

## USE OF MERCURIC BROMIDE AS A HEAVY LIQUID

DAVID E. GRANDSTÄFF, *Department of Geological and Geophysical Sciences, Princeton University, Princeton, New Jersey 08540*

### ABSTRACT

Molten mercuric bromide ( $\text{HgBr}_2$ ) has been used as a heavy liquid for separating high density minerals. The liquid has a density of  $5.08 \text{ gm/cm}^3$  at  $250^\circ \text{C}$ .

A method has been developed using mercuric bromide ( $\text{HgBr}_2$ ) as a heavy liquid in the separation of high density minerals. Mercuric bromide, a solid at room temperature, has a melting point of  $236^\circ \text{C}$  and a boiling point of  $322^\circ \text{C}$ . Mercuric bromide is moderately soluble in hot water and ethanol, and is highly soluble in methanol (Weast, 1966). The density of liquid mercuric bromide as a function of temperature ( $d_T$ ) is given by the equation  $d_T = 5.8889 - 0.0032331 T$  ( $^\circ \text{C}$ ) for the interval  $236\text{--}321^\circ \text{C}$  (Janz and McIntyre, 1962). This yields a density of  $5.08 \text{ gm/cm}^3$  at  $250^\circ \text{C}$ .

### TECHNIQUE

Two variations in technique were tried. In the first, a heavy walled glass tube about five inches long was sealed at one end. Mercuric bromide was interlayered with mineral crystals in the tube. The open end was then sealed. The closed tube was suspended entirely in an oil bath and heated to  $250\text{--}260^\circ \text{C}$ . The liquid was agitated by quickly inverting the tube and by tapping it against the sides of the oil bath.

In the second method, an open tube was used, and the mineral grains could then be stirred with a heated glass rod. This method has the disadvantage of allowing toxic mercuric bromide vapor to escape, but allows better agitation of the liquid and thus more complete mineral separation. Escape of the mercuric bromide vapor was minimized by allowing the test tube to protrude far above the surface of the oil bath. Thus, most of the escaping vapor condensed onto the sides of the test tube above the level of the oil bath. During a normal separation about 5 percent of the mercuric bromide was volatilized. Only about 0.3 percent escaped the tube entirely, the remainder recondensing onto the sides of the tube. This did not have any apparent effect on the mineral separation. All separations were done in a fume hood to minimize the danger from toxic mercuric bromide vapor.

After separation of the phases the tube was raised out of the oil bath and allowed to cool quickly to prevent denser mercuric

bromide crystals that were solidifying at the liquid-air interface from dragging floating mineral grains downward.

After cooling, the tube was scored and broken transversely between its base and the top of the mercuric bromide layer. This separated the denser crystals which had settled to the bottom of the tube from the less dense crystals which had floated to the surface of the liquid. The two halves of the tube were placed in separate beakers, and the mercuric bromide was dissolved in methanol.

By evaporation of the solvent the mercuric bromide can be recrystallized and reused. Mercuric bromide contains filaments of insoluble material; however, these filaments can be swirled into suspension, decanted, and filtered without loss of separated material. The mercuric bromide was not observed to attack or etch any of the minerals separated by this method, but it did attack the surface of aluminum weighing pans.

Liquid mercuric bromide is fluid enough for mineral separations to take place quickly. 0.1 to 0.5 mm grains were usually separated within 10 minutes. Although mercuric bromide liquid is nearly opaque, the extent of the separation can be observed by raising the tube momentarily out of the oil bath and shining a strong light through the liquid. This silhouettes suspended mineral grains. The entire procedure requires less than three hours.

The  $\text{HgBr}_2$  molecule is the predominant species in the solid, liquid, and vapor. The principal dissociation reaction is probably  $2\text{HgBr}_2 = \text{HgBr}^+ + \text{HgBr}^-$  (Thorne and Roberts, 1954). However, dissociation is slight. For example, in the liquid, the degree of dissociation at  $250^\circ\text{C}$  is  $2 \times 10^{-8}$  (Durrant and Durrant, 1962). For the reaction  $\text{HgBr}_2 = \text{Hg} + \text{Br}_2$ , releasing free mercury vapor, the degree of dissociation at  $250^\circ\text{C}$  calculated from thermochemical data (Stull, 1965) is approximately  $3 \times 10^{-14}$ . The calculated dissociation does not increase significantly below  $322^\circ\text{C}$ , the boiling point of mercuric bromide. Therefore, there is probably little physiological danger from elemental mercury released due to dissociation of mercuric bromide. However, mercuric bromide is highly toxic and care must be exercised in its use.

