



GIBBS FREE ENERGIES FOR THE SOLVATION OF KClO_3 IN MIXED $\text{DMF-H}_2\text{O}$ SOLVENTS AT 301.15 K

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The Gibbs free energies for KClO_3 were evaluated in mixed dimethylformamide (DMF)- H_2O solvents at 301.15 K from the experimental solubility measurements. From the experimental the ionic radii ratio of potassium to chlorate ions, the total free energy of the salt is divided into its individual contribution in the mixtures used. Liberation Gibbs free energy for moving KClO_3 from standard gas state to standard solution state was calculated according to specific cycle for the solvation process using the solubility product. Also the lattice energy for solid KClO_3 (cr) was also calculated and used for further evaluation. The conventional Gibbs free energies for the cation (K^+) and the anion (ClO_3^-) were estimated theoretically and also the Gibbs free energy of ClO_3^- gas was evaluated and all values were discussed.

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absolute values by the value for the absolute Gibbs solvation free energy of the proton.

The conventional Gibbs free energies of solvation for anions are shifted by an equal amount in the opposite direction.

Introduction

For neutral species experimental solvation Gibbs free energies have been tabulated large number of solutes in both aqueous¹⁻⁷ and non-aqueous^{7,8} solvents. Typically, these solvation free energies are determined experimentally⁸ and their uncertainty is relatively low (~ 0.8 kJ/mol).⁹

Determining accurate values for the Gibbs free energies of ionic solutes like KClO_3 is important than that of neutral solutes. Understanding the partitioning of single ions between different liquid phases is important in many areas of biology. For example, the electrical signals sent by nerve cells are activated by changes in cell potential that are caused by the movement of various ions across the neuronal membrane.¹⁰ The division of thermodynamic Gibbs free energies of solvation of electrolytes into ionic constituents is conventionally accomplished by using the single ion solvation Gibbs free energy of one reference ion, conventionally, the proton, to set the single ion scales.^{11,12} The aim of this work is to estimate the single ion Gibbs free energies for K^+ and ClO_3^- ions in mixed $\text{DMF-H}_2\text{O}$ solvents at 301.15 K.

Sums of solvation free energies of cations and anions are well defined through the use of thermochemical cycles involving calorimetric or electrochemical measurements.¹³⁻¹⁷ A number of different extra thermodynamic approximations have been used¹⁸⁻²⁵ to partition the sums of cation and anion Gibbs free energies into single ion contribution.

Relative and conventional solvation free energies of ions:

The Gibbs solvation free energies of ions as relative free energies by setting the free energy of solvation of some reference ion equal zero.²⁶ Proton was chosen as reference ion. For ions, this result in a set of conventional free energies of solvation that the cations are shifted from their

Conventional Gibbs free energies from reduction potentials

When the convention for the absolute Gibbs free energy of the proton is followed, the solution-phase free energy change associated with the half cell for reduction of hydrogen gas is equal to zero. Reduction potentials following this convention for hydrogen electrode are referred as standard reduction potentials. From the half cell reaction for the reduction of metal cation to crystalline phase and the half reduction reaction of hydrogen gas, the redox reaction can be illustrated through the use of thermochemical cycle.¹² This last procedure can be used to estimate the gas free energy of formation for ClO_3^- ion, to explain the ionic behaviour.

Experimental

Potassium chlorate KClO_3 , Griffin Kamp and N-N, dimethylformamide (DMF) from Merck Co, were used.

Saturated solutions of KClO_3 were prepared by dissolving different amounts of the salt in closed test tubes containing different $\text{DMF-H}_2\text{O}$ mixtures. These mixtures were then saturated with nitrogen gas as inert atmosphere. The tubes were placed in a shaking thermostat (Model Gel) for a period of four days till equilibrium reached. The solubility of KClO_3 in each mixture was measured gravimetrically by evaporating 1 ml of the saturated solution in small cup using I. R. lamp. The measurements were done by three readings for each solution at 301.15 K.

