CHEMISTRY

A. F. VOROB'EV, N. M. PRIVALOVA, A. S. MONAENKOVA, and S. M. SKURATOV

1960

SovietRxiv

Abstract

Full Text

CHEMISTRY

A. F. VOROB' EV, N. M. PRIVALOVA, A. S. MONAENKOVA, and S. M. SKURATOV

STANDARD ENTHALPIES OF FORMATION OF PERCHLORIC ACID AND OF SOME PERCHLORATES

(Presented by Academician A. N. Frumkin, July 5, 1960)

The small amount of literature data on the thermochemistry of perchloric acid and perchlorates makes a thermochemical study of these compounds highly desirable.

I. Enthalpies of formation of potassium, sodium, and barium perchlorates. The enthalpies of formation of potassium, sodium, and barium perchlorates were determined by measuring the enthalpies of their decomposition into the corresponding chlorides and oxygen, followed by calculation according to Hess' s law using literature data on the enthalpies of formation of the chlorides. The enthalpies of decomposition were measured in a specially constructed sealed massive-type microcalorimeter described previously ([1]). Decomposition of the substances in this calorimeter was achieved by heating them with an electric current by means of a special heater. (The enthalpy of decomposition of $KClO_4$ was, in addition, measured in a liquid calorimeter with a self-sealing bomb. Decomposition of the perchlorate was achieved by heating it through the combustion of benzoic acid. Both methods of measuring the enthalpy of decomposition gave concordant results.)

The perchlorate preparations used in the work were recrystallized 3–4 times from bidistilled water, after which they were dehydrated in vacuum at a temperature of about 150°. All operations with the substances were carried out in a dry chamber without exposing them to air.

The degree of purity of the substances was determined by the Dietrich–Bollenbach method ([2]), somewhat modified and checked by us. The amount of impurities in the preparations did not exceed 0.1% (the accuracy of the analysis). The calorimetric experiments were calculated from the results of analysis of the reaction products.

The enthalpies of formation of NaCl and KCl were calculated by us using the most reliable modern literature data. For the enthalpy of formation of $BaCl_2$, no fully reliable data are available. We adopted the data of Simonsen' s work ([3]), which appear to be the most reliable; however, their experimental confirmation

would be desirable. The results of the determinations are presented in Table 1 (ΔH, kcal/mole).

Table 1

Compound	ΔH of decomposition of perchlorate	ΔH of formation of chloride	ΔH of formation of perchlorate
$KClO_4$	-2.55 ± 0.18	-104.43 ± 0.06	-101.9 ± 0.2
$NaClO_4$	-7.70 ± 0.28	-98.38 ± 0.06	-90.68 ± 0.3
$Ba(ClO_4)_2$	-14.0 ± 0.4	-219.3 ± 1.6	-205.3 ± 1.6*

* The value of the enthalpy of formation of $Ba(ClO_4)_2$ may change if the enthalpy of formation of $BaCl_2$ is refined.

II. Enthalpy of formation of perchloric acid

The enthalpy of formation of perchloric acid in solution (concentration $HClO_4 \cdot H_2O > 400$) was determined by two independent routes—on the basis of data on the enthalpy of formation of $NaClO_4$ and $KClO_4$. To calculate the enthalpy of formation of perchloric acid on the basis of the enthalpy of formation of $NaClO_4$, the following system of thermochemical equations was used:

1. $Na_{[s]} + \frac{1}{2}Cl_{2[g]} + 2O_{2[g]} = NaClO_{4[s]}$ ΔH_1
2. $HClO_{4[\text{p-p}\,HClO_4\cdot 450H_2O]} + NaOH_{[\text{p-p}\,NaOH\cdot 7.65H_2O]} =$
   $= NaClO_{4[\text{p-p}\,NaClO_4\cdot 458H_2O]} + H_2O_{[\text{p-p}\,NaClO_4\cdot 458H_2O]}$ ΔH_2
3. $NaClO_{4[s]} + [458H_2O] = NaClO_{4[\text{p-p}\,NaClO_4\cdot 458H_2O]}$ ΔH_3
4. $Na_{[s]} + \frac{1}{2}O_{2[g]} + \frac{1}{2}H_{2[g]} + [7.65H_2O] = NaOH_{[\text{p-p}\,NaOH\cdot 7.65H_2O]}$ ΔH_4
5. $H_{2[g]} + \frac{1}{2}O_{2[g]} + [\text{p-p}\,NaClO_4 \cdot 457H_2O] = H_2O_{[\text{p-p}\,NaClO_4\cdot 458H_2O]}$ ΔH_5
6. $\frac{1}{2}H_{2[g]} + \frac{1}{2}Cl_{2[g]} + 2O_{2[g]} + [458H_2O] = HClO_{4[\text{p-p}\,HClO_4\cdot 458H_2O]};$ ΔH_6

$$\Delta H_6 = \Delta H_1 - \Delta H_2 - \Delta H_3 - \Delta H_4 + \Delta H_5.$$

In calculating the enthalpy of formation of perchloric acid on the basis of data on the enthalpy of formation of potassium perchlorate, an analogous system of equations was used, with the difference that the concentration of the $KClO_4$ solution was taken as $KClO_4 \cdot 4500H_2O$ owing to its low solubility; correspondingly, the concentrations of the acid and alkali in the neutralization reaction were $HClO_4 \cdot 4500H_2O$ and $KOH \cdot 25H_2O$.

