# Estimation of the lattice energy and the free energy of formation of the series $M_4P_2O_7$ (M= Li, Na, K, Rb and Cs)

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**Abstract**: Lattice energies and Gibbs energies of formation are determined for a series of alkaline diphosphate (pyrophosphate) of formula $M_4P_2O_7(s)$ where M = Li, Na, K, Rb and Cs. The lattice energy, $U_{POT}$, is calculated according to two schema of decomposition using the standard Born-Haber-Fajans (BHF) thermochemical cycle and Glasser equation. The results led to the standard molar enthalpy of formation of potassium diphosphate ($K_4P_2O_7$) as equals -3212 kJ mol$^{-1}$. This value differs only by 0.6% from literature data. Free Gibbs energy of formation of these compounds was estimated by the determination of their absolute entropy according to Jenkins and Glasser procedure.

**Keywords**: Lattice Energy, Enthalpy of formation, Entropy of formation, Gibbs Energy of formation, Alkaline Diphosphate (pyrophosphate).

## INTRODUCTION

Alkaline diphosphate of formula $M_4P_2O_7$ where M is Li, Na, K, Rb and Cs are interesting because of their various fields of application. They have been subject of many studies such as electroconductivity as pure compounds or as solid solutions such as $K_4P_2O_7$- $Rb_4P_2O_7$ system [1,2]. In literature several works were devoted to their synthesis [1,3-11]. Some focused on characterization of their crystallographic data [12-16] and others on determination of their standard molar enthalpy of formation [11,17-20]. The values reported for $\Delta_fH^\circ$ $(M_4P_2O_7)_s$ are not recent and some differ considerably for the same compound. So on, we performed to make a determination of these quantities by calorimetric measurements [21-23]. However it was impossible to perform such determination for potassium diphosphate, $K_4P_2O_7$, because of its high hygroscopicity. This work aims at calculating the lattice energies of the above compounds and to deduce this quantity for anhydrious potassium homologous one. It also concerns the determination of the free energy of formation of these compounds.

## DETERMINATION OF THE LATTICE ENERGY $U_{POT}$ OF $M_4P_2O_7$

A variety of estimation methods for lattice energy is available in literature. The earliest, and well known, was proposed in 1956 by Kapustinskii [24] in which $U_{POT}$ is expressed as:

$$U_{POT} = \frac{A\,|\,\vartheta\, z_+ z_-\,|}{<r>}\left(1 - \frac{\rho}{<r>}\right) \qquad \text{(I)}$$

Where $z_{+,}$ $z_-$ electron units are the numbers of charges of cations and anions, respectively, $\vartheta$ the number of ions per formula unit, ρ a compressibility constant depending on the repulsions between the ions, <r> the sum of the

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cation and anion thermochemical radii, and A a constant equal to 121,4 kJ $mol^{-1}$ nm.

The main limitations of this equation are, first, that it can be applied only to binary compounds and, second, it requires thermochemical radii, assuming a spherical symmetry on the ions involved. Latter, in 1984, Mallouk et al. [25] modified this equation by using the cube root of the formula unit volume rather than the cation-anion distance. In 1995, Glasser [26], extended the Kapustinskii equation to complex ionic solids and in 2000 Glasser and Jenkins [27] developed a new relationship between lattice energy, $U_{POT}$, and unit cell volume, $V_m$. The new equation (II) has the following form:

$$U_{POT} = AI(2I/V_m)^{1/3} \qquad \text{(II)}$$

Where:

A: a standard electrostatic conversion term equals to 121,4 kJ $mol^{-1}$ nm.

I: the ionic strength defined as $\frac{1}{2} \Sigma\, n_i z_i^2$ where $n_i$ is the number of ions of type i per formula unit, each one bearing the charge $z_i$. The summation is extended over all ions of the formula unit.

$V_m$ : the volume of the formula unit (the molar volume).

The lattice energy can be determined according to two paths of decomposition depending on the ions produced [28]. The material can decompose into monoatomic gaseous ions or a mixture of monoatomic and complex gaseous ions, as follows:

$$M_4P_2O_{7\,(s)} \longrightarrow 4M^+_{(g)} + 2P^{5+}_{(g)} + 7O^{2-}_{(g)} \qquad U_{POT1}$$

$$M_4P_2O_{7\,(s)} \longrightarrow 4M^+_{(g)} + P_2O_7^{4-}{}_{(g)} \qquad U_{POT2}$$

