STUDIES OF ISOTOPE EXCHANGE ON THE INTERFACE MERCURY/MERCURY(II) SALT SOLUTION

By

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Introduction

Isotope exchange is a spontaneous intersubstitution process in which the different isotopes of an element are exchanged between different states of the element being in equilibrium except their isotope distribution. The term different states includes different molecules, different bond types and different physical-chemical states, i.e. different phases too. Consequently the exchange rate is independent of the direction of the process, that is, it makes no difference which form is labelled. However, one must make certain of the equality of rates, since unforeseen unidirectional processes within the system are conceivable.

Activation energies of isotope exchange processes may vary within a wide range, whereas the change in free enthalpy is low. The latter change is the result of the configurational enthropy change due to the new distribution of the isotopes:

$$\Delta G = -T\Delta S \tag{1}$$

In the case of elements with higher atomic numbers, the isotope effect presenting itself to a very small extent may be disregarded. Neglecting this effect, the enthalpy change in the course of the exchange may be regarded zero:

$$\Delta H \approx 0 \tag{2}$$

Activation energy is usually supplied by heat movement, but can also result from the action of light, ionizing radiation or catalysts.

Isotope exchange between different phases, i.e. heterogeneous isotope exchange consists of parallel and consecutive individual processes defining the overall exchange rate. According to NERNST [1], IMRE [2] and HAISSINSKY [3] these processes are as follows:

— mass transport in the liquid phase,

— diffusion in the adhering layer (film diffusion),

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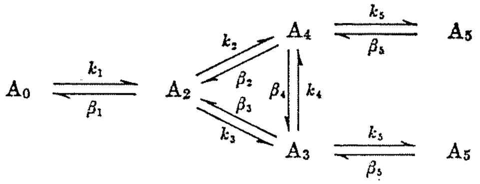
- desolvated adsorption (chemisorption),
- actual exchange,
- self-diffusion in the heavy phase.

Cross effects may also occur between these processes, and thus the total process can be characterized by the following scheme:



Due to the great number of indivual processes, the study of isotope exchange in heterogeneous systems is complex and cannot directly be evaluated in all cases. Considering the aspect of technique of measurement and evaluation, our objective was to investigate a system in which as few as possible among the mentioned individual processes should have to be taken into account as rate-controlling process of isotope exchange.

In the case of a solid heavy phase, transport rate is usually lowest in this phase, therefore it will interfere with the study of surface processes.

The study of a *liquid-liquid heterogeneous system* appers reasonable owing to the energetical homogeneity of the two phases and to higher rates of diffusion. As a result of rapid diffusion transport, the surface exchange processes can be separated, so that their direct investigation becomes possible. We therefore chose a liquid-liquid heterogeneous system, in particular, the system metallic mercury — aqueous mercury(II) salt solution for our study.

The mercury surface can be considered energetically homogeneous, and hence transversal surface processes appear to be improbable. Owing to the high self-diffusion constant of mercury at ambient temperature ($2 \cdot 10^{-5}$ $cm^2 \cdot s^{-1}$), it could be assumed and actually confirmed that mass transfer by self-diffusion is higher by several orders of magnitude than the rate-controlling step. Hence the general kinetic model becomes simpler, and — according to the initial assumption — one has to reckon with a consecutive process consisting of two or three steps.

The mechanism of the actual exchange process is complex, because the phase transition is accompanied by the change in the oxidation state, but no anion transfer occurs, since the heavy phase is metallic mercury.

Owing to the disproportionation reaction $Hg^{2+} + Hg \rightleftharpoons Hg_2^{2+}$ [4] the process is, in fact, a phase exchange process, since the mercury concentration of the aqueous phase changes during the reaction. In absence of reducing agents, in the case of the aqueous phase being labelled, the occurrence of unidirectional isotope transfer appears improbable, owing to the different oxidation states. Interfering unidirectional changes in activity could only be caused by adsorption processes.

Therefore one of the first objectives of experimental work was to find out whether the activity decrease observed in the bulk of the solution phase corresponded to a true phase transition.

