A CHEMICAL STUDY OF SOME SYNTHETIC POTASSIUM-HYDRONIUM JAROSITES

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ABSTRACT

Jarosite was synthesized at 25° C and 1 atm. Results indicate that potassium-rich jarosites are formed from solutions with $a_{K^+}/a_{H_3O^+}$ as low as 0.3 whereas hydronium substitution for potassium apparently is facilitated at higher temperatures (Kubisz 1964; Brophy & Sheridan 1965). The free energy for jarosite at 25° C, 1 atm is given a value.

INTRODUCTION

Jarosite occurs principally as a secondary mineral in the oxide zone of sulfide deposits and as a constituent of limonitic gossans associated with such deposits. Previous syntheses of jarosite were performed at temperatures and pressures considerably above the surface conditions under which jarosite naturally precipitates (Kubisz 1961*a*,*b*, 1964; Brophy & Sheridan 1965). This study presents results from the synthesis of jarosite from solutions of known chemical compositions at 25° C and 1 atm.

EXPERIMENTAL

Synthesis and chemical analysis

The starting materials for the syntheses were reagent grade K_2SO_4, $FeSO_4.7H_2O$, and $Fe_2(SO_4)_3$ dissolved in known concentrations of H_2SO_4. Table 1 summarizes the experimental conditions. At the end of a run of a few weeks to a few months duration, the jarosite was filtered through a Millipore filter (0.05 μm), washed well with distilled water and air dried.

In order to approach equilibrium from the opposite direction, *i.e.* by solution rather than by precipitation, 0.499 g of a synthesized jarosite (Syn. 4) was placed in a temperature controlled reaction cell in 100 ml 0.005 M H_2SO_4 open to the atmosphere and continually stirred for six months. The solution was analyzed at that time to determine the amount of jarosite that had gone into solution. Syn. 4 was used because there was insufficient synthetic jarosite from any of the other runs. In neither of the

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TABLE 1. CONDITIONS FOR SYNTHESES AND DISSOLUTION EXPERIMENT AT 25° C AND 1 ATM

Syn.	Initial conc. of solution	pH		Eh, mv		Oxidant	Time interval
		Initial	Final	Initial	Final		
2	0.600 M Fe^{2+} 0.200 M K^+ 0.950 M SO_4^{2-}	0.90	1.35	504	692	O_2*	5 weeks
3		0.82	1.02	516	686		4 weeks
4	0.600 M Fe^{2+} 0.200 M K^+ 0.950 M SO_4^{2-}	1.11	1.01	505	681	air*	6 months
5	0.300 M Fe^{2+} 0.100 M K^+ 0.491 M SO_4^{2-}	1.11	1.32	502	676	air	5 months
6	0.060 M Fe^{2+} 0.020 M K^+ 0.095 M SO_4^{2-}	1.72	1.52	516	626	air	6 months
8	0.600 M Fe^{3+} 0.850 M SO_4^{2-}	1.40	—	744	752	air	5 months
diss. ex.	0.005 M SO_4^{2-}	2.11	2.22	736	730	air*	6 months

*Temperature variation estimated ±1° C, other experiments ±3° C.

two types of experiments was equilibrium demonstrated. However, a bracketed value of the free energy of formation of jarosite can be calculated from them and the uncertainty involved, although large, is not excessive in view of the uncertainty in some of the analytical data together with that of the requisite thermodynamic data.

The ionic concentrations in the solutions after Syn. 6 and after the dissolution experiment were measured. These particular runs were chosen because the high ionic strength of the solutions for the other experiments made evaluation of the activity coefficients difficult. The total iron concentration was determined colorimetrically with orthophenanthroline. The sulfate was determined gravimetrically as $BaSO_4$ after the solutions were filtered through a cation exchange resin to remove the potassium and iron ions. An attempt was made to measure the potassium concentration in solution with a cation sensitive electrode but this proved to be impossible due to interfering ions. The K^+ concentration of the synthesis experiment (Syn. 6) was calculated from the volume of solution remaining, the analysis of the jarosite, and the weight of jarosite produced. In the case of the dissolution experiment, the concentration of iron in the solution was used to determine the quantity of jarosite that dissolved; from this the potassium concentration was calculated.

