Liquid-Liquid Extraction Equilibrium Data of Cobalt Nitrate–Nickel Nitrate–Nitric Acid Solutions

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Studies of the solvent extraction of cobalt and nickel nitrates from aqueous solution would add to the fundamental knowledge of extraction of metal salts. In experiments performed to determine the extractibility of these metals as nitrates from aqueous solutions by organic solvents, normal butanol was found to be the best solvent and gave equilibrium distribution coefficients *K* for cobalt or nickel nitrate of about 0.3. The presence of nitric acid tended to decrease these at high metal concentrations.

In mixtures of the two metals the *K* value of either metal was found to depend on the total metal concentration. Low separation factors of about 1.3 were obtained. Very high *K* values of over 5 were obtained for the equilibrium extraction of the nitric acid in the presence of the metal nitrates by the *n*-butanol an indication of commercial possibilities.

Solvent extraction of cobalt and nickel salts from aqueous solutions has received considerable attention in recent years, partly owing to the development of many hydrometallurgical or chemical processes which are being used to separate metals in ores. The evaluation of extraction as a potential method of removing metals from aqueous solutions has been very limited by the lack of basic equilibrium data for the distribution of the metal salts between the two imiscible solvent layers.

Detailed studies on the extraction of cobalt and nickel chlorides (*3*), thiocyanates (*5*), perchlorates (*4*), sulfates (*7*), and acetates (*5*) are available. In the first three systems the distribution coefficients of the two metals depended on the total concentration of the anion, which was the same as the anion of the nickel and cobalt salts. High separation factors or ratios of distribution coefficients were obtained in the chloride and thiocyanate systems.

The nitrates of cobalt and nickel could easily be formed from the nitric acid leaching of ores. Study of the nitrate system should add to the fund of basic knowledge of the solvent extraction of metal salts. Hence experiments were performed on the nitrate system in this work. Templeton and Daly (*10, 11*) have obtained some experimental data using *n*-hexyl alcohol as a solvent.

In the present work the distribution coefficients of cobaltous and nickelous nitrate between water and various immiscible organic solvents were determined. Then *n*-butyl alcohol was selected as the best solvent, and further studies were carried out with the cobalt and nickel nitrates and various additives such as nitric acid.

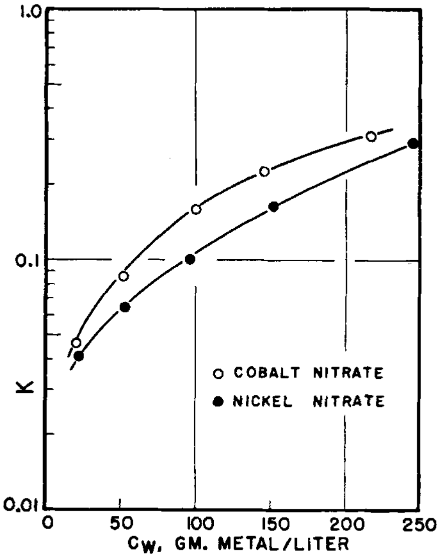

Fig. 1. Distribution coefficients in the ternary systems cobalt or nickel nitrate–water–*n*-butanol at 25.0°C. (Cobalt or nickel equilibrated separately.)

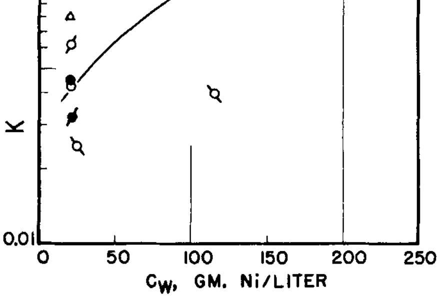

Fig. 2. Effect of additives in the system nickel nitrate–water–*n*-butanol at 25.0°C.