The choice of the system in question was also justified by the facts that the mercury surface — as shown above all by electrochemical and ion adsorption studies [5] — is well-defined from the view of adsorption, homogeneous as regards charge distribution, the true surface can readily be calculated from geometry data, a pure surface is readily obtained, it is ideal for polarization, and surface tension can readily be measured. The favourable nuclear properties of the Hg-203 radioactive isotope (half-life 47 days, $E\gamma = 0{,}279$ MeV) were also advantageous.

Experimental

A thermostated glass vessel was used for carrying out the isotope exchange between metallic mercury and aqueous solutions of mercury (II) salts (Fig. 1).

The lower limit of the concentration range was defined by the error limit of concentration determination and setting. Concentrations exceeding 10^{-3} mol · dm^{-3} could not be used, because a black coating formed on the mercury surface and the rate of the process decreased unreproducibly. The radioactive isotope Hg-203 used for labelling the solution phase was supplied, in form of the aqueous solutions of the respective salts, by the Isotope Institute of the Hungarian Academy of Sciences.

Our experimental technique was semi-continuous. After introducing the aqueous phase we removed aliquot parts (1%) using micropipettes, weighed the aliquots with an accuracy of 0.1 mg and measured counts per minute using a well-type crystal scintillation detector.

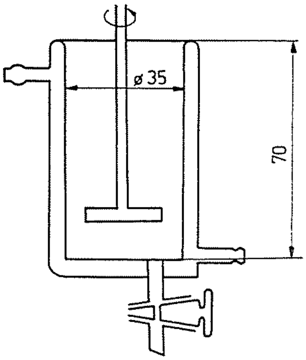


Fig. 1

The liquid phase was stirred with a constant-rpm propeller stirrer. By fixing the position of the stirrer, hydrodynamic parameters could be regarded as constant.

Since 6 to 10 samples were taken in one series of measurements, a volume correction had to be applied to improve accuracy. Corrections were calculated in knowledge of the function solution volume *vs.* exchange rate.

Subsequently we changed to a continuous technique. Here the aqueous solution was circulated by means of a pump, through polythene tubing, to pass before the scintillation detector connected to the ratemeter. Agitation of the solution was provided for by introducing the liquid tangentially into the thermostated vessel. The change of count rate with time was recorded by a compensograph connected to the ratemeter. Excat counts could be measured be means of a NK-108 counter included in the circuit.

Already the initial results unequivocally demonstrated that the activity of the solution decreased exponentially with time, and after a period of 30 to 40 minutes the aqueous phase became practically inactive.

This finding simplified the processing of the experimental data, since the half-life $t_{1/2}$ characterizing the rate of the process could simply be determined from the diagram specific intensity I *versus* time t.

This is in agreement with the McKay equation [6] describing the kinetics of isotope exchange, this being the basic equation of the homogeneous isotope exchange reaction:

$$-Rt = \frac{ab}{a+b} \ln (1 - F) \qquad (3)$$

where R is the exchange rate constant, a and b the quantities of the two substances between which isotope exchange takes place, and F the exchange fraction

$$F = \frac{x}{x_\infty} \qquad (4)$$

where x is the indicator concentration of the originally unlabelled substance. From the material balance, F can be expressed by the initially labelled substance of concentration y:

$$F = \frac{y_0 - y}{y_0 - y_\infty} \qquad (5)$$

In the case of heterogeneous isotope exchange, this equation is generally not valid, since mostly transfer processes will be the rate-controlling ones. However, for the case of liquid-liquid exchange, owing to the higher transfer rates, the spatial distribution of the isotopes in each phase will be practically constant, and hence the exchange process can be described by a formally similar equation. In this case a and b stand for the substance quantities in the individual phases.

We utilized 70 g metallic mercury and 20 to 30 cm^3 solution at concentrations of 10^{-5} to $2 \cdot 10^{-4}$ mol/dm^3. Thus the ratio $n_{Hg}/n_{Hg^{2+}} = 5.83 \cdot 10^4$— — $1.75 \cdot 10^6$. Owing to the extreme phase conditions, i.e. that a is much larger than b, and consequently $y_\infty \approx 0$, Eq. (3) can be written in a much simpler form:

$$-Rt = b \ln \frac{y}{y_0} \qquad (6)$$

or

$$\ln y = \ln y_0 - \frac{R}{b} t, \qquad (7)$$

confirming the reasonableness of presenting experimental data as lg *I. versus t.*

The error of half-life is defined primarily by the error of individual measurements and secondarily by the variance of the experimental points around the straight line.