X-ray analysis

The x-ray powder patterns were taken using a 114.6 mm camera with filtered Fe$K\alpha$ radiation. In the calculation of the initial 2θ values, a shrinkage correction was applied (Azaroff & Buerger 1958). The photograph was then completely indexed with hexagonal axes (Hendricks 1937) and a primitive unit cell, using the computer program SPACE written by D. R. Peacor. The lattice parameters were first estimated from the (006) and (220) reflections. After indexing, a least squares refinement was calculated utilizing the computer program of Burnham (1962), which included a systematic absorption term. A weighted mean value for Fe*Kα* (1.93728 Å) was used even in the back reflection region because the back reflection lines were diffuse and in some samples not resolvable. Three parameters were refined by the program: *a*, *c*, and the absorption correction term.

The final refined lattice parameters for the synthetic jarosite are listed in Table 2 with the potassium analyses. The error in the refined lattice parameters was caused in part by the diffusiveness of the lines in the back reflection region. Also, the absorption correction was of the same order of magnitude as the total error.

TABLE 2. CHEMICAL ANALYSES AND REFINED LATTICE PARAMETERS FOR A NATURAL AND SYNTHETIC JAROSITES

Syn.	Wt.%[a] K^+	Eq.[b] K^+	*a*(Å)	*c*(Å)	*c/a*
1[c]	7.1_0	0.91	7.316 ± 0.005	17.179 ± 0.018	2.348
2	7.6_7	0.98	7.328 ± 0.006	17.019 ± 0.019	2.331
3	7.5_8	0.97	7.318 ± 0.002	17.022 ± 0.008	2.326
4	7.6_4	0.98	7.300 ± 0.005	17.066 ± 0.018	2.338
5	7.5_4	0.97	7.342 ± 0.007	17.169 ± 0.019	2.338
6	7.8_2	1.00	7.302 ± 0.003	17.159 ± 0.009	2.349
7[d]	0.0	0.00	7.333 ± 0.004	16.918 ± 0.010	2.307
8[e]	0.0	0.00	7.294 ± 0.003	17.061 ± 0.015	2.339
9[f]	7.82	1.00	7.293 ± 0.004	17.192 ± 0.002	2.357
Nat.[g]	7.35	0.94	7.310 ± 0.005	17.160 ± 0.005	2.347

[a] Analyses for total K^+ performed by Spang Microanalytical Laboratory, Ann Arbor, Michigan; reported to ±0.1%.

[b] Molecular equivalent for potassium in jarosite is 1.00, that not filled by potassium was assumed to be hydronium for the synthetic jarosites.

[c] Jarosite synthesized according to Fairchild (1933).

[d] Pure hydronium end member, synthesized after Shiskin (1951).

[e] Pure hydronium end member, synthesized at 25° C, 1 atm, see Table 1.

[f] Pure potassium end member, synthesized by Brophy & Sheridan (1965) at 114° C.

[g] Natural jarosite, Walim, Poland, Kubisz (1964); the other 0.06 equivalent of univalent cation position is Na^+.

Both Brophy & Sheridan (1965) and Kubisz (1960, 1964) have stated that the lattice parameter *c* or the *c/a* ratio demonstrates the compositional variation in the univalent cation position in jarosite. No such correlation between cell-edge and hydronium-potassium composition was found for these syntheses at 25° C and 1 atm. The lack of correlation between lattice parameter and composition may possibly be due to an anomalous amount of adsorbed water or the formation of a defect structure caused by the substitution of Fe^{2+} for Fe^{3+}. The Eh conditions during the syntheses substantiate that Fe^{2+} or some ferrous complex is the dominant species of iron in solution. In addition, Kubisz & Zabinski (1958) have reported the presence of Fe^{2+} in amounts up to 0.3% in some natural jarosites.

Consideration was given to the possible presence of another phase or possibly a mixture in the synthesized samples; however all the lines on the *x*-ray photographs could be indexed as jarosite lines. Examination of the specific *x*-ray lines suggested by Warshaw (1956) and Kubisz (1962, 1964) as indicative of another phase, did not give evidence for any substance other than jarosite. DTA and IR data on the synthetic jarosites also support this conclusion, but a small amount of impurities, perhaps up to 5%, is still possible.