Results and Discussion

The molar solubility (S) for KClO_3 was measured gravimetrically in mixed $\text{DMF-H}_2\text{O}$ solvents at 301.15 K. The solubility values with an average number of the second

number often comma are cited in Table (1). The (S) value in water agreed well with that in literature values.²⁷ The activity coefficients were calculated by the use of Debye-Hückel equation.^{28, 29}

$$\log \gamma_{\pm} = -0.5062 I^{0.5} \quad (1)$$

where I is the ionic strength calculated from S values. These data ($\log \gamma_{\pm}$) were tabulated also in Table 1.

The solubility product was calculated by the use of equation (2).³⁰

$$pK_{sp} = -2\log S + 2\log \gamma_{\pm} \quad (2)$$

The solubility product (pK_{sp}) data are given in Table (1). From solubility products the Gibbs free energies of solvation and the transfer Gibbs free energies from water to mixed solvents were calculated by using Eqns. (3) and (4). Their values are tabulated also in Table 1.^{31,32}

$$\Delta G = 2.303 RT pK_{sp} \quad (3)$$

$$\Delta G_t = \Delta G_s - \Delta G_w \quad (4)$$

where s and w denote solvent and water, respectively.

It was concluded that the Gibbs free energies of transfer (ΔG_t) increases in negativity by increasing the mole fraction of DMF in the mixed DMF- H_2O solvents. This is due to more solvation behaviour in the mixed solvents than that of water (see Fig. 1).

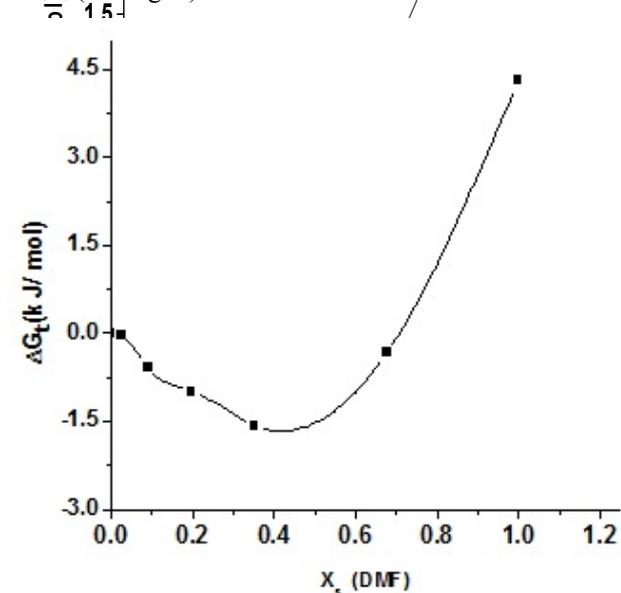


Figure 1. Gibbs free energies of transfer for $KClO_3$ versus the mole fraction of DMF at 301.15 K.

Single ion Gibbs free energies and convention free energies for K^+ and ClO_3^- ions

It was well known that the preferential single ion thermodynamic parameters depend on the ionic radii of two ions (cation and anion). Therefore the ionic radii ratio between K^+ and ClO_3^- were evaluated from exact radii values given in literature³³ and found to be 0.2788.

Multiply this ratio by the Gibbs free energies of $KClO_3$ we get the ionic free energies for K^+ ion. This last value was subtracted from the $KClO_3$ Gibbs free energy we obtain the Gibbs free energies for ClO_3^- anion in $KClO_3$. The obtained values for single ions are presented in Table 2. The conventional Gibbs free energies $\Delta G_s^{*con}(K^+)$ for potassium ion in solvents are shifted from their absolute values by the absolute free energy of the proton³⁴ according to Eqn. (5). And for ClO_3^- anion is shifted by an equal amount in the opposite direction (Eqn. 6):

$$\Delta G_s^{*con}(M^+) = \Delta G_s^0(M^+) - \Delta G_s^0(H^+) \quad (5)$$

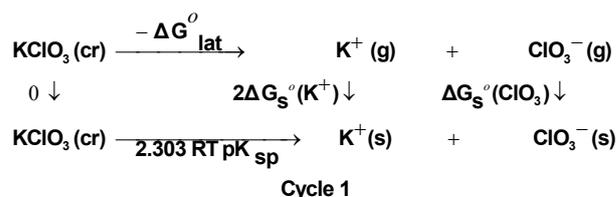
$$\Delta G_s^{*con}(X^-) = \Delta G_s^0(X^-) + \Delta G_s^0(H^+) \quad (6)$$

where $\Delta G_s^0(M^+)$, $\Delta G_s^0(X^-)$ and $\Delta G_s^0(H^+)$ are the Gibbs free energies of solvation for cation, anion and proton in solvents, respectively.

