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Kinetics of Extraction of Metals with Organophosphorus Compounds
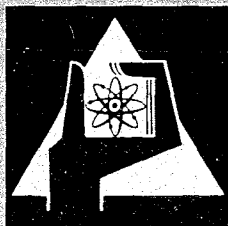
F. Baumgärtner, L. Finsterwalder

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Kinetics of Extraction of Metals with Organo-phosphorus Compounds [+)]

F. Baumgärtner, L. Finsterwalder

Kinetics of Extraction of Metals with Organophosphorus Compounds

In extraction chemistry it is common to use the term mechanism
in studies performed to describe the chemical species present at
the extraction-equilibrium.

Now however, let us discuss the mechanism of the extraction process
in respect of the chemical steps leading to the equilibrium state,
and disclosed by kinetic measurements.

It is evident that a question about chemical kinetics at the inter-
face cannot be answered by measurements alone at the equilibrium
state but needs further data from mass transfer.

However, mass transfer from one bulk phase into another always
takes place in three different steps:

1) mass transfer from bulk phase one to the interface by diffusion

2) interfacial mass transfer which may involve a chemical reaction

3) mass transfer from the interphase into the bulk phase two by
   diffusion.

To each of these steps, one can assign a resistance, as figure 1
shows schematically. The sum of these resistances controls the rate
of mass transfer.

It is generally assumed, however, that the diffusion processes preceeding and succeeding the interfacial reaction obscure the mass transfer data of the interfacial chemical process because of their magnitude.

Nevertheless, we thought this problem is worthy of further discussion as W. Nitsch [1,2,3] in Munich has already successfully demonstrated by the elucidation of the chemical steps taking place in the extraction of carbonic acids.

The chemical conditions for the investigation of a chemical reaction at the interface are certainly provided in a favourable manner for the extraction of metals with organophosphorus compounds. In some experiments, especially those with TBP, an interfacial resistance has already been observed by some authors [4,5].

In addition the study of extraction kinetics of uranium and plutonium with TBP is stimulated by its industrial importance.

Mass transfer measurements dealing with the extraction of uranylnitrate from an aqueous phase into a hydrocarbon solution of tributylphosphate were first carried out by Hahn [6] and later by Lewis [4], Burger [5], McKay [7] and Knoch [8].

The results, however, were interpreted in all cases in terms of the theory of hydrodynamical models which state nothing on the chemical reaction at the interface we are asking for now.

From all methods of mass transfer measurements the most suitable one for elucidating the chemical reaction at the interface is the well known single drop method as W. Nitsch[9] has shown.

The method of evaluating the results of mass transfer in single rising or falling drops in order to obtain an information about the interface reaction is briefly summarized in fig. 2.

First, the integral mass transfer is determined at different throughputs and different contact-times and extrapolated to infinite throughput.

In the second step the contact-time-mass-transfer curve is constructed, giving the intial transfer rate. The possibility to determine the initial transfer rate which is represented in the initial slope of the mass transfer curve is one of the particular advantages of the single drop method.

The third step is repetition of the procedure with varied concentrations for all components under consideration.

Then, in the last step, as it is common practice in chemical kinetic studies the reaction order of a single component is obtained by plotting the initial reaction rate versus the concentration in a double logarithmic scale. The resulting slope represents the reaction order of the chemical component under consideration.

Following this method we studied the extraction kinetics of uranyl-nitrate and plutonium-IV-nitrate with TBP. As fig 3, 4, 5 show, however, we did not obtain such nice straight lines with a distinct slope.

Therefore, we were faced with the problem, as it is often the case in studies of chemical kinetics, to draw consistent conclusions from the experimental results.

To survey the conclusions more easily, let me arrange the experimental results in a clear schematic diagramm as it is shown in fig 6.

The key to the interpretation of the kinetic results of mass transfer in terms of a chemical interface-reaction, as we will try here, is offered by the organic to aqueous transfer reaction which we will call the reverse reaction or back-extraction.

If we consider the nominal equation number (1) which represents the back extraction, then the reaction rate should - according to a pure dissociation - depend only on the metal concentration in the organic phase, as it is expressed in equation (2).

The experiments show however, additional influence of repelling character by nitrate or nitric acid in the aqueous phase and by unbound TBP in the organic phase that is considered in equation (3).