EXPERIMENTAL METHODS

Cobalt, alone in the aqueous or organic phase, was determined colorimetrically in a sulfuric acid solution by using the method of Gagnon (*2*). When the organic solvent was present, it was removed by evaporation with nitric acid. For very dilute solutions the method of Yoe (*12*) was used. When the ferric ion was present, it was removed by extraction with isopropyl ether. Also cupric ion, when present, was removed by precipitation as the sulfide.

In the solvent search phase, when nickel nitrate was alone in either layer, it was analyzed colorimetrically by the method

TABLE 1. SOLVENT SEARCH DATA AT 25.0°C.

(Metals equilibrated separately)

Solvent	Metal	C_w, g./liter	C_0, g./liter
	Alcohols		
n-Butanol	Ni	21.15	8.76×10^{-1}
n-Butanol	Ni	96.50	9.76
n-Butanol	Co	20.70	9.75×10^{-1}
n-Butanol	Co	99.60	16.00
n-Amyl alcohol	Ni	20.30	3.97×10^{-2}
n-Amyl alcohol	Co	22.00	6.47×10^{-2}
Isoamyl alcohol	Ni	20.75	4.33×10^{-2}
Isoamyl alcohol	Co	22.00	5.76×10^{-2}
n-Hexyl alcohol	Ni	96.00	6.80×10^{-2}
n-Hexyl alcohol	Ni	20.20	1.29×10^{-2}
n-Hexyl alcohol	Co	21.20	2.15×10^{-2}
Cyclohexanol	Co	21.80	2.80×10^{-1}
2-Octanol	Ni	20.85	9.78×10^{-3}
n-Decyl alcohol	Ni	20.78	6.91×10^{-3}
	Ketones		
Methyl ethyl ketone	Ni	15.15	1.18×10^{-1}
Methyl isopropyl ketone	Co	22.55	$<1.0 \times 10^{-3}$
3-Pentanone	Ni	19.38	2.60×10^{-3}
4-Methyl, 2-pentanone	Ni	18.85	6.04×10^{-3}
4-Methyl, 2-pentanone	Co	21.30	1.52×10^{-3}
Diisobutyl ketone	Ni	19.70	1.98×10^{-3}
	Ethers		
Diethyl ether	Ni	18.18	8.7×10^{-4}
Isopropyl ether	Ni	19.52	8.84×10^{-4}
Isopropyl ether	Co	20.7	$<1.0 \times 10^{-3}$
Ethylene glycol monoethyl ether	Ni	16.35	1.05×10^{-2}
	Nitrogen Compounds		
2-Nitropropane	Ni	19.60	6.07×10^{-4}
	Others		
Carbon tetrachloride	Ni	19.65	2.59×10^{-4}
Benzene	Ni	19.23	4.66×10^{-4}
Ethyl acetate	Ni	18.97	3.5×10^{-4}

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of Snell and Snell (*9*). When *n*-butanol was the solvent, the method of Gagnon (*2*) in sulfuric acid solution was adopted for use with nickel. In the presence of iron, nickel was analyzed by the dimethylglyoxime gravimetric method. This was necessary, since even traces of ferric ion interfere in the colorimetric determination of nickel sulfate at 397 mμ. (*6*).

A colorimetric procedure was developed for the analysis of cobalt and nickel when together in sulfuric acid solution. Beer's law can be written for the peak absorbance of nickel sulfate solution at 397 mμ., another Beer's law equation can be written for the relatively weak absorbance at 518 mμ., separate equations can be written for cobalt sulfate at its peak of 518 and at 397 mμ., and these four equations can then be combined. Then the absorbance of solutions containing both metals was measured at the two peaks of 397 and 518 mμ. and the concentrations calculated from the combined equations. Known mixtures were analyzed and gave an average deviation of 1.8% and a maximum of 2.8% (*6*).

Nitric acid was determined by using 0.2*N* sodium hydroxide and an electrotitrimeter. Ferric ion was analyzed by the dichromate method and copper by electrodeposition. The *n*-butyl alcohol and metal salts used were reagent grade.

