti-alkali glass vessel
 - : 50-ml solution in Hario glass vessel
 - △-△- : 25-ml solution in Hario glass vessel
 - : 5-ml solution in Hario glass vessel
- Capacity of vessel: about 40 ml each

with different V_i , shaken in Hario or Anti-alkali glass vessel at 100°C for long hours. The pH of the solution in Hario glass vessel decreases rapidly as the volume of solution is much smaller. The pH of the solution in Anti-alkali glass vessel, together with the pH of the solution with large amount in Hario glass vessel, scarcely decreases for hours.

Titration of the solution treated in glass vessel for long consecutive hours was conducted with preliminary dilution, since otherwise an abundance of flocculent precipitates formed on addition of hydrochloric acid made the titration impossible. On sufficient dilution of the resultant solution, there was neither the trouble of flocculation nor the considerable decrease in titer of the solution. Probably this was the case with ABE's work; he used 0.5 to 2 ml of heavy alkaline solution and reported neither the above trouble nor his actual procedure in the titration of solution by the Winkler method.

Table III summarizes results of tests for the alleged catalytic effect of

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TABLE III Effect of Impurities and OH⁻ on Exchange
Rate of D₂-H₂O at 100°C

$P = 15$ to 35 cmHg, $D_0 = 0.998$

Anti-alkali glass reaction vessel

Series -Run No.	OH ⁻ [g ion/l]	Concn. Ratio of Impurities	V _l [ml]	t [hr]	-ΔDV _g /V _l t [hr ⁻¹]
1-1	1	1	5	20	0.083
-2	"	"	"	"	0.076
-3	"	"	"	17	0.069
-4	"	"	"	20	0.064
2-1	0.1	0.1	20	17	0.0078
-2	"	"	"	20	0.0085
3-1	0.1*)	1*)	20	17	0.0073
-2	"	"	"	20	0.0075
4-1	0.07	0**)	20	25	0.0057
-2	"	"	"	20	0.0048
-3	"	"	"	"	0.0052

*) "Control" KOH solution, partially neutralized by HCl.

***) The solution of KOH diffused through collodion membrane.

impurities. Every exchange reaction was carried out in an Anti-alkali glass reaction vessel of about 40 ml capacity at 100°C. Column 2 shows the hydroxyl ion concentration of solution, column 3 the ratio of the concentration of impurities, if any, in the solution to that in standard 1 N potassium hydroxide solution, column 4 the volume of solution, column 5 the reaction time, and the last column the specific rate of exchange, $-\Delta DV_g/V_l t$.

In contrast to the series 3 in Table I, series 1 shows insignificant decrease in the specific rate of exchange from run to run. Series 2 was conducted with standard 0.1 N potassium hydroxide solution, and series 3 with the control potassium hydroxide solution prepared by neutralizing 1 N potassium hydroxide solution with hydrochloric acid partially to reduce hydroxyl-ion concentration to 0.1 gram ion per liter; the alleged impurities, if any, should be retained at the equal concentration with that of standard 1 N potassium hydroxide solution. Series 4 was conducted with "diffused" potassium hydroxide solution from which the impurities, if any, should have been removed.

Results of series 2, 3, and 4 indicate that the impurities, if any, have no effect on the rate of exchange.

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It may be concluded that the isotopic exchange reaction between gaseous deuterium and aqueous alkaline solution is homogeneous, with the rate proportional to the partial pressure of deuterium gas and to the concentration of hydroxyl ion; and that the decay of catalytic activity of potassium hydroxide solution in a glass vessel at 100°C is due to the decrease in hydroxyl-ion concentration by reaction of alkali with glass.

Acknowledgement

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