

Reaction volume in aqueous solutions in problem solving

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The volumes of reactions in solution are usually ignored in problem solving. Neglecting reaction volumes may lead to errors on the order of 1 % in the final result. Calculation of the volume of neutralization reaction based on the specific densities of solutions from chemical tables is demonstrated.

Keywords: problem solving; physical chemistry; acid-base reactions; thermodynamics; chemical tables

1. INTRODUCTION

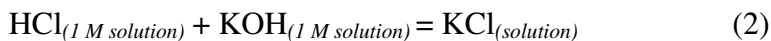
The fact that the volume of the products of reaction in solution is not equal to the sum of volumes of reactants is well-known, and numerous studies of reaction volumes in solution have been reported in the scientific literature [1-3]. However, the volume of chemical reaction in solution is ignored in classroom teaching. Most students (and probably also many teachers) are not aware that the volumes of products on the one hand and of reactants on the other, can be substantially different, even in solution reactions. In chemical calculations involving chemical reactions in solution, demonstrated in handbooks of chemistry at various levels, the volume of the final solution is calculated as a sum of volumes of initial solutions, e.g., [4-5]. In other words, the following assumption:

$$\Sigma V_{(products)} = \Sigma V_{(reactants)} \quad (1)$$

is tacitly introduced. The present paper shows that eq. (1) is false, and the volume of chemical reaction in solution can be relatively high (on the order of 1 % of the volume of the reactants). The following solution of a problem introduces the student into the topic. It can be demonstrated as a part of a lecture in solution chemistry (1 unit of 45 min.) or using the guided inquiry approach (2 units 45 min. each). It can also serve as a basis for problems for Chemistry Olympiad or similar contests at the level of high school.

2. PROBLEM

Calculate the volume of reaction:



in which the reactants are mixed in stoichiometric proportions at 20°C.

Hint: use specific densities of solutions from Handbook of Chemistry and Physics [6].

3. SOLUTION

For any reaction:

$$\Delta V_{(\text{reaction})} = \Sigma V_{(\text{products})} - \Sigma V_{(\text{reactants})} \quad (3)$$

(by definition). For specific reaction (2):

$$\Delta V_{(\text{reaction } 2)} = V_{(\text{KCl solution})} - V_{(1\text{ M HCl})} - V_{(1\text{ M KOH})} \quad (4)$$

In reaction in solution, relatively small number (l.h.s. of eq. 3) is calculated as a difference between large and almost equal numbers (r.h.s. of eq. 3). In such a subtraction, the difference is often on the same order of magnitude as the accuracy of the data, and the final result may be sensitive to any rounding in the course of calculations. In the present example any rounding will be avoided until we arrive at the final result. This approach is different from the usual approach, in which only significant digits are taken into account, and the insignificant digits are dropped.

$V_{(1\text{ M HCl})}$ and $V_{(1\text{ M KOH})}$ in equation (4) can be easily determined. By definition:

$$V = \text{number of moles}/c \quad (5)$$

Let us consider 1 mole of each reactant. From eq.(5) we have $V_{(1\text{ M HCl})} = V_{(1\text{ M KOH})} = 1\text{ dm}^3$. The calculation of $V_{(KCl\text{ solution})}$ in eq. (4) will be more complicated. The volume of the solution is not additive, but the mass is additive, that is,

$$m_{(KCl\text{ solution})} = m_{(1\text{ M HCl})} + m_{(1\text{ M KOH})} \quad (6).$$

Obviously

$$m_{(1\text{ M HCl})} = V_{(1\text{ M HCl})} \times d_{(1\text{ M HCl})} \quad (7),$$

and

$$m_{(1\text{ M KOH})} = V_{(1\text{ M KOH})} \times d_{(1\text{ M KOH})} \quad (8).$$

At this point we have to refer to chemical tables to determine the specific densities d in eqs. (7) and (8). The chemical tables explicitly report d only for several discrete values of c . In the specific source we are using, the specific densities are available for round mass fractions of HCl, and this is why the molarities in our Table 1 are not round numbers. The specific densities of HCl solutions are summarized in Table 1, and plotted in Fig. 1.

Table 1 Specific density of HCl solutions at 20°C.

c [M]	d [kg/dm ³]
0	0.99821
0.137	1.0007
0.275	1.0031
0.553	1.0081
0.833	1.013
1.117	1.0179
1.403	1.0228

