520. *The Dissolution of Beryllium in Aqueous Solutions of Mineral Acids and Ammonium Fluoride.*

By C. J. Hardy and D. Scargill.

The rates of dissolution of beryllium metal in aqueous solutions of nitric, sulphuric, hydrochloric, and hydrofluoric acid, and of ammonium fluoride, have been measured and the relative rates for equimolar concentrations of the acids under similar conditions found to be $HF > H_2SO_4 \approx HCl > HNO_3$. The rate varies with the source and method of fabrication of the metal. Dissolution of beryllium in nitric acid has been examined in detail as a function of acid concentration, temperature, surface properties of the metal, and the presence of hydrofluoric acid.

Metallic beryllium was first prepared by Wöhler [1] in 1828. Since then many conflicting statements have appeared, particularly in recent textbooks, on the dissolution of the metal in aqueous acids. All the published work has been qualitative and, since the purity of the metal has rarely been stated, impurities may account for much of the conflict in the early work.

Wöhler noted that beryllium powder, prepared by the reduction of beryllium chloride by potassium in a platinum crucible, is readily attacked by dilute hydrochloric or sulphuric acid with evolution of hydrogen, and is dissolved by cold dilute nitric acid with evolution of nitric oxide. Metal prepared by Debray,[2] by passing the chloride vapour over molten sodium, dissolved with difficulty in boiling concentrated nitric acid. Lebeau [3] found that metal produced electrolytically, in a nickel crucible, from the molten double fluoride of beryllium with sodium or potassium readily dissolved in concentrated sulphuric acid, liberating sulphur dioxide, but was only superficially attacked by concentrated nitric acid. Fichter and Jablczynski,[4] and Bodforss,[5] in work reviewed in Gmelin's " Handbuch " [6] state that freshly cleaned beryllium metal undergoes no visible attack by cold

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[1] Wöhler, *Pogg. Annalen*, 1828, **13**, 577.

[2] Debray, " Du Glucinum et ses Composés," Mallet-Bachelier, Paris, 1855; *Compt. rend.*, 1854, **38**, 784; *Ann. Chim.*, 1855, **44**, 1.

[3] Lebeau, *Compt. rend.*, 1898, **126**, 744; *Ann. Chim.*, 1899, **16**, 495.

[4] Fichter and Jablczynski, *Ber.*, 1913, **46**, 1604.

[5] Bodforss, *Z. phys. Chem.*, 1926, **124**, 68.

[6] Gmelin, "Handbuch der Anorganischen Chemie," 8th edn., System-Nummer 26, " Beryllium," Verlag-Chemie, Berlin, 1930, p. 70.

concentrated nitric acid, that reaction in cold 2N-nitric acid occurs at first with evolution of gas that soon subsides, and that hot concentrated or dilute nitric acid rapidly dissolve the metal with the formation of nitric oxide and/or ammonia.

Textbooks by Mellor,[7] Remy,[8] and Sidgwick [9] contain conflicting statements on the dissolution of beryllium in nitric acid, but it appears to be generally accepted that the metal dissolves readily in sulphuric and in hydrochloric acid. We have therefore examined in detail the rate of dissolution of the purest available metallic beryllium in aqueous mineral acids, and particularly nitric acid, under a variety of conditions.

EXPERIMENTAL

Materials.—The beryllium metal used was in the form of sheet, tube, or disc, prepared from beryllium " flake " from the Pechiney Co. (France), or powder from the Brush Beryllium Corporation (U.S.A.). Pechiney " flake " metal is prepared by electrolysis of the mixed chlorides of beryllium and sodium at 350° in a nickel crucible as cathode with a graphite rod anode. The Brush powder is prepared by reduction of beryllium fluoride at 1300° with magnesium. The beryllium sheet was prepared by Metallurgy Division, Harwell, by powdering, sintering, and hot-rolling the Pechiney " flake " to give a laminated product 0·026″ thick with a rough, dark grey surface. Beryllium tube was prepared by the Research and Development Branch, Springfields Works, U.K.A.E.A., from Pechiney powdered " flake " or Brush powder by loose-sintering into billets and extrusion into tubes of 0·3″ internal diameter and 0·04″ wall thickness. The surfaces were dark grey and rough with longitudinal striations. Two batches of tube produced at different times from Brush powder were examined: they are designated A and B below. The beryllium discs were made from Pechiney " flake " by vacuum-melting in a beryllia crucible, casting into an alumina-lined vessel, and extrusion into bars from which the discs were cut (2·44″ in diameter × 0·635″ thick; surface area 14·2 cm.^{2}; 5·4 g.) after removal of surface scale.