From the mean values of proton solvation free energies in water and other solvents in literature^{12,35,36} relation between these values and the diameter for each solvent taken from,³⁷ straight line was obtained. From this line the proton solvation free energies in pure water and DMF were obtained and found to be 1523 and 1561 kJ mol^{-1} , respectively. Multiplying these value by the mole fraction of each solvent and then sum the results. The mixed solvent proton free energies in DMF- H_2O mixtures were obtained and their values are given in Table 2. Apply Eqns. (5) and (6) we get the conventional Gibbs free energies for the cation and anion and their values are given also in Table 2. Cation conventional free energy values are negative indicating exothermic character and anion values are positive indicating endothermic character. Both values increase with increase in the mole fraction of DMF due to more solvation and the sum of them gives the values for the neutral salt.

Liberation Gibbs free energies for $KClO_3$ in mixed DMF- H_2O solvents

The liberation Gibbs free energies for $KClO_3$ in mixed DMF/ H_2O solvents at 301.15 K were calculated following thermochemical cycle 1 as done before¹² for silver salts following solubility product concept:



where ΔG_{lat}^0 is the lattice free energy in kJ mol^{-1} , (g) and (s) denote the gas and solution cases. The lattice energy was calculated following Bartlett's relationship following equation (7).³⁸

Table 1. Solubility and Gibbs free energies for $KClO_3$ in mixed DMF- H_2O solvents at 301.15 K.

X_s DMF	S , mol L ⁻¹	$\log \gamma \pm$	pK_{sp}	ΔG kJ mol ⁻¹	ΔG_f kJ mol ⁻¹
0	0.244	-0.2514	1.7282	9.8647	0
0.0253	0.246	-0.2524	1.7229	9.8356	-0.0291
0.0909	0.290	-0.2741	1.6234	9.2675	-0.5971
0.3527	0.326	-0.2906	1.5547	8.8756	-0.9891
0.6773	0.391	-0.3183	1.4522	8.2904	-1.5742
0.6773	0.266	-0.2609	1.6720	9.5451	-0.3196
1.0	0.080	-0.1439	2.4816	14.1668	4.3021

Table 2. Single ion Gibbs free energies for K^+ , ClO_3^- and their conventional energies at 301.15 K. in mixed DMF- H_2O solvents (in kJ mol⁻¹).

X_s DMF	$\Delta G(K^+)$	$\Delta G(ClO_3^-)$	$\Delta G_s^{*con}(K^+)$	$\Delta G_s^{*con}(ClO_3^-)$	$\Delta G_s^*(H^+)$
0	2.7502	7.1164	-1520.2	1530.11	1523
0.0253	2.7421	7.0934	-1520.2	1530.09	1523
0.0909	2.5837	6.6837	-1520.2	1525.60	1523
0.1965	2.4745	6.4011	-1526.4	1529.40	1529
0.3529	2.3114	5.9790	-1535.5	1543.90	1538
0.6773	2.5511	6.8839	-1549.32	1558.90	1552
1.0	3.9437	10.2170	-1557.05	1571.20	1561

$$\Delta G_{lat} = \frac{232.8}{\sqrt[3]{V}} + 110 \quad (7)$$

The volume of $KClO_3$ was calculated by dividing its molecular weight by the density of solid given in literature⁴ and apply it in equation (7) to obtain (168.996 kJ mol⁻¹) as ΔG_{lat} for $KClO_3$.