The change in exchange rate due to the volume decrease caused by sampling is a systematical error, while the statistical character of radioactive decay and measurement causes random errors. Determinations of sample weight and time were satisfactorily accurate so that they could be disregarded in error calculations.

Taking into account the error margins, a vertical section corresponds to each point of the diagram lg I *vs.* t. Maximum and minimum half-life can then be computed from the straight lines with maximum and minimum slopes that can be drawn through these sections.

The exponential course only indicated that the number of individual processes did not presumably exceed 2, but gave no information on the rate-controlling process.

An inspection of Eqs (3), (6) and (7) discloses which parameters are of importance with respect to the process.

Since $b = cV$, where c is the concentration of the solution and V its volume, Eq. (7) can be written in the following form:

$$\ln y = \ln y_0 - kt \qquad (8)$$

where $k = \frac{R}{cV}$ is the rate constant in formal kinetics.

It is equal to the slope in the representation ln y *vs.* t.

It appears therefore necessary to experimentally determine the functions exchange rate *vs.* volume of solution and concentration of solution, and to determine the activation energy by measuring the temperature dependence of k.

Results

Effect of the volume of the solution on the rate constant

To study this relationship we determined the rate constant with different solution volumes, without changing the concentration. The volume was increased by maximum 50%, since a larger change would have affected the efficiency of stirring. To evaluate the results, we calculated the products of the volumes and the corresponding rate constants. The results are listed in Table I.

Table I

Concentration mol · dm^{-3} · 10^5	Volume of solution, V cm^3	Rate constant, k min^{-1}	k · V cm^3 · min^{-1}
8.93	20.6	0.093—0.096	1.92—1.98
8.93	24.7	0.077—0.081	1.90—1.99
9.20	20.0	0.085—0.090	1.70—1.80
9.20	30.0	0.062—0.064	1.86—1.90
8.93	20.0	0.098—0.105	1.95—2.01
8.93	24.7	0.082—0.084	2.01—2.11

The experimental results demonstrate that the product of the rate constant and the volume of the solution is constant within the limits of experimental error.

A similar statement was made by KREEVOY and WALTERS [7] for the exchange between organic mercury compounds and metallic mercury: they found that the ratio of the rate constant and the mercury surface was constant at unchanged concentration and volume of the solution.

Effect of the degree of dissociation on the rate constant

Measurements were made with aqueous solutions of $Hg(NO_3)_2$ and $HgCl_2$, these salts being chosen because $Hg(NO_3)_2$ dissociates practically completely in aqueous solution, whereas the dissociation equilibrium constant of $HgCl_2$ is

$$K = \frac{[HgCl_2]}{[Hg^{2+}]\,[Cl^-]^2} = 1{,}7 \cdot 10^{13}\,M^{-2} \quad (M = mol \cdot dm^{-3})\,.$$

Thus the degree of dissociation in for instance, 10^{-4} M and 10^{-5} M solutions is $\alpha = 0.018$ and 0.082, respectively.

Table II

Concentration mol · dm^{-3} · 10^5	Volume of solution, V cm^3	Anion	Rate constant, k min^{-1}
8.93	24.7	NO_3^-	0.077—0.081
8.93	24.7	Cl^-	0.081—0.086
8.93	20.0	NO^-	0.096—0.099
8.93	20.0	Cl^-	0.098—0.104
9.92	18.0	NO_3^-	0.104—0.107
9.92	18.0	Cl^-	0.100—0.106

The results presented in Table II indicate that no essential difference exists between data obtained with the two anions.

These data are in apparent contradiction with OKASHITA's results [8] who, in nitric acid, hydrochloric acid and potassium chloride solutions, found substantially different rate constants for exchange between metallic mercury and mercury(I) and mercury(II), resp. This difference might be explained by the use of 1 mol · dm^{-3} concentrations, so that the results cannot directly be compared with our results obtained in the concentration range of 10^{-5} — 10^{-4} mol · dm^{-3}.