Impurities in random samples of the beryllium tube determined by mass-spectrometry by R. & D.B., Springfields Works, U.K.A.E.A., in p.p.m. (except oxygen in % w/w) were as tabulated.

The beryllium sheet contained Cl, ~1100, and Fe, 300—400 p.p.m., and the beryllium discs had approximately the same specification as the Pechiney tube.

														Carbon	
Impurity	O_2 (%)	Fe	Al	Cl	F	Si	Mn	Ni	N	H	Mg	B	Ag	combined	free
Pechiney	0·45 ± 0·09	485	705	<30	90	30	15	45	50	210	<50	—	—	255	210
Brush A	0·50 ± 0·09	800	950	30	50	1020	115	120	95	135	185	0·66	5	315	40
Brush B	0·25 ± 0·05	1100	800	—	90	225	—	—	100	90	350	—	—	365	45

Solutions of nitric, sulphuric, hydrochloric, and hydrofluoric acids were prepared by dilution of "AnalaR " acids with demineralised distilled water.

Apparatus and Procedure.—Samples of metal were dissolved in glass flasks with water-cooled condensers, except that for hydrofluoric acid Polythene vessels were used. Temperatures up to 75° were thermostatically controlled in a water-bath, and a boiling-water bath was used for experiments at 97° ± 1°. Temperatures above 100° were measured under reflux. The samples were suspended in the solutions in stainless-steel or platinum mesh cages. The amount of beryllium dissolved was determined by weighing, after washing them with water and acetone, and drying in a stream of hot air. Rates of dissolution were calculated in mg. cm.$^{-2}$ min.$^{-1}$ based on the initial geometrical surface area measured by steel rule and micrometer. All the experiments refer to dissolution in an unstirred system. However, a sample of Pechiney beryllium tube gave an identical dissolution rate in 12M-nitric acid at 97° whether unstirred or stirred at 600 r.p.m.; hence a diffusion barrier does not appear to be set up under these conditions. A 20-fold molar excess of acid was used except where otherwise stated.

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[7] Mellor, " A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, London, 1946, Vol. IV.

[8] Remy, " Treatise on Inorganic Chemistry," Elsevier Publ. Co., Amsterdam, 1956, p. 249.

[9] Sidgwick, " Chemical Elements and their Compounds," Oxford, 1950, Vol. I.

RESULTS AND DISCUSSION

Dissolution of Beryllium Sheet and Tube in Nitric Acid.—The rate of dissolution of the Pechiney beryllium sheet and Brush beryllium tube A during the first 0·5—1 hr. was usually greater than the final constant value (as shown in curve 1 of Fig. 3). This is thought to be due to the surface film or scale, and later samples of Brush beryllium tube B and Pechiney tube did not show this effect, possibly because of improved fabrication techniques. Rates of dissolution for a range of acid concentrations and temperatures are given in Tables 1 and 2, together with the initial rates and amounts dissolved before the constant rates were reached. The constant rates of dissolution of beryllium sheet and tube are plotted against the nitric acid concentration in Fig. 1 and against the temperature in Fig. 2. The constant rates for the tube are generally lower than for the sheet but follow the same trends, being approximately independent of acid concentration from 6M to 14M, and increasing markedly with temperature.

