

Thermodynamics of Extraction of ReO_4^- from Aqueous Sulfuric Acid Media with Tri-*n*-Butyl Phosphate Dissolved in Kerosene

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Rhenium distribution between Tri-*n*-butyl phosphate (TBP) dissolved in kerosene and sulfuric aqueous media is investigated under different temperatures, acidities, and TBP concentrations. Results show an exothermic extraction reaction with a distribution factor that decreases with the increase of the temperature and increases with the increase of the acidity and the TBP concentration. The stoichiometry of the reaction indicates neutralization of 1 mole of H^+ with 1 mole of ReO_4^- and solvating of a neutral molecule with four molecules of TBP. The structure of the complexes formed is, therefore, $4\text{TBP} \cdot \text{HReO}_4$. The apparent Gibbs free energy of the formation of $4\text{TBP} \cdot \text{HReO}_4$ from TBP, ReO_4^- , and H^+ is determined to be equal to $-66,989 + 219.8 T$ J/mole.

I. INTRODUCTION

MOLYBDENITE concentrate is an important source for rhenium. Roasting changes the concentrate from molybdenum disulfide to molybdenum trioxide. Rhenium disulfide also oxidizes to rhenium hepta-oxide, which sublimates with other volatile materials such as MoO_2 and SeO_2 at the oxidation temperature. The exhausting gas contains N_2 , O_2 , SO_2 , volatile materials, and dust. The gas is usually cleaned up by filtration. Most of the sublimated rhenium remains in the filtrate dust. Rhenium is subsequently extracted through leaching of the dust. During leaching, rhenium dissolves in aqueous media. Other soluble materials such as molybdenum, iron, copper, and selenium also dissolve into their ionic forms. The solution is generally treated for extraction of the valuable materials. Purity of the rhenium depends on the method of extraction and the type of reagents used.

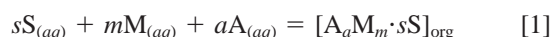
A commercial method for recovery of rhenium is solvent extraction. Different extractants have been used for this purpose. These include organic materials such as Tri-*n*-butyl phosphate (TBP),^[1-12] Tri octyl amine (TOA),^[13-18] Bis-2-ethylhexyl phosphoric acid (D2EHPA),^[19-24] Alamin 336,^[22-28] Tri alkyl amine (TAA),^[29] mixture of TBP with Tri octyl phosphin oxide (TOPO),^[30-33] TBP with D2EHPA,^[34-36] TBP with TOA,^[30,32] TBP with primary Amine,^[37-41] TBP with CMPO,^[42,43] TOA with Alamin 336,^[25-27] TOA with TBP and TOPO,^[30] Tri-octyl arsine,^[44] and other organic compounds.^[45-62] Many investigators have studied solvent extraction of rhenium from aqueous media containing sulfuric acid,^[9,13-15,17-18,20,24,29,36,37,45,48,62-80] nitric acid,^[3,5,7,12,13,20,26,39,42,43,62,63,79,81-83] hydrochloric acid,^[2,5,13,20,30,31,46,62,64,69,84-91] and perchloric acid.^[17,33,41,62,69] These studies have shed light on the

extraction of rhenium from solutions containing U, W, Mo, Tc, Al, and Fe.

There are, however, no quantitative details on the effect of temperature, TBP concentration, and sulfuric acid molarity on the distribution factor in the literature. Thermodynamic properties such as enthalpy, entropy, and equilibrium constant of extraction reaction are required for detailed scientific studies and industrial applications. These properties can conveniently be utilized for the estimation of the distribution factor prevailing under practical extraction conditions. Extensive research has been carried out during the past few years in our laboratory to evaluate these properties. The results corresponding to extraction of ReO_4^- from sulfuric acid media with TBP are given in this article.

II. CHEMICAL EQUILIBRIA

The extraction reaction is



where S is the extractant, M is the ion being extracted (anion or cation), and A is any counter ion or other species that may be present in the organic phase. The equilibrium constant of the extraction Reaction [1] may be written as

$$K_P = \frac{a_{[\text{A}_a\text{M}_m \cdot s\text{S}]_{\text{org}}}}{a_{\text{S}}^s a_{\text{M}}^m a_{\text{A}}^a} = \frac{[\text{A}_a\text{M}_m \cdot s\text{S}]_{\text{org}}}{[\text{S}]^s [\text{M}]^m [\text{A}]^a} \frac{\gamma_{[\text{A}_a\text{M}_m \cdot s\text{S}]_{\text{org}}}}{\gamma_{\text{S}}^s \gamma_{\text{M}}^m \gamma_{\text{A}}^a} \quad [2]$$
$$= \frac{[\text{A}_a\text{M}_m \cdot s\text{S}]_{\text{org}}}{[\text{S}]^s [\text{M}]^m [\text{A}]^a} \cdot Q$$

where Q is the quotient of the activity coefficients and square brackets indicate molar concentrations. The distribution factor of species M may be written as

$$D_M = \frac{\sum [\text{M}]_{\text{org}}}{\sum [\text{M}]_{\text{aq}}} \quad [3]$$