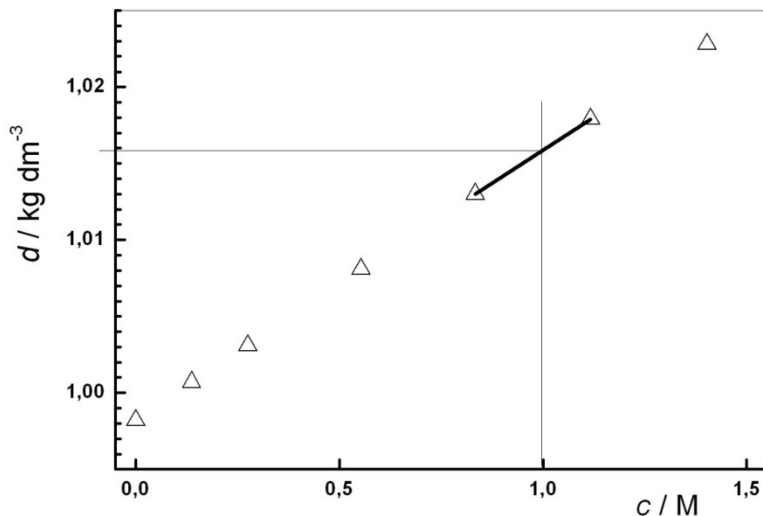


Fig. 1. Specific density of HCl solutions at 20°C.

The plot in Fig. 1 is nearly linear, but not exactly linear. Table 1 does not explicitly report d of 1 M HCl, and this is typical, that chemical tables do not explicitly report d of a solution of interest (concentration c). Interpolation is required to calculate d of 1 M HCl. To this end we assume that the $d(c)$ plot is linear over a narrow concentration range from c_1 to c_2 where c_1 is the highest concentration lower than c , and c_2 is the lowest concentration higher than c , for which the specific density is explicitly reported in the tables. In Table 1 c_1 , c_2 and corresponding specific densities are marked by boldface. Graphical interpolation of data from Table 1 is illustrated in Fig. 1. Table 2 illustrates the interpolation carried out by means of a spreadsheet application. Most commercial spreadsheet applications offer a linear regression function, e.g., FORECAST in MS Excel.

Table 2. Linear regression of data from Table 1. Calculation of specific density of 1 M HCl.

c	d
0.833	1.013
1.117	1.0179
1	1.015881

Mathematically oriented students will probably prefer the following “two-point” version of linear equation:

$$d(1\text{ M}) = d_1 + [(d_2 - d_1)/(c_2 - c_1)](1\text{ M} - c_1) \quad (9).$$

A procedure analogous to that discussed above for 1 M HCl, leads to specific density of 1 M KOH. The data used in calculations and the result are reported in Table 3.

Table 3. Linear regression. Calculation of specific density of 1 M KOH.

<i>c</i>	<i>d</i>
0.929	1.0419
1.124	1.0509
1	1.045177

The specific densities of 1 M solutions from Tables 2 and 3 (all decimal digits displayed in the spreadsheet included) are used in eq. (7) and (8) to calculate the masses of 1 M solutions of HCl and KOH, which are equal to 1.015881 and 1.045177 kg, respectively, and from eq. (6) we have: $m(\text{KCl solution}) = 2.061058$ kg. Calculation of the volume of final KCl solution is the next step. To this end we have to calculate its specific density. The KCl solution contains 1 mole of KCl (it was obtained from solutions containing 1 mole of HCl and 1 mole of KOH), thus the KCl mass fraction in the solution is:

$$(0.0745513 / 2.061058) \times 100\% = 3.617138\% \quad (10),$$

where 0.0745513 is the molar mass of KCl expressed in kilograms. At this point we will refer to the chemical tables again to find the specific density of 3.617138% solution of KCl. We use linear interpolation as described above for HCl and KOH solutions, except in this step, mass concentrations are used rather than molarities. The data used in calculations and the result are reported in Table 4.

Table 4. Linear regression. Calculation of specific density of the final KCl solution.

Mass %	<i>d</i>
3	1.0174
4	1.0239
3.617138	1.021411

The volume of the final KCl solutions equals to m/d , that is, 2.017854 dm^3 . This value is used in eq. (4) along with the volumes of initial HCl and KOH solutions (1 dm^3 each), and it produces:

4. ANSWER

$$\Delta V_{(\text{reaction } 2)} = 17.9 \text{ cm}^3/\text{mol} \quad (11)$$

We rounded the final result to 3 significant digits. This is because several numbers used as the data (molarities in Tables 1-3) are only reported with 3 significant digits. The volume of the solution increased by 0.9 % in the course of reaction. This means that eq.(1) may result in an error on the order of 1 % in the final result (e.g. calculated molarity of the final solution) [5]. Eq.(1) is a good approximation for very dilute solutions millimolar range, when the amount of reacted substances per unit of volume is low.

5. THE SIGNIFICANCE OF THE RESULT

The above calculations have been carried out for a reaction of 1 M solutions of acid and base, and the aforementioned numerical value of ΔV (eq. 11) is only valid for this specific concentration. Similar calculations can be carried out for different concentrations of HCl and KOH, and the calculated ΔV (reaction) is a function of the concentration of reagents. ΔV of reaction of stoichiometric volumes of equimolar HCl and KOH as a function of concentrations of reactants is plotted in Fig. 2. Each data point in Fig. 2 can be calculated by an individual student during an guided-inquiry-lesson.