## RESULTS

Table 1 gives the densities of several heavy minerals, indicating those which may be separated by this technique. This technique has been used to separate uraninite from zircon in artificial mixtures, and to separate monazite, uranothorite, microlite, and polycrase from a fluvial sand from British Columbia. The artificial mixture yielded

Table 1. Representative Heavy Minerals

	density (gm/cm <sup>3</sup> )	references*
uraninite	7.5 - 9.7	1
galena	7.5	2
microlite	4.3 - 5.7	1
euxenite	5.0 - 5.9	3
thorite	5.2 - 5.4	1
monazite	5.2 - 5.4	1
hematite	5.25 (usually less)	2
magnetite	5.2	2
mercuric bromide	5.08 (250° C)	
pyrite	4.95 - 5.03	2
ilmenite	4.7 - 4.78	2
zircon (non-metamict)	4.6 - 4.7	2
rutile	4.23 - 5.5	2
garnet	3.58 - 4.32	2
forsterite	3.22	2
diopside	3.22	2
apatite	3.1 - 3.35	2
hornblende	3.02 - 3.45	2

\*references for densities

1. Frondel, 1958
2. Deer, Howie, and Zussman, 1966
3. Weast, 1966

virtually pure mineral separates (>99 percent). Contamination of the dense fraction of the separated fluvial sand with minerals of density less than 5.1 was also minor. Pyrite was the major contaminant with subsidiary zircon and ilmenite. Although these three minerals represented about 90 percent of the material introduced into the mercuric bromide liquid, they usually represented no more than 4 percent of the material in the dense fractions obtained in a single stage separation.

## ACKNOWLEDGMENTS

The author acknowledges the receipt of an N.D.E.A. Fellowship and the financial support of the Department of Geology. Dr. H. D. Holland critically

reviewed the manuscript and made numerous helpful suggestions for its improvement.

## REFERENCES

- DEER, W. A., R. A. HOWIE, AND J. ZUSSMAN (1966) *An Introduction to the Rock-Forming Minerals*. Wiley, New York, 528 p.
- DURRANT, P. J., AND B. DURRANT (1962) *Introduction to Advanced Inorganic Chemistry*. William Clowes and Sons, Limited, London, 1171 p.
- FRONDEL, C. (1958) Systematic mineralogy of uranium and thorium. *U. S. Geol. Surv. Bull.* 1064, 400 p.
- JANZ, G. J., AND J. D. E. MCINTYRE (1962) Mercuric halides as molten electrolytes: physical properties, vibrational spectra, constitution, and electrical conductance. *J. Electrochem. Soc.* 109, 842-849.
- STULL, D. R., (1965) JANAF Thermochemical Tables. *U. S. Nat. Tech. Inform. Serv.* PB 168 370.
- THORNE, P. C. L., AND E. R. ROBERTS (1954) *Inorganic Chemistry*. Oliver and Boyd, London, 955 p.
- WEAST, R. C., ed. (1966) *Handbook of Chemistry and Physics, 47th ed.* Chemical Rubber Co., Cleveland.

*American Mineralogist*  
Vol. 57, pp. 1902-1908 (1972)

THE EFFECT OF REDUCED H<sub>2</sub>O FUGACITY ON THE BUFFERING  
OF OXYGEN FUGACITY IN HYDROTHERMAL EXPERIMENTS

JAMES A. WHITNEY, *Dept. of Geology, Stanford University,  
Stanford, California 94305*

## ABSTRACT

The effect of varying H<sub>2</sub>O fugacity on the oxygen fugacity in hydrothermal experiments is analyzed for both the solid external buffer and the controlled hydrogen pressure methods. Lowering of H<sub>2</sub>O fugacity in the experimental charge either by a second species in the vapor phase, or by the absence of a free vapor phase, lowers the oxygen fugacity in the charge.

## INTRODUCTION

Within the last fifteen years, great strides have been made in the study of the geochemistry of elements with variable oxidation states by means of the solid buffer technique (Eugster, 1957) and by the use of gas mixtures (Shaw, 1967). One of the basic assumptions inherent in the use of these buffering techniques to control oxygen fugacity is that the charge contains abundant water. (Shaw, 1967; Eugster, 1957) Recently, experiments have been conducted in which the availability of water has been purposely limited (Whitney and