Equal volumes of initial aqueous-phase solution and pure solvent were used in the equilibrium experiments. The equilibrium extractions were performed in rubber-sealed, glass-stoppered flasks agitated by magnetic stirrers and totally immersed in a bath. The densities were determined by weighing the contents from calibrated pipettes. The ternary-phase diagram was determined by titrating known amounts of one phase with another until the solution became cloudy. Experimental details are available elsewhere (*6*).

DISCUSSION OF SOLVENT SEARCH DATA

To select the best solvents distribution ratios (ratio of concentration in organic to concentration in aqueous phase) of cobalt nitrate and nickel nitrate alone were obtained between water and a variety of solvents (Table 1) at 25.0°C. The solvents used were restricted to those known to have some ability to extract metal salts.

The ketones gave distribution ratios *K* of about 0.008 as a maximum, and the ethers gave values less than 0.001 for the cobalt and nickel nitrates. The alcohols were the best solvents with maximum *K* values of about 0.2, the *K* value decreasing with increasing solvent molecular weight. *N*-butyl alcohol was selected for further studies because of its high *K* value compared with that of other solvents. This solvent was also used in the studies of the sulfate system (*7*).

N-BUTANOL–COBALT OR NICKEL NITRATE–WATER–ADDITIVE SYSTEM

No Additives

Distribution data from the solvent *n*-butanol when either the cobalt or nickel is alone are given in Table 2. Figure 1 shows that the *K* for nickel or cobalt increases markedly as the concentration of the metal in the water increases. At about 250 g. metal/liter the *K* is approximately 0.3. The *K* of cobalt is slightly greater than that of nickel.

TABLE 2. DISTRIBUTION OF COBALT NITRATE OR NICKEL NITRATE IN *N*-BUTANOL–WATER AT 25.0°C.

(Metals equilibrated separately)

Water phase concentration before extraction		Phases at equilibrium					
		Water phase			Alcohol phase		
C_w', g./liter Metal	HNO$_3$	C_w, Metal	g./liter HNO$_3$	ρ_w, g./ml.	C_0, Metal	g./liter HNO$_3$	ρ_0, g./ml.
			N-Butanol–nickel nitrate–water system				
20	0	21.15	0		0.876	0	
50	0	52.5	0		3.42	0	
100	0	96.5	0		9.76	0	
150	0	152.2	0	1.350	25.25	0	0.888
260.5*	0	244.5	0	1.555	71.50	0	0.996
			N-Butanol–nickel nitrate-water–nitric acid system				
150	197.0	182.5	35.21	1.441	7.25	135.2	0.917
150	49.48	161.2	6.87	1.372	17.37	37.70	0.889
150	98.5	175.5	15.22	1.402	12.49	71.20	0.895
100	197.0	130.0	60.75	1.327	5.46	119.2	0.910
100	49.48	114.2	11.90	1.260	8.93	33.45	0.871
100	98.5	119.5	26.72	1.281	7.18	63.3	0.883
50	98.5	61.3	43.25	1.156	3.44	52.30	0.877
50	197.0	66.6	91.5	1.192	3.73	100.8	0.910
50	49.48	55.2	20.39	1.132	3.17	27.05	0.857
20	98.5	24.90	54.5	1.072	1.40	44.2	0.876
20	197.0	27.45	111.1	1.101	2.34	90.8	0.911
20	49.48	23.15	28.55	1.057	0.948	22.01	0.857
			N-Butanol–cobalt nitrate–water system				
20	0	20.7	0		0.975	0	
50	0	52.0	0	1.118	4.50	0	0.841
105	0	99.6	0		16.00	0	
150	0	145.5	0	1.352	33.05	0	0.913
236*	0	217.0	0	1.503	68.5	0	1.009
			N-Butanol–cobalt nitrate–water–nitric acid system				
150	49.48	151.2	7.52	1.360	21.35	36.3	0.906
150	98.5	167.8	16.05	1.387	16.71	70.0	0.913
150	197.0	188.7	37.60	1.441	10.35	131.6	0.923
100	49.48	107.9	12.05	1.262	10.87	32.7	0.879
100	98.5	113.9	26.68	1.278	9.31	62.95	0.890
100	197.0	122.5	61.0	1.319	6.35	117.5	0.917
50	49.48	54.8	20.45	1.132	3.88	27.00	0.861
50	98.5	58.7	42.80	1.157	3.95	52.20	0.880
50	197.0	65.1	90.80	1.188	4.375	100.0	0.910
20	49.48	23.21	28.05	1.057	0.942	21.75	0.856
20	98.5	23.95	55.5	1.069	1.645	44.1	0.876
20	197 0	26.80	110.1	1.101	2.66	91.0	0.912