Fig. 2 demonstrates that the volume of reaction is always positive (the solution expands in the course of reaction), and it is sensitive to the concentration of the reagents, especially over the range of low concentrations. Reaction (2) can be written as:



Namely, both acid and base are dissociated in solution, and only protons and hydroxyl ions participate in the reaction, and chloride anions and potassium cations do not. Therefore the ΔV (reaction) shown in

Fig. 2 is a good approximation of ΔV of any reaction of strong acid and strong base (reaction 12), especially in the low-concentration range.

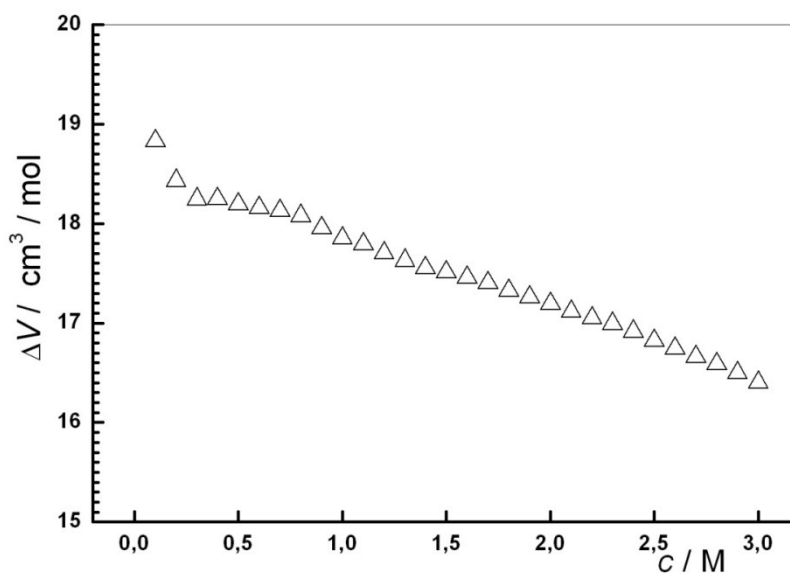


Fig. 2. ΔV of reaction of stoichiometric volumes of equimolar HCl and KOH.

6. THE PHYSICAL EXPLANATION

The protons in HCl solution and hydroxyl anions in KOH solution are hydrated, and the structure of water around the ions is different from the structure of bulk water. As the result of strong Coulombic attraction between the ions and water dipoles, the specific density of the hydration water is higher than the specific density of bulk water. This phenomenon is common for all ions, that is, the hydration water around cations other than proton has also higher specific density than bulk water. In the course of chemical reaction between acid and base, two ions produce a water molecule, and the original hydration water (high specific density) turns into bulk water (lower specific density). This is why the solution expands. The degree of hydration of ions is a function of electrolyte concentration. In dilute solutions the ions are fully hydrated, and the amount of hydration water is high. In concentrated solutions, the degree of hydration is low due to limited availability of water molecules. For example in 3 M acid or base solution (Fig. 2) only about 10 water molecules per ion are available. Consequently in concentrated solution fewer molecules of

hydration water (per mole of reagents) are turned into bulk water. This explains high volume of reaction in dilute solution, and lower volume of reaction in concentrated solution. Particular monovalent cations and anions differ in their affinity to water molecules, and they may have different effects on the hydration of hydroxyl anions and of protons, respectively. Therefore the plots analogous to Fig. 2 are different for various 1-1 salts (LiCl, CsNO₃, etc.). On the other hand, the ΔV (reaction 12) extrapolated to $c=0$ does not depend on the nature of the 1-1 electrolyte.

7. REVERSED REACTION AND PRESSURE EFFECT

Reversed reaction (12) is the reaction of water dissociation. The volume of water dissociation has the same value but opposite sign to the volume of reaction (12), that is, it equals about $-19 \text{ cm}^3/\text{mole}$ (in the presence of dilute 1-1 electrolyte).

According to the Le Chatelier's principle the negative value of volume of reaction implies that the water dissociation reaction shifts to the right at elevated pressures. Yet, since the absolute value of ΔV (reaction) is low in absolute value, the pressure effect on the equilibrium constant becomes significant only at very high pressures (>100 bars) [7].

8. EXPERIMENTAL

The above calculations can be verified by direct measurement of volume in a specially designed dilatometer. The dilatometric effect of neutralization is not exceptionally high as compared with other reactions in solution. For example, ΔV of precipitation of heavy metal hydroxides is on the order of $60 \text{ cm}^3/\text{mole}$ [8].

9. CONCLUSIONS

Eq. (1) is an approximation. Neglecting of reaction volume in solution may result in under- or overestimation of the final volume of solution by about 1 %.

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