Effect of the concentration of the solution on the rate constant

The concentrations dependence of the rate constant was measured in the concentration range 9.2 · 10^{-6} to 2.10^{-4} mol · dm^{-3}, at a constant solution volume of 20 cm^3.

It may be seen from the data in Table III that the rate constant decreases with increasing concentration. However, the decrease is not linear, but proportional to some fractional power of the concentration.

Table III

Concentration, c mol · dm^{-3} · 10^6	$c^{1/2}$ mol$^{1/2}$ · dm$^{-3/2}$ · 10^3	Rate constant, k min^{-1}	$\bar{k}$ min^{-1}	$\bar{k} \cdot c$ mol · dm^{-3} min$^{-1}10^6$
9.2	3.2	0.101—0.111	0.106	0.975
40.0	6.3	0.099—0.104	0.101	4.03
89.3	9.4	0.096—0.099	0.097	8.65
92.0	9.6	0.092—0.095	0.094	8.70
200.0	14.1	0.086—0.091	0.088	17.40

Effect of temperature on the rate of isotope exchange

To confirm the assumption that the rate-controlling step is film diffusion, we determined the activation energy of process by means of the rate constants measured at various temperatures (Table IV).

Table IV

Concentration mol · dm^{-3} · 10^5	Rate constant, min^{-1}			Activation energy H kcal · mol^{-1}
	20°C	35°C	50°C	
1.0	0.108—0.113	0.132—0.142	0.232—0.250	5.0
4.0	0.096	0.144	0.194	4.2
10.0	0.094—0.098	0.119—0.124	0.175—0.181	4.2

Discussion

Only the various parameters of the aqueous solution were varied in the course of experimental work, since metallic mercury does not occur in the kinetic equation. For a concentration of 10^{-5} mol · dm^{-3} of the solution and the described experimental scheme, the quantity of substance present in the solution phase corresponds — according to the lattice constants of metallic mercury — to a layer of ten atoms, and hence the possibility of a pure adsorption process cannot be excluded. It had therefore to be decided whether the total amount of the heavy phase took part in the exchange.

This question was decided by tapping the mercury phase. Some minutes after the start of the experiment, a sample taken from the lower mercury layer proved to be active. This was, of course, only qualitative proof.

A quantitative study of the self-diffusion in the metallic mercury phase was carried out utilizing geometry data, measured half-lives and the self-diffusion coefficient of mercury.

The solution of the problem is provided by the second Fick law, based on the model of diffusion from a solution with homogeneous concentration into a plate [9].

When the symmetrical model lending itself to simpler mathematical treatment is applied, the initial conditions at $t = 0$ are $c = 0$; $-l < x < l$; where l is the height of mercury measured from the bottom of the vessel. The boundary condition is

$$\frac{a}{k}\frac{\partial c}{\partial t} = \pm D \frac{\partial c}{\partial x} \quad x = \pm l \quad t \neq 0 \tag{9}$$

where c is the concentration of the indicator, a the height of the solution phase, and

$$\mathrm{k} = \frac{\text{mercury concentration in the heavy phase}}{\text{mercury concentration in the light phase}}$$

If A_t is total activity measured in the time t, and A_∞ is equilibrium activity in the metallic mercury, then

$$-\frac{A_t}{A_\infty} = 1 - \sum_{n=1}^{\infty} \frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2 q_n^2} \exp\left(-Dq_n^2 t/l^2\right) \tag{10}$$

where q_n represents the non-zero roots of $\mathrm{tg}\, q_n = -\alpha q_n$ (tabulated in [8]), and

$$\alpha = \frac{a}{kl}\,. \tag{11}$$

From the material balance equation

$$\frac{A}{2ac_0} = \frac{1}{1+\alpha}\,. \tag{12}$$

For the given problem, it is more expedient to use the expression

$$\frac{A_t}{A_\infty} = (1-\alpha)\left[1 - \frac{\alpha}{\pi^{1/2}T^{1/2}} \frac{\alpha^3}{\pi^{1/2}T^{3/2}} - \frac{3\alpha^5}{4\pi^{1/2}T^{5/2}}\right] \tag{13}$$

where $T = Dt/l^2$. This expression can favourably by used for small values of α.