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*Water phase saturated with metal nitrate before extraction.

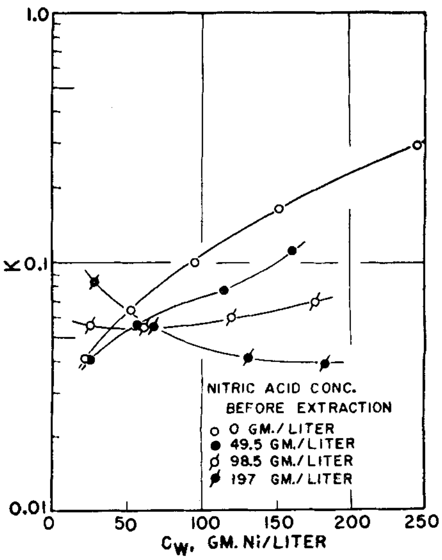

Fig. 3. Effect of nitric acid in the system nickel nitrate-water-nitric acid-*n*-butanol at 25.0°C.

If the distribution coefficient is assumed to follow the equation

$$K' = C_0/(C_w)^n \qquad (1)$$

than a log-log plot of C_0 vs. C_w should be a straight line with slope *n*. Plots of the cobalt nitrate and nickel nitrate data give straight lines which are almost parallel with an *n* value of 1.69 for cobalt and 1.82 for nickel. The chloride data (*3*) give slopes of about 7 for both cobalt and nickel. The values for the nitrates

Table 3. Distribution in the System: *N*-Butanol-Nickel Nitrate-Cobalt Nitrate-Water at 25.0°C.

(One run made with nitric acid as an additive)

Water phase before extraction C_w', g./l. Co	Water phase before extraction C_w', g./l. Ni	Phases at equilibrium C_w, g./l. Co	Phases at equilibrium C_w, g./l. Ni	Phases at equilibrium C_w, g./l. Co and Ni	Density ρ_w, g./ml.	Density ρ_0, g./ml.	K Co	K Ni	β, K_{Co}/K_{Ni}
20	20	21.4	21.9	43.3	1.069	0.8361	7.77×10^{-2}	6.30×10^{-2}	1.233
50	50	47.3	51.2	98.5	1.027	0.8641	1.51×10^{-2}	1.20×10^{-1}	1.258
100	100	92.0	97.7	189.7	1.445	0.9586	2.73×10^{-1}	2.15×10^{-1}	1.270
100	25	97.3	26.4	123.7	1.293	0.8887	1.84×10^{-1}	1.46×10^{-1}	1.260
25	100	25.2	99.8	125.0	1.293	0.8768	1.84×10^{-1}	1.44×10^{-1}	1.278
50*	50*	56.1	57.2	113.3	1.278	0.8880	7.78×10^{-2}	6.14×10^{-2}	1.266

*98.5 g. HNO_3/liter before extraction.

which are near 2 might possibly be explained by dissociation of the salt in the aqueous phase. However the real significance of these *n* values is not yet apparent.

Runs made at different temperatures show that the *K* vaules for cobalt and nickel both decreased by approximately 30% in going from 5.5° to 69.5°C. (*1*) with little effect on the separation factor of *K* of cobalt over *K* of nickel. The data for the sulfates (*7*) show the reverse trend with the *K* values approximately doubling in this temperature range.