For the enthalpy of reaction 1, the data of the present work (Section I) were used; the enthalpies of reactions 2 and 3 were measured experimentally; the enthalpies of reactions 4 and 5 were reliably estimated from literature data. The sample of perchlorate in determining the enthalpies of dissolution, or of hydroxide solution in determining the enthalpies of neutralization, was placed in the calorimetric vessel in a thin-walled glass ampoule, sealed with a stopper made of a picein alloy with paraffin.

The weights of the hydroxide solutions and the concentration of perchloric acid in measuring the enthalpies of neutralization (reaction 2) were selected in such a way that the concentration of the perchlorate solution formed as a result of the neutralization reaction was the same as in determining the enthalpy of its dissolution (reaction 3).

Solutions of perchloric acid for neutralization were prepared by diluting twice-distilled perchloric acid dihydrate.

The concentration of perchloric acid was not the same in determining the enthalpy of its formation through $NaClO_4$ and $KClO_4$ ($HClO_4 \cdot 450H_2O$ and $HClO_4 \cdot 4500H_2O$, respectively). However, literature data (4) indicate that the enthalpy of dilution of perchloric acid at concentrations below $HClO_4 \cdot 400H_2O$ is practically equal to zero.

The agreement of the results of determining the enthalpy of formation of perchloric acid by two independent routes confirms the reliability of the value obtained. The results of the determinations, as well as the quantities used for the calculation, are presented in Table 2 (ΔH, kcal/mole). Using the data

Table 2

Cation	ΔH of formation of $ECl O_4$	ΔH of neutralization	Concentration of alkali used	ΔH of dissolution of $ECl O_4$	ΔH of formation of alkali solution	ΔH of formation of perchloric acid
K^+	-101.9 ± 0.2	-13.35 ± 0.03	$KOH \cdot 25H_2O$	12.14 ± 0.01	-115.00 ± 0.05	-29.73 ± 0.21
Na^+	-90.68 ± 0.3	-13.66 ± 0.04	$NaOH \cdot 7.65H_2O$	3.26 ± 0.011	-112.19 ± 0.05	-29.82 ± 0.3

Average $\Delta H = -29.77 \pm 0.17$ kcal/mole

from the recently published work (5) on the determination of the enthalpy of dissolution of anhydrous $HClO_4$, it is possible to calculate the standard enthalpy of formation of anhydrous $HClO_4$: -8.62 ± 0.18 kcal/mol.

III. Enthalpies of formation of lithium, ammonium, calcium, and magnesium perchlorates. The enthalpies of formation of lithium, ammonium, cal-

cium, and magnesium perchlorates were calculated by Hess' s law using systems of thermochemical equations similar to those indicated in Section II. The enthalpies of dissolution of these perchlorates and the enthalpies of neutralization of perchloric acid by calcium and magnesium oxides and by solutions of lithium and ammonium hydroxides were measured experimentally. For the enthalpy of formation of the perchloric acid solution, the value obtained in the present work was used (-29.77 ± 0.17 kcal/mol). The enthalpies of formation of calcium and magnesium oxides, solutions of lithium and ammonium hydroxides, and liquid water were estimated with sufficient reliability from literature data.

The preparation of samples for the study, as well as their characteristics, are analogous to those indicated in Sections I and II. The results obtained are given in Table 3 (ΔH, kcal/mol).

Table 3

Cation	State of oxide or hydroxide	ΔH of formation of oxide or hydroxide solution	ΔH of dissolution of perchlorate	ΔH of neutralization	ΔH of formation of perchlorate
Li^+	Solution $LiOH \cdot 15H_2O$	-120.65 ± 0.05	-6.296 ± 0.009	-14.18 ± 0.03	-89.98 ± 0.18
$NH_4{}^+$	Solution $NH_4OH \cdot 6.5H_2O$	-87.46 ± 0.08	$+7.984 \pm 0.008$	-12.65 ± 0.01	-69.54 ± 0.18
Ca^{++}	CaO_{solid}	-151.79 ± 0.23	-15.42 ± 0.007	-46.35 ± 0.01	-173.94 ± 0.41
Mg^{++}	MgO_{solid}	-143.82 ± 0.04	-37.08 ± 0.16	-36.11 ± 0.12	-134.07 ± 0.31

In the present work the relation 1 cal = 4.1840 absolute joules has been adopted. All errors are expressed in the form of twice the "standard deviation."

Moscow State University
named after M. V. Lomonosov

Received
5 VII 1960

REFERENCES

1. A. F. Vorob' ev, N. M. Privalova, S. M. Skuratov, ZhFKh, **34**, No. 5, 1142 (1960).

2. M. Dittrich, H. Bollenbach, Ber., **38**, 751 (1905).

3. H. Siemonsen, Zs. Elektrochem., **55**, 327 (1951).

4. M. Berthelot, Ann. Chim. phys., **27**, 214 (1882).

5. N. V. Krivtsov, V. Ya. Rosolovskii, A. A. Zinov' ev, ZhNKh, **5**, No. 4, 772 (1960).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.