Solution to the beryllium valence challenge

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Solution

The quest in this column is to elucidate the valence of beryllium from the density measurements of the *soluble* chlorides, as suggested by Mendeleev in 1889 [1, 2]. From the composition of beryllium oxide we gather that the atomic weight of beryllium is either 9 or 13.5 Da, depending on the valence of beryllium, or simply $4.5x$ Da where x is the valence [2]. Now, it is known that solutions of beryllium chloride, prepared by dissolving 2.00 g and 3.00 g anhydrous salt in 90.0 g water, have densities 1.0138 and 1.0211 g mL^{-1} , respectively at 15°C . Because dilute equimolar solutions of metal chlorides will have densities increasing in the order of their molecular weights it is necessary to calculate the amount of beryllium chloride in these two solutions:

$$n_1(\text{BeCl}_x) = \frac{2.00 \text{ g}}{(4.5x + 35.5x) \text{ g mol}^{-1}} = 0.050 \cdot x^{-1} \text{ mol},$$
$$n_2(\text{BeCl}_x) = \frac{3.00 \text{ g}}{(4.5x + 35.5x) \text{ g mol}^{-1}} = 0.075 \cdot x^{-1} \text{ mol}.$$

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In both cases the amount of water is $90.0 \text{ g}/18.0 \text{ g mol}^{-1} = 5.00 \text{ mol}$. If $x=2$, the first solution has 200 mol water per mol BeCl_2 . If, however, $x=3$, the second solution has exactly 200 mol water per mol BeCl_3 . Now we need to compare the densities of these solutions with those of KCl ($M=75$), MgCl_2 ($M=93$), CaCl_2 ($M=111$), and MnCl_2 ($M=126$), all containing 200 mol (3600 g) water per mol salt. The mass fraction of chlorides in such solutions is:

$$w(\text{KCl}) = \frac{75 \text{ g}}{3600 \text{ g} + 75 \text{ g}} = 2.0\%, \quad w(\text{MgCl}_2) = \frac{93 \text{ g}}{3600 \text{ g} + 93 \text{ g}} = 2.5\%,$$
$$w(\text{CaCl}_2) = \frac{111 \text{ g}}{3600 \text{ g} + 111 \text{ g}} = 3.0\%, \quad w(\text{MnCl}_2) = \frac{126 \text{ g}}{3600 \text{ g} + 126 \text{ g}} = 3.4\%.$$

The densities of these solutions (15°C) can be obtained from chemistry handbooks, and are 1.012, 1.020, 1.024, and 1.029 g mL^{-1} , respectively. If beryllium is divalent (BeCl_2 , $M=80$), the density of BeCl_2 solution with $n(\text{H}_2\text{O})$: $n(\text{BeCl}_2) = 200:1$ must be slightly above that of KCl yet below that of MgCl_2 —which is the case. Alternatively, for trivalent beryllium (BeCl_3 , $M=120$) the density of its chloride solution must be above that of CaCl_2 —which is not the case. Thus, density measurements of aqueous chlorides are (correctly) in support of divalent beryllium.

References

1. Mendeleev D (1889) J Chem Soc 55:634–656
2. Meija J (2010) Anal Bioanal Chem 396:185–186