Additives

Data where additives were put into the *n*-butanol–metal nitrate–water system are plotted in Figure 2 for nickel (*1*), and the curve for no additives from Figure 1 is shown for comparison. A plot of the cobalt data gave very similar curves. The data show that the additive cupric nitrate has the largest effect, approximately doubling the *K* value. A mixture of nitric acid and sodium chloride decreased the *K*, and other additives such as calcium nitrate, calcium chloride, sodium nitrate, and ferric nitrate had little effect (*1*).

Since the cobalt and nickel nitrate salts would often occur in nitric acid solution, data were obtained for nitric acid as an additive; this also allows comparison with other studies where the acid counterpart of the anion of the cobalt and nickel salts was used. Figure 3 for nickel shows the effect of initial nitric acid concentration on the *K* value. Initial rather than equilibrium acid concentrations were used as parameters, since it is extremely difficult to control experimentally the final equilibrium acid concentrations. A similar type of plot for cobalt, which is not shown, gave the same trends as nickel. At low metal concentrations the *K* value increases with increasing acid concentration, but at higher metal concentrations the trend reverses and *K* decreases with increasing nitric acid concentration. These effects are quite different from the sulfate system, where the *K* of both cobalt and nickel sulfate increased a hundredfold in going from low to high sulfuric acid concentrations. In the chloride system the *K* and the separation factor also increased greatly with increases in hydrochloric acid concentration.

Distribution Coefficient for Nitric Acid

The distribution coefficient data for nitric acid in the presence of nickel nitrate (Table 2) are plotted in Figure 4. This plot shows a very large increase in *K* with increasing nickel concentration in the aqueous phase with *K* values over 5. A similar curve is obtained when only cobalt nitrate is present, an indication of a very high extraction of nitric acid by *n*-butanol with metals present. This could be the basis for a good extraction process to recover nitric acid from aqueous salt solutions. Methods such as distillation or addition of a second solvent might then be tried to recover the acid from the *n*-butanol solvent, but further research would be needed. At zero concentration of metal the *K* value approaches approximately 0.7.

N-BUTANOL–COBALT NITRATE–NICKEL NITRATE–WATER SYSTEM

Distribution Coefficients

In Table 3 the *K* values are given for the complex system *n*-butanol–cobalt nitrate–nickel nitrate–water. The absolute concentrations of the cobalt and nickel were varied fivefold, and the ratio of concentration of cobalt to nickel was varied from 4 : 1 to 1 : 4. Only one run was made with nitric acid present.

In Figure 5 the *K* value of nickel from Table 3 is plotted vs. the total cobalt plus nickel concentration in the water at equilibrium. For comparison curves *A* and *B* from Figure 3 are shown for nickel when equilibrated in the absence of the cobalt. A similar type of plot for cobalt, which is not shown, was made, the *K* of

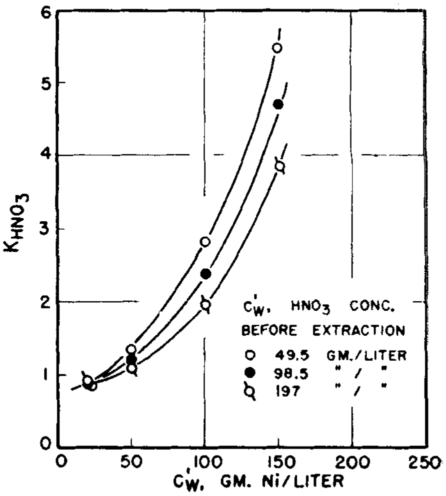

Fig. 4. Distribution coefficient of nitric acid in the system nickel nitrate–water–nitric acid–*n*-butanol at 25.0°C.