If the value of the coefficient m in Eq. [2] equals one, then

$$\frac{K_P}{Q} = K_C = \frac{D_M}{[\text{A}]^a [\text{S}]^s} \quad [4]$$

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Manuscript submitted January 31, 2000.

Rearranging and taking logarithms yields

$$\ln D_M = a \ln [A] + s \ln [S] + \ln [K_p] - \ln Q \quad [5]$$

The term K_p is a function of temperature, so at equilibrium condition,

$$\begin{aligned} \Delta G^\circ &= \Delta H^\circ - T \Delta S^\circ = -RT \ln [K_p] = -RT \ln [K_C \cdot Q] \\ &= -RT \ln [K_C] - RT \ln [Q] \end{aligned} \quad [6]$$

Generally, Q is a function of temperature and concentration. We assume that $-RT \ln [Q]$ can be written in a standard form such as

$$-RT \ln [Q] = A - BT \quad [7]$$

which can be subtracted from the standard values of Gibbs free energy:

$$-RT \ln [K_C] = (\Delta H^\circ - A) - (\Delta S^\circ - B)T \quad [8]$$

given the apparent standard change value of enthalpy ΔH_{app}° and entropy ΔS_{app}° when

$$\Delta H_{app}^\circ = \Delta H^\circ - A \quad [9]$$

and

$$\Delta S_{app}^\circ = \Delta S^\circ - B \quad [10]$$

Since $\ln (K_C)$ is a function of temperature, Eq. [5] can be written as

$$\ln D_M = -\frac{\Delta H_{app}^\circ}{RT} + \frac{\Delta S_{app}^\circ}{R} + a \ln [A] + s \ln [S] \quad [11]$$

By measuring the distribution factor of an ion, one can determine the relationship between the stoichiometric coefficients and the apparent standard enthalpy and entropy of the reaction.

III. EXPERIMENT

A. Materials and Reagents

Aliquot samples containing 5 g/L rhenium in ionic form were prepared by dissolving analytical grade potassium perchlorate ($KReO_4$) made in Fluka AB (Switzerland) in distilled water. In order to avoid the reduction of metal ions, 5 M sulfuric acid solution was prepared with diluting analytical grade sulfuric acid from Baran Chemical Company (Tehran, Iran) in doubly distilled water. Acidic solutions of rhenium were prepared by diluting the 5 g/L aliquot solution with 5 M sulfuric acid to produce the desired final concentrations. Small quantities of analytical grade TBP were dissolved in aromatic kerosene, both obtained from Fluka AB (Switzerland). All reagents and indicators such as potassium thiocyanate and stannous chloride (II) were produced by Merck Chemical Inc.

B. Experimental Procedure

Batch experiments were carried out in a flask containing equal volumes (20 mL) of both aqueous and organic phases. The mixture was agitated at a constant temperature with a mechanical shaker. The experiments were allowed to run for one hour in order to reach equilibrium.^[5] The samples were retained for 3 hours and passed through a separation

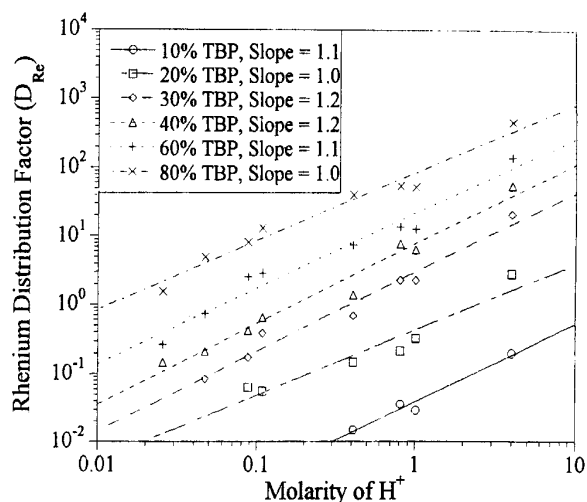


Fig. 1—The effect of molarity of sulfuric acid on distribution of rhenium between aqueous and organic phases (kerosene containing TBP) at 27 °C.

funnel, which separated the two phases. Experiments were performed at 27, 40, and 60 ± 0.5 °C.