TABLE 1. *Dissolution of Pechiney beryllium sheet in nitric acid.*

		Initial variable dissolution rate			Final constant dissolution rate	
HNO_3 concn. (moles/l.)	Dissn. temp.	Time (hr.)	Wt. dissolved (%)	Average rate (10^{-2} mg. cm.$^{-2}$ min.$^{-1}$)	Wt. % dissolved/hr.	Rate (10^{-2} mg. cm.$^{-2}$ min.$^{-1}$)
1	~97°	0·75	2·5	3·14	1·75	1·67
2	,,	0·75	2·0	2·54	1·75	1·67
4	,,	1·0	7·4	7·03	4·33	4·14
6	,,	1·0	8·2	7·8	5·5	5·2
8	,,	0·5	2·5	4·73	3·75	3·55
8	,,	—	—	—	6·0	5·0
10	,,	0·75	5·0	6·3	5·6	5·25
12	,,	1·0	13·0	12·2	8·0	7·53
14	,,	1·0	10·75	10·2	6·25	5·95
8	25	—	—	—	0·08	0·06
8	50	—	—	—	0·33	0·307
8	75	—	—	—	2·5	2·28
14	25	—	—	—	0·125	0·118
14	50	—	—	—	0·80	0·752
14	75	—	—	—	3·0	2·8

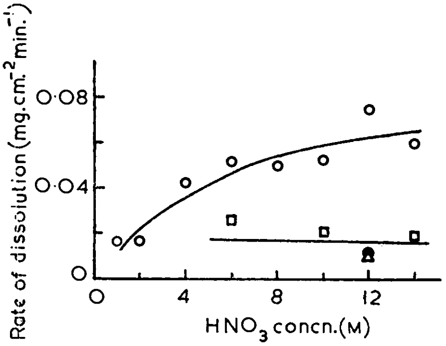
TABLE 2. *Dissolution of Brush beryllium tube A in nitric acid.*

		Dissolution rate in first hour		Constant dissolution rate	
HNO_3 concn. (moles/l.)	Dissn. temp.	Wt. dissolved (%)	Average rate (10^{-2} mg. cm.$^{-2}$ min.$^{-1}$)	Wt. % dissolved/hr.	Rate (10^{-2} mg. cm.$^{-2}$ min.$^{-1}$)
6	approx. 97°	6·5	10	1·7	2·6
10	,,	5·2	7·9	1·4	2·1
14	,,	5·4	8·25	1·27	1·94
14	50	1·5	2·3	0·3	0·46
8	115 (reflux)	7·5	11·4	1·75	2·68
12	123 (reflux)	7·8	11·8	2·4	3·65

The removal of the surface film or scale was examined in an attempt to understand the difference between the initial and the final rate of dissolution, and to reduce the large amount of beryllium rapidly dissolved at high temperature and high acidity. The dissolution of an untreated Brush beryllium tube A as a function of time is compared in Fig. 3 with the dissolution of tubes treated as follows: (2) descaled with a solution 2M in nitric and 0·05M in hydrofluoric acid at 20°, and (3) chemically " polished " with chromic oxide–phosphoric acid–sulphuric acid at about 60° for 5 min., which gave a smooth, bright, silvery surface. The dissolution rates of the descaled tubes were constant from the start and almost the same as the final constant rate of the untreated tube. The mechanism of dissolution at high temperature cannot simply be an initial fast removal of scale because only 3 wt. % of the tube was removed in descaling process (2), whereas amounts up to 8%

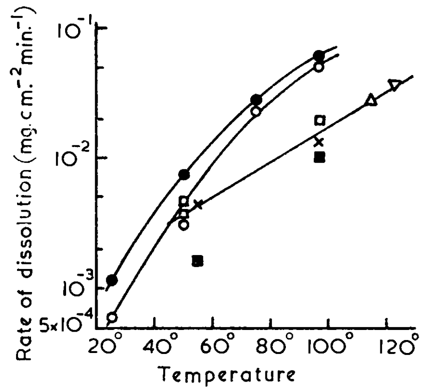
were removed at the rapid rate (Table 1) at high temperature from untreated tubes. The dissolution rate of the chemically polished tube is lower than that of the descaled tube owing to the lower acidity used in the dissolution of the former and the rougher surface of the latter. The rate of the polished sample increased slightly with time as the surface became etched and pitted ($5{\cdot}8 \times 10^{-3}$ for the first hour and $6{\cdot}8 \times 10^{-3}$ mg. cm.$^{-2}$ min.$^{-1}$ after the first hour).