In order to derive a rate equation which should fit this experimental data therefore an additional reaction which is opposing the back-extraction from the beginning has to be assumed. The reason why it is an opposing reaction to the back-extraction is revealed by the decrease in initial reaction rate with increasing concentrations of nitrate or TBP.

Furthermore, this opposing reaction is driven by components of both phases. Hence, we have to infer that this opposing reaction comes into action at the interface.

That or those chemical species at the interface where the opposing
reaction sets in we will call furtheron interfacial complex, short
IFC. Thereby the singular noun IFC indeed may comprise several
complexes with different numbers of nitrate and TBP ligands
attached to the uranyl moiety. Generally speaking the IFC is the
junction of the extraction and back-extraction processes. Hence
it follows that the opposing reaction for instance to the extrac-
tion process is identical to that part of the back-extraction which
takes place towards the aqueous phase as it is shown in fig 7.

To avoid a wrong interpretation of what I have just described I
should like to repeat the process once more: There is certainly
not from the material balance in the state of equilibrium, but
rather from the kinetic point of view during start up of the
extraction process, a distinct difference between the back-extrac-
tion, and the reaction opposing the forward-extraction. The back-
extraction rises with the build up of solute in the primarily un-
loaded phase and is essential for a dynamical equilibrium.

The opposing reaction, however, starts up already at the very
beginning of the extraction process if still no solute is trans-
ferred to the other phase but only the interface is loaded. In
other words, the opposing reaction can be compared to the desorption
step in a cycle of adsorption and desorption at a surface.

Later then at the equilibrium state, the opposing reaction of
the extraction step is that part of the back-extraction which
carries off the metal-complex from the interface to the aqueous
phase.

But if this interpretation is true, hence it follows a far-reaching
conclusion namely that the kinetics in one direction has already
to include the essential part of the kinetics in the opposite
direction.

If this conception is true, a calculation of the extraction rate should be possible already using only the data gained from back-extraction and vice versa.

Before setting out the corresponding rate-equation, however, it is necessary to gain the most fundamental term of this equation, namely the concentration of the interfacial complex.

For this purpose we have modified the derivation of Langmuir's Adsorption Isotherm, that is we have to take into account that the withdrawal of the IFC from the interface takes place with different probabilities namely $\vec{f}-$ and $\overleftarrow{f}-$ directed to the organic and aqueous phase.

The interfacial concentration during start up of extraction or back-extraction then can be obtained from the balance between the entrance into the interface from one direction and the withdrawal from the interface in two directions as it is shown in equation (4) of fig 8.

Finally we reach equation (5) for the IFC concentration.

Utilizing this result of the IFC concentration we finally arrive at the kinetic equations (8) of mass transfer, fig 9. Equation number 8 represents the equation of back-extraction. A quite similar equation results for the extraction process which has instead of the metal concentration in the organic phase the product of the aqueous metal concentration and the organic TBP and aqueous nitrate concentrations.

Starting with the back-extraction now let us compare how
the theoretical equation (8) fits with the experimental data.
Fig 10 shows calculated curves of mass transfer velocities of
the uranium back-extraction with various nitrate and TBP concen-
trations and corresponding experimental data.

In fig 11 the theoretical curve of plutonium transfer velocities
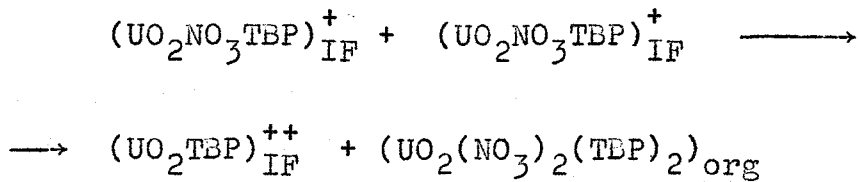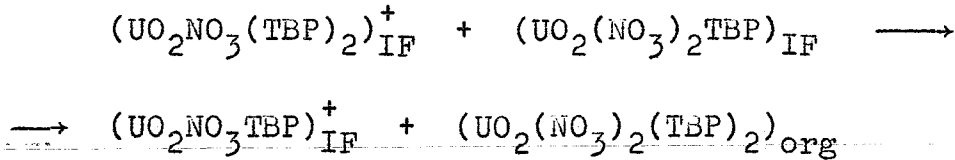is compared with the experimental values. The agreement is quite
satisfactory.