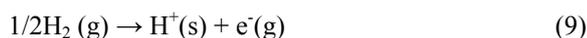
$$\Delta G_s(K^+) + \Delta G_s(ClO_3^-) = 2.303RTpK_{sp} - \Delta G_{lat} - 2\Delta G^{0 \rightarrow *}$$

On the use of Eqn. (8) cycle (1), the liberation free energy for $KClO_3$ was obtained (84.498 kJ mol⁻¹).

The $\Delta G^{0 \rightarrow *}$, the free energy change associated with moving $KClO_3$ from standard gas phase at 1 atmosphere to solution phase. This free energy change has been referred as "compression" work of the gas or liberation free energy.

Conventional free energies from reduction potentials

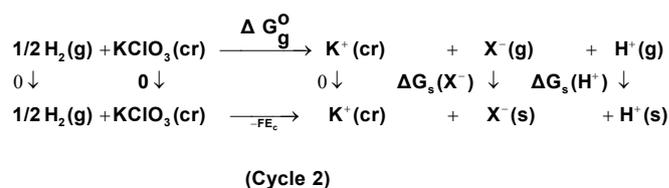
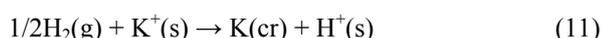
The absolute Gibbs free energy of the proton is followed solution phase free energy change associated with the following half cell.



The half cell reaction for the reduction of cation is:



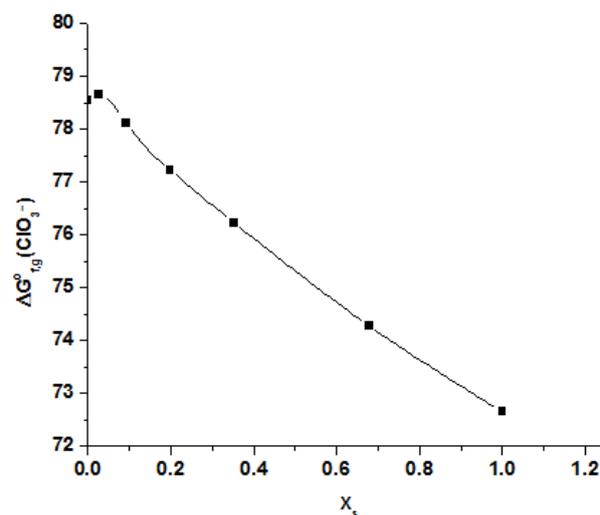
The symbol (cr) denotes the crystalline phase. The sum of the two half cells is:



Through the thermochemical cycle 2, the conventional free energy of K^+ ion can be written as:

$$\Delta G_s^{*con}(K^+) = \Delta G_f^0(H_g^+) - \Delta G_f^0(K_g^+) - FE_c \quad (12)$$

where $\Delta G_f^0(H_g^+)$, $\Delta G_f^0(K_g^+)$ are the gas free energy of formation for H^+ and K^+ ions. F is the Faraday's constant, 96.485 kJ per gram equivalent and E_c is the standard reduction potential of K^+ .

**Figure 2.** Relation between $\Delta G_{f,g}^0(ClO_3^-)$ against the mole fraction of DMF at 301.15 K.

Also the conventional free energy of the chlorate ion can be written following Truhlar¹² explanation as:

$$\Delta G_s^{*con}(ClO_3^-) = -\Delta G_{f,g}^0 - FE_C - 2\Delta G^{0 \rightarrow *}$$
 (13)

Apply last equation the $\Delta G_{f,g}^0$, gas free energies of formation for the anion ClO_3^- and K^+ estimated in the mixed DMF- H_2O solvents and their values are given in Table 3 and Fig. 2. The $\Delta G_{f,g}^0$ values increase by increase of the mole fraction of DMF favouring less solvation.

Table 3. Gas formation free energy for ClO_3^- anion in mixed DMF- H_2O solvents at 301.15 K (in kJ mol^{-1}).

X_2 , DMF	$\Delta G_{f,g}(ClO_3^-)$
0	-1731.94
0.0253	-1731.89
0.0909	-1731.49
0.1975	-1731.20
0.3527	-1774.69
0.6773	-1760.59
1.0	-1773.10

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