FIG. 1. *Variation of the dissolution rate of beryllium with nitric acid concentration at 97°.*



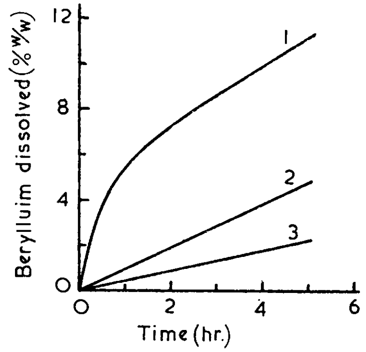
○ Pechiney beryllium sheet; ● Pechiney beryllium tube; □ Brush beryllium tube A; △ Brush beryllium tube B.

FIG. 2. *Variation of the dissolution rate of beryllium with temperature.*



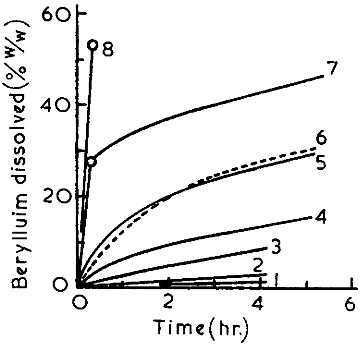
○ Pechiney beryllium sheet, 8M-HNO$_3$; ● Pechiney beryllium sheet, 14M-HNO$_3$; × Pechiney beryllium tube, 12M-HNO$_3$; ■ Brush beryllium tube B, 12M-HNO$_3$; △ Brush beryllium tube A, 8M-HNO$_3$; ▽ Brush beryllium tube A, 12M-HNO$_3$; □ Brush beryllium tube A, 14M-HNO$_3$.

FIG. 3. *Dissolution of untreated and descaled Brush beryllium tube* A *in nitric acid.*



1, Untreated, 14M-HNO$_3$ at 97°. 2, Descaled in 2M-HNO$_3$–0·05M-HF, then 14M-HNO$_3$ at 97°. 3, Chemically polished, 6M-HNO$_3$ at 97°.

FIG. 4. *Effect of hydrofluoric acid on the dissolution of Pechiney beryllium tube in* 14M-HNO$_3$ *at* 50°.



1, No HF; 2, 0·001M-HF; 3, 0·01M-HF; 4, 0·05M-HF; 5, 0·1M-HF; 6, 0·01M-HF–12M-HNO$_3$, 97°; 7, 0·25M-HF; 8, 0·5M-HF.

○ indicates that temperature increased to near the b. p.; samples were removed for weighing after reaction abated, and solution was cooled to 50° before continuation.

Effect of Hydrofluoric Acid on the Dissolution of Beryllium in Nitric Acid.—The effect of hydrofluoric acid in 14N-nitric acid at 50° on the dissolution of Pechiney beryllium tube is shown in Fig. 4. Above 0·1M-hydrofluoric acid the reaction became very vigorous and caused the temperature to rise almost to the b. p. The rate of dissolution in solutions containing >0·01M-hydrofluoric acid was initially fast but became constant at about 0·04 mg. cm.$^{-2}$ min.$^{-1}$. This did not occur, however, until the molar ratio Be : HF in solution exceeded 3. This effect was more pronounced at 97°, where the rate for 0·01M-hydrofluoric in 12M-nitric acid is equal to that for 0·1M-hydrofluoric acid at 50°. The reaction was very vigorous with 0·05M-hydrofluoric acid at 97°, and the temperature rapidly increased to the b. p.

Dissolution of Beryllium in Aqueous Sulphuric, Hydrochloric, and Hydrofluoric Acid.—Brush beryllium tube A dissolved rapidly in 3M-sulphuric acid at 50° with evolution of hydrogen, and the temperature rapidly increased to the b. p. The dissolution rate was 13 mg. cm.$^{-2}$ min.$^{-1}$. The reaction was also fast when started at room temperature, because the temperature also rose rapidly to the b. p. The molar ratio of acid used to beryllium dissolved was 0·75.