Now we have to come to the crucial test of the theory. As I
mentioned before a calculation of the extraction rate should be
possible from data gained solely from the back-extraction.

In fig 12 you will see the result of the test using plutonium-
extraction under various conditions. I think the agreement is
quite acceptable.

In the case of uranium-extraction, however, as you may see on fig
13 the experiments show reaction orders of 1.25 up to 1.3 for
the metal instead of 1.0 as it should be expected according to
our simple chemical model.

Our primary model of pure adsorption and desorption, however,
is able to yield a first and only a first order reaction for the
metal. The deviation in the case of uranium, therefore, suggests
that also higher reaction orders have to be considered at the
interface.

The most obvious interpretation is an exchange reaction
according to:

$$(UO_2NO_3(TBP)_2)^+_{IF} \quad + \quad (UO_2(NO_3)_2TBP)_{IF} \quad \longrightarrow$$

$$\longrightarrow \quad (UO_2NO_3TBP)^+_{IF} \quad + \quad (UO_2(NO_3)_2(TBP)_2)_{org}$$

$$(UO_2NO_3TBP)^+_{IF} \quad + \quad (UO_2NO_3TBP)^+_{IF} \quad \longrightarrow$$

$$\longrightarrow \quad (UO_2TBP)^{++}_{IF} \quad + \quad (UO_2(NO_3)_2(TBP)_2)_{org}$$

IF = interface
org = organic phase

Let me summarize now the chemical picture of interface reactions
we can use to interpret the kinetic mass transfer data of uranium
and plutonium-extraction with TBP.

As soon as the metal enters the interface either in ionic or
neutral form it belongs to the IFCs, which add by degrees TBP
molecules from the organic phase as well as nitrate anions from
the aqueous phase. There is no evidence that a distinct sequence
exists in the addition of the ligands, that means the addition
of TBP does not only start at the neutral metal compound but also
may start at ionic species.

The entrance of a metal into the interface does not necessarily
lead into the other phase. At any step the reaction may reverse
leading the interfacial complex back to its original phase.

Furthermore, beside the addition of the nitrate or TBP from both
phases to the interfacial complex also exchange reactions between
IFCs may occur. The result is a sort of disproportionation reac-
tion concerning the number of ligands. That means on one metal
the number of necessary ligands is build up and on the other
it is decreased.

The IFCs cannot be distinguished according to the phase, they came
from. Consequently the dynamical extraction equilibrium is not
composed as it is often represented by two reactions running
independently parallel and in opposite directions.

But the dynamical equilibrium is obtained rather by a dual trans-
formation of the IFC common to the forward and back-extraction.

In retrospect, the preceeding conclusions drawn form chemical
kinetic measurements may seem to be quite evident. Such arguments,
however, well justify our interpretation of the kinetic data
which were not all so obvious at the beginning of the experimental
work.

References

1) Nitsch, W.   Dechema Monographien, Vol. 55, 1965

2) Nitsch, W.   Z. Elektrochemie 69, 884 (1965)

3) Nitsch, W.   Chem.Ing.Techn. 38, 525 (1966)

4) Lewis, J.B.   AERE-CE/3-1366 (Nov. 1956)

5) Burger, L.L.   HW-62087 (Nov. 1959)

6) Hahn, H.T.   HW-32626 (July 1954)

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8) Knoch, W., Lindner, R.   Z. Elektrochemie 64, 1020 (1960)

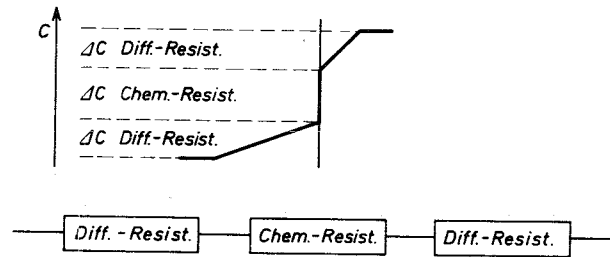9) Nitsch, W., K. Matschke   Chem.Ing.Techn. 40, 625 (1968)

ΔC Diff.-Resist.

ΔC Chem.-Resist.