Assuming that

— the volume of the solution is 20 cm^3, its concentration is 10^{-8} $\mathrm{mol \cdot cm^{-3}}$,

— the thickness of the metallic mercury layer is 0.5 cm, and

— $D = 2 \cdot 10^{-5}$ $\mathrm{cm^2 \cdot s^{-1}}$,

we obtain

$$\frac{A_t}{A_\infty} \approx 1 - 10^{-5}$$

that is, during a measured half-life practically the total quantity can diffuse into the heavy phase.

The correctness of the model seems to be confirmed by the fact that in the given experimental scheme, self-diffusion would be rate-controlling at a concentration of 4 $\mathrm{mol \cdot dm^{-3}}$. This value is in a good agreement with the measurements of HAISSINSKY and COTTIN [10]. According to them, self-diffusion is the rate-controlling step in the concentration range of 0.05 to 0.2 mol · dm^{-3}. When comparing the data it should be taken into account that they worked with different molar conditions and substance quantities, and that — owing to intense stirring — the heavy phase consisted of mercury droplets.

From the discussed experiences and considerations it appeared that the possibility of an independent adsorption process and self-diffusion of the metallic mercury as the rate-controlling step could be dismissed. An inspection of Eq. (5) shows that the measured rate constant k depends on the amount of the substance in the solution. Since this can be expressed as product of concentration by volume, the rate constant depends on these quantities, and the product kV, at unchanged concentration, as well as the product kc, at unchanged volume, should be constant.

Our experiments confirmed the constancy of the product kV (Table I), but did not confirm that of the product kc. Table III shows a change in the value of kc exceeding one order of magnitude. Consequently the surface exchange process described by the McKay equation had to be denied as a rate-controlling step.

The fact that concentration dependence and solution volume dependence differ makes it probable that the rate-controlling step is solution-phase diffusion or film diffusion. In this case, the integrated form of the first Fick equation is the kinetic equation of the process:

$$y = y_0 e^{-\frac{AD}{\delta V} t} \tag{14}$$

where y is the concentration of the indicator, A the surface, D the diffusion constant of the solution, δ the thickness of the laminar layer (film), V the volume of the solution and t the time. The rate constant is

$$k = \frac{AD}{\delta V} . \tag{15}$$

Since the surface and the volume, as well as — owing to small concentrations — the thickness of the adhering layer are independent of the concentration, we considered the concentration dependence of the diffusion coefficient in the formula as the rate constant. The diffusion coefficient of electrolytes in the concentration range of interest is proportional to the square root of concentration [11], therefore we plotted the value of the rate constant *versus* $\sqrt{c}$. In view of the error limits, the function k *vs.* $\sqrt{c}$ is well approached by a straight line described by the equation

$$k = k_0(1 - B\sqrt{c}) \tag{16}$$

with the numerical value

$$k = 0.112(1 - 15\sqrt{c})\ \mathrm{min}^{-1}.$$

From Eqs (15) and (16)

$$\delta = \frac{AD}{V k_0(1 - B\sqrt{c})}$$

At a concentration of 10^{-5} mol · dm^{-3} a value of $4 \cdot 10^{-3}$ cm is obtained for the thickness of the adhering layer. This is in good agreement with the values of 10^{-2} to 10^{-3} cm found in the literature.

The thickness of the laminar surface layer is defined by the hydrodynamic parameters of stirring, and hence, if film diffusion is the rate-controlling step, a change in the rpm value of the stirrer should affect the rate of the process. This was confirmed by our measurements.

Kreevoy and Walters made a similar statement. They measured the rate of isotope exchange between aryl mercury compounds dissolved in an organic solvent and metallic mercury as a function of rpm of the stirrer [7].

Okashita's measurements also indicated an important effect of stirring on the exchange rate between metallic mercury and aqueous solutions of mercury salts. Half-life was reduced by almost two orders of magnitude when he applied ultrasonic instead of mechanical stirring.