Samples of Pechiney beryllium tube, Brush tube B, and Pechiney discs were partially dissolved in N-sulphuric-, hydrochloric-, and hydrofluoric-acid at 30—33° and gave the following dissolution rates (mg. cm.$^{-2}$ min.$^{-1}$):

FIG. 5. *Variation of the dissolution rate of Pechiney beryllium tube with hydrofluoric acid concentration in* 14M-HNO$_3$ *at* 50°.

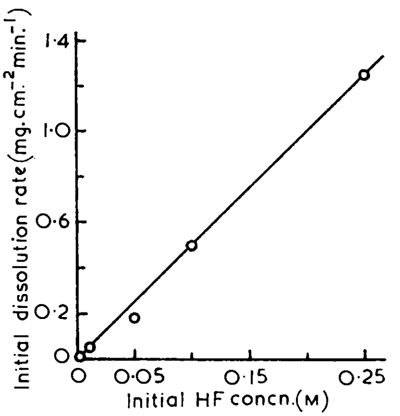
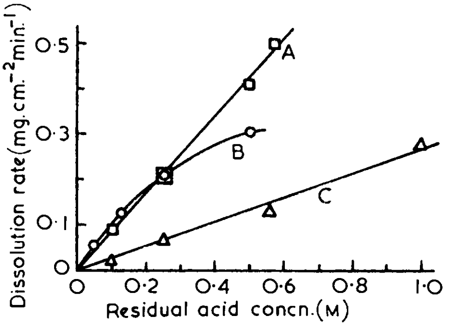


FIG. 6. *Dissolution of Pechiney beryllium discs in* N-*aqueous mineral acids at* 30—33°.



A, HF. B, H$_2$SO$_4$. C, HCl.

	Initial dissolution rate		
	1 N-H$_2$SO$_4$	1 N-HCl	1 N-HF
Pechiney tube	0·37	0·54	1·0
Brush tube B	0·24	0·16	0·8
Pechiney disc	0·31	0·28	0·8

The dissolution rate decreased linearly with decreasing acid concentration for both hydrochloric and hydrofluoric acid, but non-linearly for sulphuric acid (Fig. 6). The dissolution rate in hydrochloric acid fell to zero at the theoretical equivalence point given by the equation, $Be + 2HCl \longrightarrow BeCl_2 + H_2$, but at the equivalence point in hydrofluoric acid, dissolution continued at a constant rate of 0·03 mg. cm.$^{-2}$ min.$^{-1}$ until 0·6 g.-atom of Be had dissolved per mole of acid, and similarly in sulphuric acid until 1·15 g.-atoms had dissolved.

The differences in rate for the different samples are probably mainly due to structural differences arising in the beryllium during fabrication, since the attack by the acid caused particles to break away from the surface, giving a black suspension. The surface of the Pechiney tube was pitted to a greater extent than the surfaces of the other samples at the end of the dissolution period.

The relative rate of dissolution of a given sample of beryllium in equimolar solutions of various mineral acids under similar conditions is therefore $HF > H_2SO_4 \sim HCl > HNO_3$.

Dissolution of Beryllium in Aqueous Ammonium Fluoride.—The dissolution of Brush beryllium tube A in 5M-ammonium fluoride is fairly rapid, with evolution of hydrogen at initial rates of 0·6 and 2·4 mg. cm.$^{-2}$ min.$^{-1}$ at 50° and 97° respectively. The rate of dissolution at 50° decreases exponentially with time and approaches zero as the molar ratio of fluoride to dissolved beryllium approaches 4. However, at 97° a precipitate was formed and the final molar ratio tended towards 3. The molar ratios of dissolved beryllium, ammonium fluoride consumed, hydrogen evolved, and ammonia produced were therefore quantitatively determined as 1 : 3·96 : 0·96 : 1·9, which indicates the reaction:

$$Be + 4NH_4F + 2H_2O \longrightarrow (NH_4)_2BeF_4 + H_2 + 2NH_4{\cdot}OH$$

Since at 97° the reaction tends to go further with the formation of a precipitate, it seems probable that beryllium hydroxide is formed, thus liberating more ammonium fluoride for further attack of the beryllium, *e.g.*, $(NH_4)_2BeF_4 + 2NH_4{\cdot}OH \longrightarrow 4NH_4F + Be(OH)_2$.

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