ΔC Diff.-Resist.

| Diff. - Resist. | Chem.-Resist. | Diff.-Resist. |

Fig.1

Sequence in kinetic measurements

$$\frac{1}{A} \cdot \frac{dm}{dt} = v = \vec{v} - \overleftarrow{v} = \vec{k}\, c_i^m\, c_j^n \cdots - \overleftarrow{k}\, c_a^r \cdot c_v^s \cdots$$

①

$\frac{m}{A}$ $\left[\frac{mg}{cm^3}\right]$

$\frac{1}{Throughput}$ $\left[\frac{sec}{cm^3}\right]$

②

$\frac{m}{A}$

Contact time [sec]

③

$\frac{m}{A}$

C=3

C=2

C=1

Contact time

④

log v(t=0) = log $\vec{v}$

C

m

log C
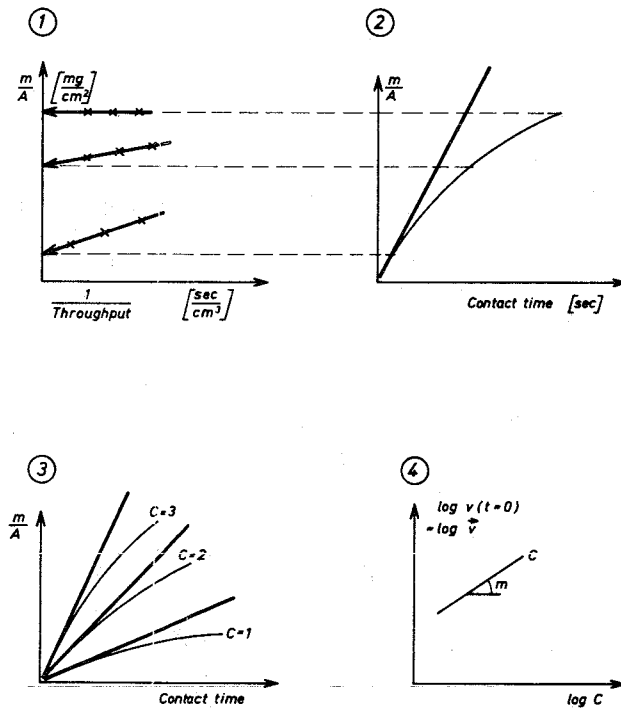
Fig.2

Experimental Transfer Rate of Forward Reaction

$$U(VI)_{aq} \longrightarrow UO_2(NO_3)_2\,TBP_{2\,org}$$
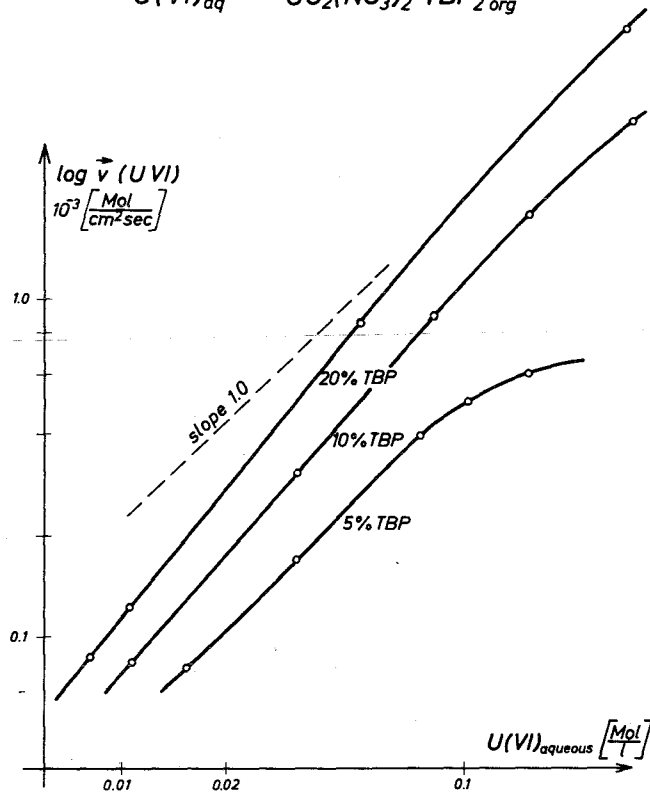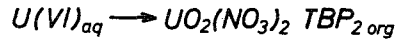