Discussion

Table 3 enumerates the synthesis conditions for the previous work on the synthetic jarosites. In those syntheses ferric iron was used as the reacting species rather than ferrous iron. However, the cation ratio of 1:3 (K^+:$Fe^{2+,3+}$) was maintained in all the synthetic work. A comparison of Tables 1 and 3 indicates that the difference between the previous investigations and the present study is primarily that of temperature and initial concentration of reacting ions. It is significant that the concentrations and temperatures previously used in the syntheses did not seem geologically reasonable for the surface occurrences of jarosite. This investigation demonstrates that high concentrations and temperatures are not necessary.

TABLE 3. CONDITIONS FOR PREVIOUS SYNTHESES OF VARIOUS POTASSIUM-HYDRONIUM JAROSITES

Jarosite	Initial conc. of solution	Temp., °C	Pressure, atm	Reference
$K_{0.19}(H_3O)_{0.81}$	0.009 M K^+ 0.904 M Fe^{3+} 1.361 M SO_4^{2-}	145	8	Kubisz (1961*a*)
$K_{1.00}$	0.505 M K^+ 1.948 M Fe^{3+} 3.279 M SO_4^{2-}	105	1	Brophy *et al.* (1962)

It was found that the incorporation of potassium into the jarosite structure was consistently greater than that of hydronium even for a ratio $a_{K^+}/a_{H_3O^+}$ in solution as low as 0.3 (*e.g.*, Syn. 6). Kubisz (1961*b*) and Brophy & Sheridan (1965) have shown the same results for higher temperatures with the hydronium activity greater than potassium. However, it appears that perhaps elevated temperatures are required for the synthesis of the hydronium-rich jarosites or solutions very deficient in alkali (Kubisz 1960; 1961*a*,*b*; Brophy & Sheridan 1965). It has been demonstrated also that the pure hydronium jarosite can be synthesized only in the absence of alkali in the temperature range 25–170°C (Shiskin 1951; Shiskin *et al.* 1958; Posnjak & Merwin 1922; this study). These data indicate that the preference for substitution in the jarosite structure is $K^+ \gg H_3O^+$ which is also the frequency of occurrence of these jarosites in nature (Kubisz 1964).

FREE ENERGY OF FORMATION OF JAROSITE

In the following series of calculations, jarosite precipitation and dissolution data from the six month runs are used. The activity of jarosite and water are assumed to be unity. $\gamma_{Fe^{2+}}$ was obtained from the ferrous chloride data (Latimer 1952) and calculated by the mean salt method (Garrels & Christ 1965), $\gamma_{Fe^{3+}}$ was taken from Hem (1960) and Krauskopf (1967), γ_{K^+} and $\gamma_{SO_4^{2-}}$ were obtained from Garrels & Christ (1965) and $\gamma_{HSO_4^-}$ was determined from the data of Sherill & Noyes (1926). The activities of the ions were calculated from the activity coefficients and the determined molalities of the ions. Then, the activity of the sulfate and bisulfate in solution can be calculated from the total sulfate and the second ionization constant for sulfuric acid (Krauskopf 1967). Similarly, the activity of Fe^{3+} and Fe^{2+} can be determined from the measured Eh and total iron. The reference states for the free energy of formation ($\Delta F_f°$) of the compounds are the elements in their standard state at 25° C, 1 atm.