The initial concentration of rhenium in the aqueous phase in all experiments was 1 g/L. Rhenium content of the aqueous phase was analyzed with thiocyanate indicators extracted with chloroform. Rhenium contents of each sample were measured by the spectrophotometric adsorption method. Analysis of the organic phase was determined through mass balance calculations. Spectrophotometry was done with a Unicam 8700 series UV/VIS spectrophotometer.

IV. RESULTS AND DISCUSSION

A. The Effect of H^+ Concentration on the Rhenium Distribution Factor

The effect of the concentration of H^+ on the extraction of rhenium was investigated by keeping the extraction temperature constant at 27 °C, 40 °C, and 60 °C in both phases and retaining the TBP concentration constant within 10 to 80 pct. The concentration of acid in this set of experiments changed between 0.02 to 4 M. The concentration of H^+ is calculated from equilibrium data of dissociation of sulfuric acid in aqueous media given by Harned and Owen.^[92] The experimental results at 27 °C are demonstrated in Figure 1. From this figure, it may be concluded that $\log D_{Re}$ has a linear relationship with $\log [H^+]$. This effect looks the same at all acid and TBP concentrations. The values of the slopes for different TBP concentrations and temperature are given in Table I. The average slope of the lines corresponds to the parameter (a) in Eq. [11]. The mean values of the slopes at 27 °C, 40 °C, and 60 °C are 1.1, 1.2, and 1.1, respectively. The slope at different temperatures is averaged to be equal to 1.1. Since the stoichiometric constant of the neutralized agent in Eq. [1] (value of (a)) must be an integer number, we estimate it to be one. The constant (a) indicates the number of moles of H^+ required for extraction of 1 mole of rhenium.

B. The Effect of TBP on the Rhenium Distribution Factor

Equation [11] shows that at constant temperature and acid molarity, the distribution factor of rhenium is proportional

Table I. Values of the Slope $\ln D_{Re}$ vs $\ln [H^+]$ Evaluated at Different Temperatures and TBP Concentration

TBP Concentration (Pct)	Temperature, °C		
	27	40	60
10	1.1	—	—
20	1.0	1.2	—
30	1.2	1.1	0.9
40	1.2	1.2	1.2
60	1.1	1.4	1.3
80	1.0	1.1	1.1
mean	1.1	1.2	1.1

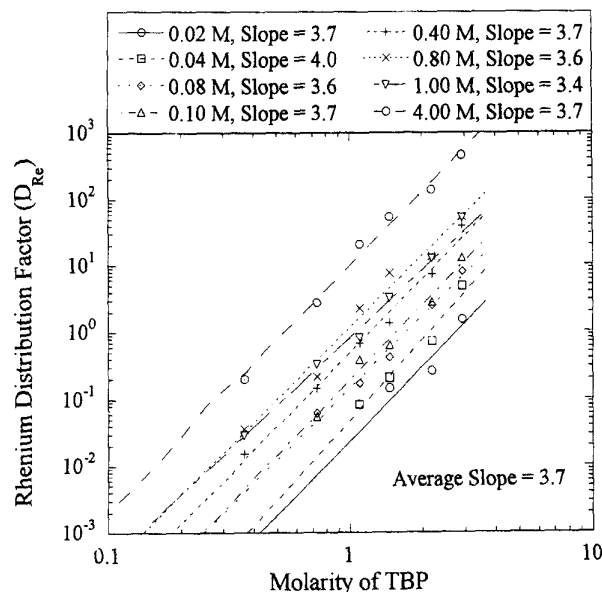


Fig. 2—The effect of molarity of TBP on the distribution factor of rhenium at 27 °C for aqueous sulfuric acid media.

to the concentration of TBP. In this study, the effect of concentration of TBP (0.365 to 2.923 M = 10 to 80 vol pct) on the extraction of rhenium was determined at constant temperature and acid concentration. The results at 27 °C are shown in Figure 2. This figure indicates that $\log D_{Re}$ vs $\log [TBP]$ is a straight line. This effect seems to be the same at all acid concentrations and temperatures. The values of the slopes for different acid concentrations and temperatures are given in Table II. The mean values of the slopes at 27 °C, 40 °C, and 60 °C are 3.7, 3.7, and 3.9, respectively. The average of the slopes of these lines at different temperatures is equal to 3.7. This value can also be interpreted as an indication for the existence of both tri-solvate and tetra-solvate extraction. The mean values of the slopes given in Table II indicate that at higher temperatures, the tetra-solvate mechanism is prevailing. Since the stoichiometric constant of the solvent in Eq. [1] (s) must be an integer number and the mean solvating number is greater than 3.5, it is assumed that its value is equal to four. This quantity indicates the required moles of TBP for extraction of 1 mole of rhenium.