Fig. 3

Experimental Transfer Rate of Inverse Reaction

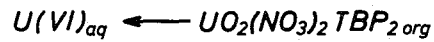$$U(VI)_{aq} \longleftarrow UO_2(NO_3)_2\,TBP_{2\,org}$$
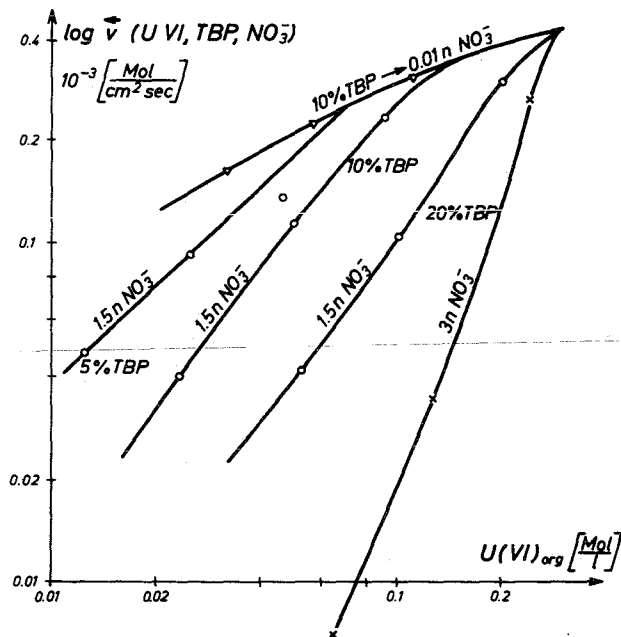
Fig. 4

Experimental Transfer Rate of Inverse Reaction

$$Pu(IV)_{aq} \longleftarrow Pu(NO_3)_4 TBP_{2\,org}$$
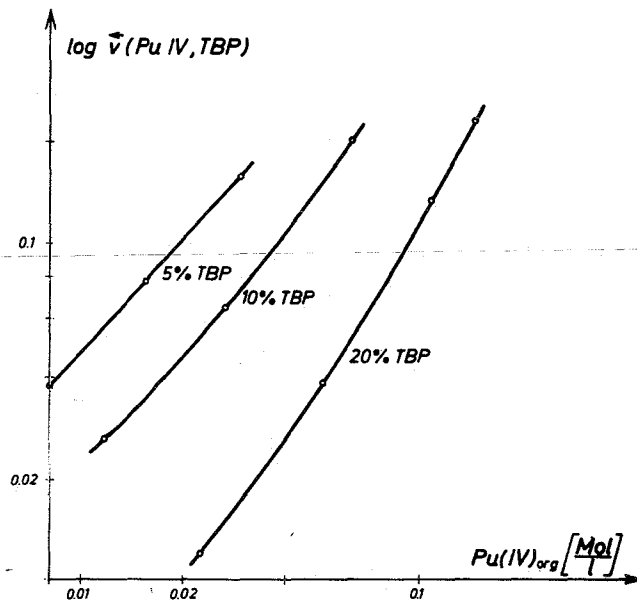
Fig. 5

Reverse Reaction Kinetics

$$M_{aq} + nS \longleftarrow M_{org} \qquad (1)$$

nominal $\qquad \overleftarrow{v} = \overleftarrow{k} \cdot M_{org} \qquad (2)$

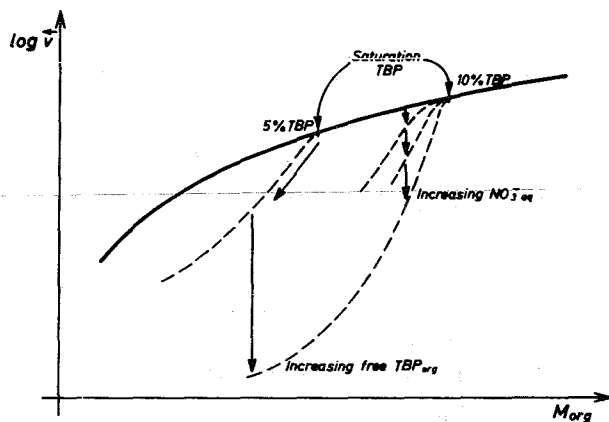experim. $\qquad \overleftarrow{v} = (M_{org}, \dfrac{1}{TBP^2}, \dfrac{1}{(NO_3^-)^x}) \qquad (3)$