The values of activation energy determined from the temperature dependence of the rate constant are comparable — owing to small concentrations — with the activation energy of the self-diffusion of water which is 4.6 kcal/mol in the range 0 to 55 °C [12]. This agreement confirms the assumption of film diffusion as the rate-controlling step.

Summing up the results obtained by changing various parameters, the rate-controlling step of the isotope exchange reaction in the heterogeneous system metallic Hg/aqueous solution of Hg(II) salt, within the studied concentration range can be stated to be the film diffusion.

Investigation of the surface exchange process

Owing to slow diffusion transport, the described experimental results did not yield data on the processes passing on the interface of the phase. We therefore complemented our work by electrode potential measurements to study the disproportionation process $Hg + Hg^{2+} \rightleftharpoons Hg_2^{2+}$ taking place on the interface. At a concentration of 10^{-4} mol · dm^{-3} $Hg(NO_3)_2$, the electrode potential between the platinum electrode immersed into the mercury and the calomel electrode immersed into KCl solution and connected with the solution phase continuously decreased. This finding confirmed that disproportionation took place.

Homogeneous isotope exchange in the system Hg^{2+}/Hg_2^{2+} formed at the interface is an extremely rapid process, and heterogeneous exchange Hg/Hg_2^{2+} taking place at the interface is also rapid [4], therefore the phase transition between metallic mercury and mercury(II) salt should presumably be attributed to one disproportionation and two isotope exchange processes.

Data concerning the rate of the interface exchange process could be obtained from the exchange current values measured by GERISCHER and KRAUSE [13] between metallic mercury and the aqueous solution of mercury(I) salt. Since equilibrium concentrations of Hg^{2+} and Hg_2^{2+} will be established on the interface at rest, owing to the reaction $Hg + Hg^{2+} \rightleftharpoons Hg_2^{2+}$, the exchange current measurements carried out with Hg(I) ions are comparable with our own isotope exchange measurements.

At $2 \cdot 10^{-4}$ mol $\cdot$ dm^{-3}, the measured exchange current density was $4.5 \cdot 10^{-2}$ A $\cdot$ cm^{-2}. This is the charge transfer per second through unit interface. Charges are transported by ions, and hence mass transfer and half-life can be calculated from this value. At the above concentration, half-life calculated from the exchange current and in conformity with the actual geometry dimensions is 1.23 s, and the rate constant is 34 min^{-1}. Our own measurements resulted in the value $k = 0.088$ min^{-1} for this concentration. The comparison of the two values confirms our conclusion, since it indicates that surface charge transfer and mass transfer is faster by two orders of magnitude, so that film diffusion is the slowest step of the process.

Summary

The reasons for choosing the model system metallic mercury — aqueous solution of a mercury(II) salt were the rapid transport processes in the phases, the well-defined surface of metallic mercury and the energetic homogeneity of the surface.

A suitable semi-continuous technique has been developed for quantitative measurement of the kinetics of the heterogeneous isotope exchange process.

Based on theoretical considerations the formal kinetic rate constant has been measured as a function of volume and concentration, of the solution, of the temperature resp., and for Hg(II) salts having different degrees of dissociation.

The exchange rate has been stated to depend on the rpm value of the stirrer and to be inversely proportional to the volume of the solution. Its dependence on concentration is not linear, but proportional to the square root of the concentration. No difference was found between rate constants measured with Hg(II) salts differing in the degree of dissociation.

From the different rate constant to volume, or concentration of the solution relationships as well as from the dependence on the speed of the stirrer it was assumed that the rate-controlling step was film diffusion. This assumption was confirmed by determining the activation energy: the measured values were in good agreement with the activation energy of the self-diffusion of water. Electrode potential measurement demonstrated that Hg_2^{2+} ions formed on the interface participated in the Hg/Hg^{2+} exchange process.

The rate of the surface exchange process was calculated from exchange current values taken from the literature. This rate was found to be higher by more than two orders of magnitude than our measured exchange rates. This also confirms the correctness of the assumption that film diffusion is the rate-controlling step in the isotope exchange process.

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