C. The Effect of Temperature

The effect of temperature on the extraction of rhenium is determined by changing the temperature between 27 °C and

Table II. Values of the Slope $\ln D_{Re}$ vs $\ln [TBP]$ Evaluated at Different Temperatures and Acid Molarities

Acid Molarity (Mole/L)	Temperature, °C		
	27	40	60
0.02	3.7	3.6	3.9
0.04	4.0	3.6	3.9
0.08	3.6	3.7	3.8
0.10	3.7	3.6	3.9
0.40	3.7	4.0	3.6
0.80	3.6	3.6	3.9
1.00	3.4	3.4	3.9
4.00	3.7	3.4	3.9
Mean	3.7	3.7	3.9

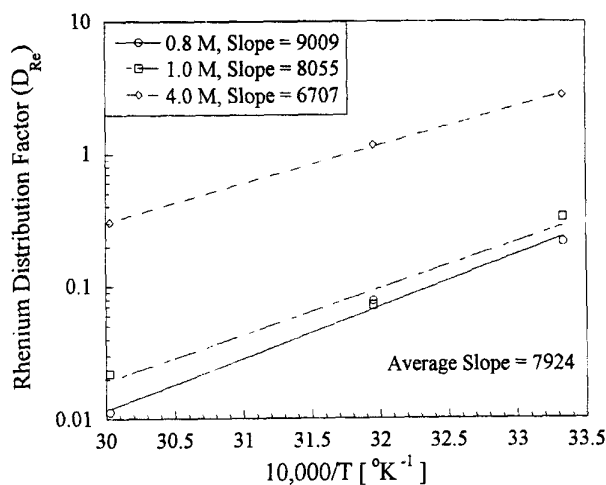


Fig. 3—The effect of temperature and molarity of sulfuric acid on rhenium distribution factor with 20 vol pct TBP in kerosene.

Table III. Values of the Slopes of $\ln D_{Re}$ vs $1/T$ Evaluated at Different TBP Concentrations and Acid Molarities

Acid Molarity (Mole/L)	TBP Concentration (Pct)				
	20	30	40	60	80
0.02	—	—	—	8892	8769
0.04	—	—	8381	8892	8042
0.08	—	—	6520	9778	7104
0.10	—	—	7191	9196	9976
0.40	—	6441	7422	9196	9976
0.80	9009	6749	7835	8058	7225
1.00	8055	6458	6441	6515	7071
4.00	6707	10,270	7240	5584	6744
Mean	7924	7479	7290	7988	7935

60 °C and keeping the concentration of TBP constant. It can be seen from Figure 3 that $\ln D_{Re}$ increases with the decreasing of the temperature. This effect, for all acid and TBP concentrations, is the same. The values of the slopes for different acid and TBP concentrations are given in Table III. The mean value of the slope of the distribution factor vs the inverse of the temperature ($1/T$) is 7924, 7479, 7290, 7988, and 7935 for 20, 30, 40, 60, and 80 pct TBP, respectively. The average of the slopes is 7737. The apparent standard enthalpy of the extraction reaction is, therefore,

Table IV. Coefficients Computed to Determine the Distribution Factor of Rhenium with TBP Diluted in Kerosene from Aqueous Sulfuric Acid Media at Different Temperatures

Value	Computed Coefficient	Standard Error
1/T	8057.3	369.1
ln [H ⁺]	1.2	0.03
ln [TBP]	3.7	0.09
Intercept	-26.47	1.19

equal to -64.32 kJ/mole. The negative value shows that the extraction of rhenium from sulfuric aqueous media with TBP is exothermic and the reaction is, therefore, favored by reducing the temperature.