Fig. 6

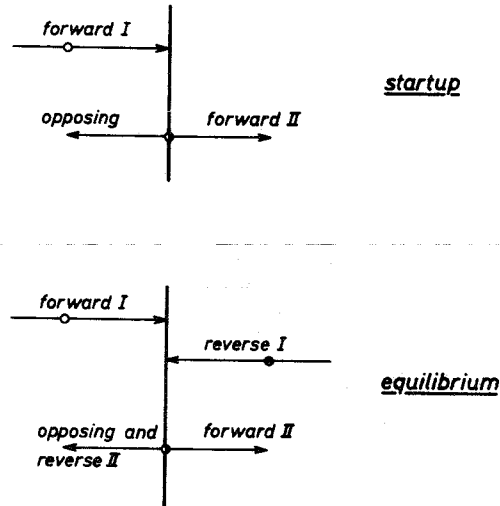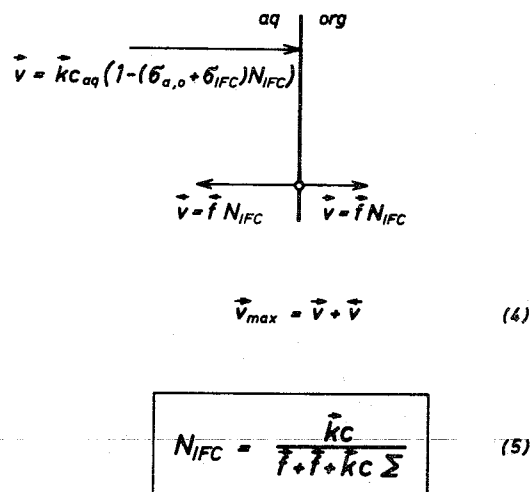## Mass Transfer during Startup and
Equilibrium State of Extraction

forward I

opposing | forward II

startup

forward I

reverse I

opposing and | forward II
reverse II

equilibrium

Fig. 7

Derivation of Interfacial Complex
Concentration

aq | org

$$\vec{v} = \vec{k}c_{aq}(1-(\sigma_{a,o}+\sigma_{IFC})N_{IFC})$$

$$\overleftarrow{v} = \overleftarrow{f} N_{IFC} \qquad \overrightarrow{v} = \overrightarrow{f} N_{IFC}$$

$$\vec{v}_{max} = \vec{v} + \overleftarrow{v} \qquad (4)$$

$$N_{IFC} = \frac{\vec{k}c}{\overleftarrow{f}+\overrightarrow{f}+\vec{k}c\,\Sigma} \qquad (5)$$

$\sigma_{a,o}$ — Collision cross sections in
aqueous or organic phase

σ_{IFC} — Collision cross section of IFC

Σ — $\sigma_a + \sigma_o$

Fig. 8

The Reverse Reaction and IFC Concentration

$$M_{aq} + nS \quad \longleftarrow \quad M_{org} \qquad (1)$$

organic

aqueous

$\overleftarrow{V}_{max}$

$[M_{aq}]$ $[M_{org}]$

$\overleftrightarrow{V}$ directly measured by chemical analysis

$\overrightarrow{V}$ deduced from $\overrightarrow{v}$ by influence of participating components (TBP, NO_3^-)
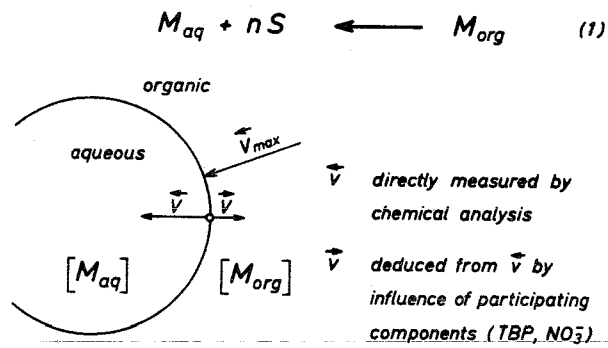
$$\overleftarrow{v} = \overleftarrow{f}\left[\overleftrightarrow{N}_{IFC}\right] = \overleftarrow{f} \cdot \frac{\overleftarrow{k}\left[M_{org}\right]}{\overrightarrow{f} + \overleftarrow{f} + k\left[M_{org}\right]\Sigma} \qquad (6)$$

$$\overleftarrow{v} = \overleftarrow{f}\left[\overleftrightarrow{N}_{IFC}\right] = \overleftarrow{k}\left[\overleftrightarrow{N}_{IFC}\right]\cdot\left[TBP\right]^2\cdot\left[NO_3^-\right]^x \qquad (7)$$

$$\boxed{\overleftarrow{v} = \frac{1}{A}\frac{d\overleftarrow{m}}{dt} = \frac{\overrightarrow{f}\ \overleftarrow{k}\cdot\left[M_{org}\right]}{\overrightarrow{f} + \overleftarrow{k}\left[TBP\right]^2\cdot\left[NO_3^-\right]^x + \left[M_{org}\right]\Sigma}} \qquad (8)$$