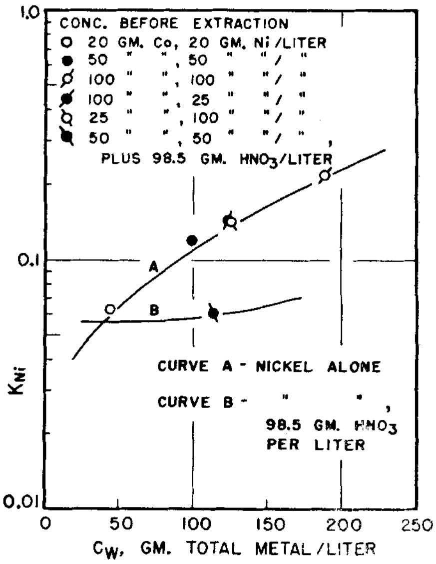

Fig. 5. Distribution coefficient of nickel nitrate in the system nickel nitrate–cobalt nitrate–water–*n*-butanol at 25.0°C.

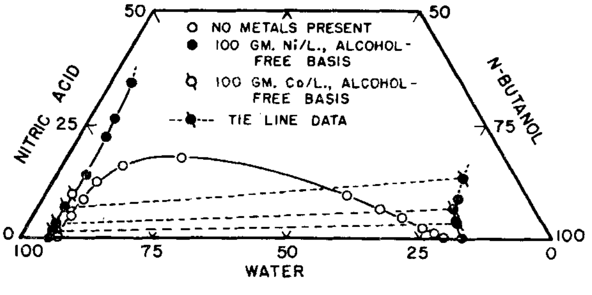

Fig. 6. Phase diagram for the system nitric acid–water–*n*-butanol at 25.0°C. (Data on a weight-percentage metal-free basis.)

cobalt being plotted vs. the total metal concentration in the water at equilibrium. This gave the same trends as nickel. That the distribution coefficient of cobalt or nickel in a mixture of the two depends only on the total metal concentration is concluded.

Separation Factors

When cobalt and nickel were equilibrated separately with no nitric acid present, and the initial concentration was 100 g. each metal/liter, the calculated separation factor was a maximum at 1.49. When the two metals were equilibrated together, the actual separation factor was 1.27 for the same concentrations. Hence having both metals present decreased the maximum separation factor by about 15%. These separation factors in Table 3 are all low and constant at about 1.26. The separation factor for sulfates increased slightly when the metals were equilibrated together and was between 1.2 to 1.5 depending on the sulfuric acid concentration (*7*). The separation factor for the chlorides increased very greatly with increases in hydrochloric acid concentration (*3*).

Phase Diagram

The phase diagram (Figure 6) is shown for the ternary system *n*-butanol–nitric acid–water on a metal-free basis; it is very similar to the *n*-butanol–sulfuric acid–water system (*8*). When the metal salts cobalt or nickel nitrate are present, the solubilities of the alcohol in the aqueous phase and the aqueous phase in the alcohol phase are lowered and change the phase diagram markedly (Figure 6). Densities were determined and reported in Tables 2 and 3 and elsewhere (*6*).

Inspection of experimental phase solubility and tie line data, reported elsewhere (*1*) and used to plot Figure 6 show that the ratio of the nitric acid content to the water content in the phases at equilibrium are as follows. In the aqueous phase the ratio varies from 0.03 to 0.08 depending on the concentration of nitric acid. In the organic phase the ratio is about 0.2 to 0.8. Hence at equilibrium the nitric acid to water ratio is considerably higher in the organic than in the aqueous phase, and the acid is extracted preferentially by the organic solvent.

Using the triangular diagram (Figure 6) and Figures 1, 3, 4, or 5 one can predict the compositions and amounts of the two phases resulting from the equilibrium of equal volumes of an aqueous solution and the solvent. Density data can then be used to calculate relative volumes of the resultant equilibrium solutions.

ACKNOWLEDGMENT

Grateful acknowledgement is made to the American Cyanamid Company for their fellowships which aided in this work.