D. An Estimated Equation for the Computation of Distribution Factor

In order to compute the coefficients used in Eq. [11] more accurately, it can be rewritten as

$$\ln D_M = \frac{7737}{RT} + \frac{\Delta S_{app}^\circ}{R} + 1.1 \ln [H^+] + 3.7 \ln [TBP] \quad [12]$$

in which all of the constants are substituted with figures, except $\Delta S_{app}^\circ/R$. It must be noted that the constants are defined at the very special case where one parameter is being changed while the others are fixed. It is more appropriate to assign new values to all parameters specified in the equation. To determine these coefficients, we gathered a data bank with different acid molarities and analyzed the data with SPSS for windows V. 8.0. The results are shown in Table IV. The final equation for the rhenium distribution is

$$\ln D_{Re} = -26.47 + \frac{8057.3}{T} + 1.2 \ln [H^+] + 3.7 \ln [TBP] \quad [13]$$

The measured and calculated values of the logarithm of the rhenium distribution factor are compared in Figure 4.

Comparing Eqs. [11] and [13] indicates that the apparent standard molar enthalpy of extraction of rhenium anions is -66,989 J/mole and the apparent standard entropy of rhenium extraction with TBP from sulfuric acid aqueous media is -229.3 J/mole K. The apparent standard Gibbs free energy of extraction of rhenium from the solution is, therefore,

$$\Delta G_{app}^\circ = \Delta H_{app}^\circ - T \Delta S_{app}^\circ = -66,989 + 220.1 T \text{ (Joules)} \quad [14]$$

The equilibrium constant of the extraction reaction can be calculated from

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ = RT \ln K_p \quad [15]$$

Based on Eq. [14], the apparent standard equilibrium constants at 27 °C, 40 °C, and 60 °C are, therefore, 1.468, 0.481, and 0.103, respectively.

E. Estimation of the Stoichiometric Equation for Extraction of Rhenium

Regression analysis of the data given in Table IV shows that the constant (*a*) is equal to 1. These data indicate that

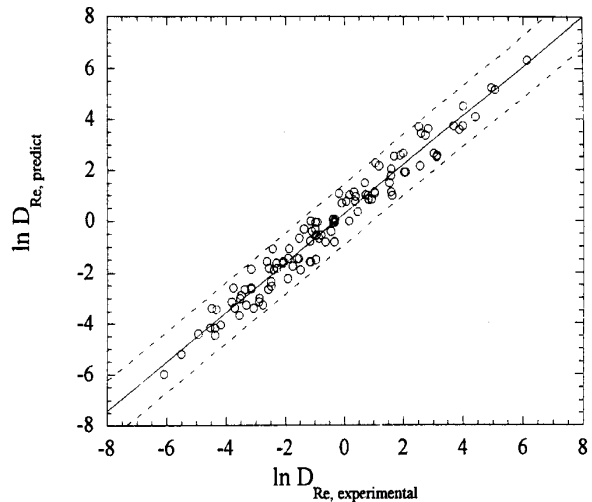
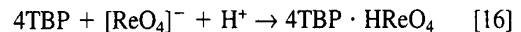


Fig. 4—Comparison of the measured and calculated values of rhenium distribution factor with TBP in kerosene in aqueous sulfuric acid media.

constant (*s*) is equal to 4. The formula of the complex produced, therefore, may be 4TBP · HReO₄ and the stoichiometric equation for extraction of rhenium, therefore, may be



V. SUMMARY

The rhenium extraction reaction with TBP is an exothermic reaction. The apparent standard enthalpy of the extraction reaction is -66,989 J/mole. Based on regression analysis of the experimental data, the rhenium distribution factor depends on temperature, H⁺ concentration, and TBP concentration according to

$$\ln D_{Re} = -26.47 + \frac{8057.3}{T} + 1.2 \ln [H^+] + 3.7 \ln [TBP]$$

The extraction of rhenium at acid concentrations between 0.02 and 4 M with constant temperature and constant TBP concentration indicates that neutralization of each mole of rhenium anion needs only 1 mole of H⁺ cation. At these molarities, the molecules formed react with 4 moles of TBP and the complexes formed may be 4TBP · HReO₄. The extraction reaction of the rhenium insinuated the apparent standard entropy of rhenium extraction with TBP from aqueous sulfuric acid media to be equal to -229.3 J/mole K. The apparent standard Gibbs free energy of the extraction reaction at the conditions specified in the article can be obtained from

$$\Delta G_{app}^\circ = \Delta H_{app}^\circ - T \Delta S_{app}^\circ = -66,989 + 220.1 T \text{ (Joules)}$$

and the apparent standard equilibrium constants of the extraction reaction at 27 °C, 40 °C, and 60 °C are equal to 1.468, 0.481, and 0.103, respectively.

ACKNOWLEDGMENTS

The authors thank Mrs. Z. Moshefi Shabestari, Amirkabir University of Technology, for her useful recommendations made on the analysis of the materials.

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