Fig. 9

Calculated and Experimental Values of Transfer Rates of Inverse U(VI) Extraction

$$U(VI)_{aq} \longleftarrow U(VI)_{org}$$
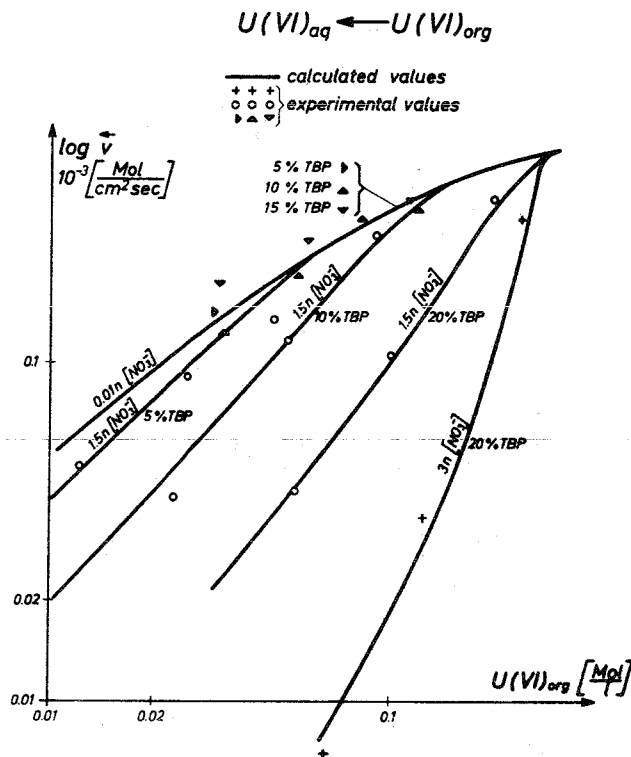
Fig. 10

Calculated and Experimental Values of Transfer Rates of Inverse Pu(IV) Extraction
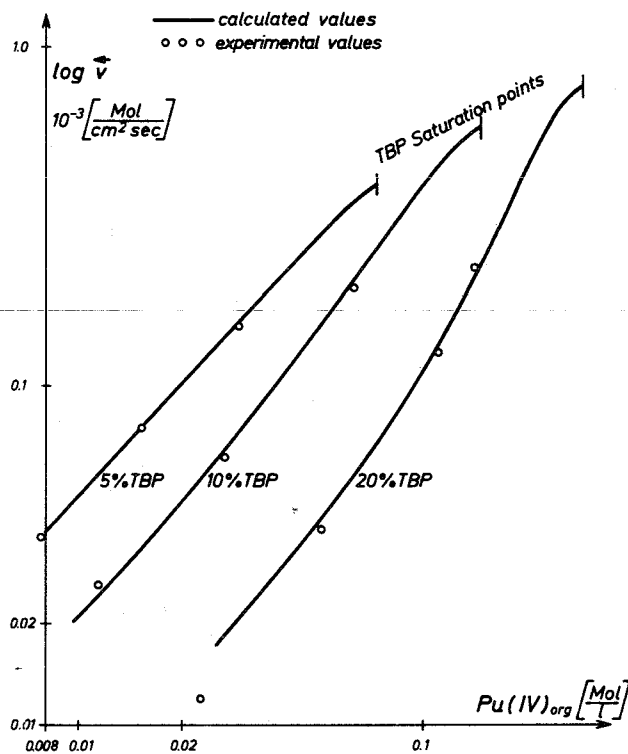
$$Pu(VI)_{aq} \longleftarrow Pu(IV)_{org}$$

Fig. 11

Calculated and Experimental Values of Transfer Rates of Forward Pu(IV) Extraction

$$Pu(IV)_{aq} \longrightarrow Pu(IV)_{org}$$

Fig. 12

Experimental Values of
Tranfer Rates of Pu(IV) Extraction

Fig. 13