NOTATION

C = concentration, g. metal/liter (not g. metal salt/liter)
C_0 = equilibrium concentration of metal or nitric acid in organic phase, g./liter
C_w = equilibrium concentration of metal or nitric acid in aqueous phase, g./liter
C_w' = concentration of metal or nitric acid in aqueous phase before extraction, g./liter
K = distribution coefficient, C_0/C_w
K' = distribution coefficient, $C_0/(C_w)^n$
n = constant

Greek Letters

β = separation factor = K(cobalt)/K(nickel)
ρ_0 = density of organic phase at equilibrium, g./ml.
ρ_w = density of aqueous phase at equilibrium, g./ml.

LITERATURE CITED

1. Geankoplis, C. J., and E. J. Scharf, *Doc.* 5827, A.D.J. Auxiliary Publications Project, Washington, D. C.; $1.25 for photoprints or 35-mm. microfilm.
2. Gagnon, J., *Chemist Analyst*, No. 1, **43**, 15 (1954).
3. Garwin, Leo, and A. N. Hixson, *Ind. Eng. Chem.*, **41**, 2298, 2303 (1949).
4. Moore, T. E., R. J. Laren, and P. C. Yates, *J. Phys. Chem.*, **59**, 90 (1955).
5. Rigamonti, R., and E. Spaccemela-Marchetti, *Chim. e ind. (Milan)*, **36**, 91 (1954).
6. Scharf, E. J., Ph.D. dissertation, Ohio State Univ., Columbus, Ohio (1957).
7. Schlea, C. S., and C. J. Geankoplis, *Ind. Eng. Chem.*, **49**, 1056 (1957).
8. Schlea, C. S., Ph.D. dissertation, Ohio State Univ., Columbus, Ohio (1955).
9. Snell, F. D., and C. T. Snell, "Colorimetric Methods of Analysis," 3 ed., Vol. II, p. 346, D. Van Nostrand, New York (1948).
10. Templeton, C. C., and L. K. Daly, *J. Am. Chem. Soc.*, **73**, 3989 (1951).
11. ———, *J. Phys. Chem.*, **56**, 215 (1952).
12. Yoe, J. H., "Photometric Chemical Analysis," Vol. I, p. 172, John Wiley, New York (1948).

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Heat and Mass Transfer from Wall to Fluid in Packed Beds

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Experiments of heat and mass transfer from the tube wall to the fluids flowing through the packed beds were carried out separately. In heat transfer air was used as the fluid, and several kinds of solid particles with low and high thermal conductivities were investigated to determine effective thermal conductivities and wall heat transfer coefficients. In mass transfer the dissolution rate of the coated material on the inner wall of the packed tube to the water stream was measured, and wall mass transfer coefficients were analyzed. It was found that a close similarity exists between the J_H and J_D factor for the wall coefficients in the turbulent-flow region.

The rate of heat transfer in a packed bed is of particular interest in the process design not only of heat exchangers but also of catalytic reactors. The problem of the rate of heat transfer from the tube wall to a fluid flowing through a packed tube has been the subject of considerable study. The first work of heat transfer in a packed bed was made by Colburn (*6*) in 1931. He correlated the data as the over-all heat transfer coefficients, which are similar to those for an empty tube. Thereafter several investigators (*4, 12, 13*) reported the correlations for over-all coefficients.

For the calculation of the temperature distributions and explanation of the mechanism of heat transfer in the bed, the concept of the so-called "effective thermal conductivity" was introduced. Smith et. al. (*21*) determined values of the local effective thermal conductivity in the packed bed and found that the resistance to heat transfer increased greatly near the wall. Hatta and Maeda (*15*), Coberly and Marshall (*5*), and later workers (*2, 9, 18, 19, 23*) found that an additional resistance to heat transfer existed at the wall. They assumed the effective thermal conductivity to be constant within the bed and expressed the additive effect in the wall vicinity as the wall heat transfer coefficient.

This paper reports the results of both heat and mass transfer from the wall of