$\Delta F_f°$*(jarosite) as calculated from its formation*

The half-cell reaction for the formation of jarosite may be written as:

$$3Fe^{2+} + HSO_4^- + SO_4^{2-} + K^+ + 13H_2O = KFe_3(SO_4)_2(OH)_6 + 7H_3O^+ + 3e^- \qquad (1)$$

The redox potential for equation (1) is:

$$Eh = E° + \frac{RT}{n\mathfrak{F}} \ln \frac{(a_{H_3O^+})^7}{(a_{Fe^{2+}})^3 (a_{SO_4^{2-}}) (a_{HSO_4^-}) (a_{K^+})} \qquad (2)$$

where Eh is the measured redox potential for the reaction in volts, $E°$ is the redox potential in volts when all ions are at standard activity ($E° = \Delta F_r°/n$), R is the gas constant in kcal/°K, T is temperature °K, n

TABLE 4. DATA FOR THE CALCULATION OF $\Delta F_f°$ (JAROSITE), 1 is ionic strength, a is activity, all values in the table are multiplied by 10^4

Experiment	1	$^*a_{H_3O^+}$	$a_{Fe^{2+}}$	$a_{Fe^{3+}}$	a_{K^+}	$a_{HSO_4^-}$	$a_{SO_4^{2-}}$
synthesis 6	2480	295.	145.	0.53	95.2	285.	121.
dissolution	129	60.3	—	0.50	0.35	6.8	27.5

*Determined from measured pH.

is the number of electrons exchanged, $\mathfrak{F}$ is the faraday constant in kcal/volt g-eg, (a_{K^+}) is the activity of the ionic species, K^+, and $\Delta F_r°$ is the standard free energy of the reaction in kcal/mole. From the data in Table 4 for synthesis 6 and the measured Eh from Table 1, solving for $E°$ in equation (2) at 25° C and 1 atm,

$$E° = 0.624 \text{ v.}$$

$$\text{From } \Delta F°(\text{reaction}) = n\mathfrak{F}E° \text{ (in kcal/mole using above units)}, \tag{3}$$

$$\Delta F°(\text{reaction}) = 43 \pm 19 \text{ kcal/mole for (1).}$$

$$\text{Then } \Delta F_f°(\text{jarosite}) = [(3\Delta F_f°{}_{Fe^{2+}}) + (\Delta F_f°{}_{HSO_4^-}) + (\Delta F_f°{}_{SO_4^{2-}}) + (13\Delta F_f°{}_{H_2O})] - [(7\Delta F_f°{}_{H_3O^+}) - \Delta F°(\text{reaction})]. \tag{4}$$

Obtaining $\Delta F_f°$ for products and reactants at 25° C, 1 atm from Robie & (Waldbaum 1968),

$$\Delta F_f°(\text{jarosite}) = -783 \pm 20 \text{ kcal/mole.}$$

$\Delta F_f°$(jarosite) as calculated from its dissolution to equilibrium

The reaction for the dissolution experiment can be written:

$$K_{0.98}(H_3O)_{0.02}Fe_3(SO_4)_2(OH)_6 + 6.98H_3O^+ = 0.98K^+ + 3Fe^{3+} + HSO_4^- + SO_4^{2-} + 13H_2O. \tag{5}$$

Then the equilibrium constant for the reaction is given by:

$$K = \frac{(a_{K^+})^{0.98}(a_{Fe^{3+}})^3(a_{HSO_4^-})(a_{SO_4^{2-}})}{(a_{H_3O^+})^{6.98}}. \tag{6}$$

From the data in Table 4 for the dissolution experiment, the equilibrium constant is

$$K = 3.205 \times 10^{-8}.$$

The free energy for the reaction is determined by:

$$\Delta F_r° = -RT \ln K \tag{7}$$

and at 25° C and 1 atm

$$\Delta F°(\text{reaction} = -1.364 \log K \text{ (in kcal/mole)}, \tag{8}$$

then $\Delta F°(\text{reaction}) = 10 \pm 5.8$ kcal/mole for (5),
and $\Delta F°(\text{jarosite}) = -763 \pm 6$ kcal/mole.

Discussion

The probable errors above are given at the 95% confidence level. They were calculated as two times the square root of the sums of the squares of the uncertainties in the individual measurements and in the ΔF_f° of the reactants and products (Robie & Waldbaum 1968). The two values for the ΔF_f°(jarosite) suggest that equilibrium was nearly approached from both directions. By comparison, an independent estimate of the ΔF_f°(jarosite) is -798 kcal/mole obtained by summation of the entropies and enthalpies at 25° C, 1 atm of the component oxides as suggested by Fyfe *et al.* (1958) and Helgeson (1969).

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