## 1. Schema 1

Glasser equation and the BHF cycle were used for the determination of the lattice energy $U_{POT}$. For decomposition into monoatomic gaseous ions, the BHF cycle could be schematisized as:

$$\begin{tikzcd}
M_4P_2O_{7\,(s)} \arrow[rr, "U_{POT1}"] \arrow[dr, "-\Delta_fU°(M_4P_2O_7)"'] & & 4M^+_{(g)} + 2P^{5+}_{(g)} + 7O^{2-}_{(g)} \\
& 4\,M_{(s)} + 2\,P_{(w)} + 7/2O_{2(g)} \arrow[ur, "\begin{array}{l}4\,\Delta_fU°(M^+_g)\\ 2\,\Delta_fU°(P^{5+}_g)\\ 7/2(\Delta_{diss}U°(O_{2g}))\\ 7\,(\Delta_{atta}U°(O_g))\end{array}"'] &
\end{tikzcd}$$

Combining the standard molar energy of $M_4P_2O_{7(s)}$ [21-23] with literature data [29] the lattice energy, following the BHF cycle can be derived as:

$$U_{POT1} = -\Delta_fU°(M_4P_2O_7) + 4\,\Delta_fU°(M^+_g) + 2\,\Delta_fU°(P^{5+}_g) + 7/2(\Delta_{diss}U°(O_{2g})) + 7\,(\Delta_{atta}U°(O_g)) \qquad \text{(III)}$$

With

$$\Delta_fU°(M_4P_2O_7) = \Delta_fH°(M_4P_2O_7) - RT\Delta n_{(g)} \qquad \text{(IV)}$$

On Glasser equation (II), for the schema 1, I is equal to 41.

Values of $U_{POT1}$ according to the BHF cycle and to Glasser equation are reported in Table I, column 3 and 4 respectively.

The lattice energy was not determined for $Rb_4P_2O_7$ and $Cs_4P_2O_7$, using the Glasser equation because the lack of their crystallographic data.

## 2. Schema 2

For a decomposition leading to a mixture of monoatomic and complex gaseous ions, the BHF cycle is:

$$\begin{tikzcd}
M_4P_2O_{7\,(s)} \arrow[rr, "U_{POT2}"] \arrow[dr, "\begin{array}{l}4\,\Delta_fU°(M^+_g)\\ -\,\Delta_fU°(M_4P_2O_7)\end{array}"'] & & 4M^+_{(g)} + P_2O_7^{4-}{}_{(g)} \\
& 4\,M_{(s)} + 2\,P_{(w)} + 7/2\,O_{2(g)} \arrow[ur, "\Delta_fU°(P_2O_7^{4-}{}_g)"'] &
\end{tikzcd}$$

To close the cycle and determine the lattice energy according to schema 2 the knowledge of the energy of formation of gaseous ion of $P_2O_7^{4-}$ is required. As the standard molar enthalpy of formation of $Mg_2P_2O_7$ (-3155 kJ $mol^{-1}$) and its lattice energy are available in literature (8519 kJ $mol^{-1}$) [27,30], $\Delta_fU°(P_2O_7^{4-}{}_g)$ could be estimated according to this expression:

$$\Delta_fU°(P_2O_7^{4-}{}_g) = U_{POT} - 2\,\Delta_fU°(Mg^{2+}_g) + \Delta_fU°(Mg_2P_2O_7) \qquad \text{(V)}$$

So on $\Delta_fU°(P_2O_7^{4-}{}_g)$ is equal to 2177 kJ $mol^{-1}$ and $U_{POT2}$ can be calculated as:

$$U_{POT2} = -\Delta fU°(M4P2O7) + 4\,\Delta_fU°(M^+_g) + \Delta_fU°(P_2O_7^{4-}{}_g) \qquad \text{(VI)}$$

**Table I**. Molar volume, $U_{POT1}$ and $U_{POT2}$ for the series $M_4P_2O_7$

|  | Vm ($nm^3$) [31] | $U_{POT1}$ (kJ $mol^{-1}$) |  | $U_{POT2}$ (kJ $mol^{-1}$) |  |
|---|---|---|---|---|---|
| Compound |  | BHF | Glasser | BHF | Glasser |
| $Li_4P_2O_{7(s)}$ | 0.142 | 25379 | 41449 | 8033 | 6316 |
| $Na_4P_2O_{7(s)}$ | 0.170 | 25138 | 39035 | 7792 | 5948 |
| $K_4P_2O_{7(s)}$ | 0.223 | 24758* | 35659 | 7412* | 5434 |
| $Rb_4P_2O_{7(s)}$ | - | 24633 | - | 7288 | - |
| $Cs_4P_2O_{7(s)}$ | - | 24575 | - | 7229 | - |

(*) Values determined by linear interpolation.

**Table II.** Molar energy of formation of the cation

| Cation | $Li^+_{(g)}$ | $Na^+_{(g)}$ | $Rb^+_{(g)}$ | $Cs^+_{(g)}$ |
|---|---|---|---|---|
| $\Delta_fU°(M^+_g)$* kJ $mol^{-1}$ | 679.45 | 603.27 | 483.93 | 452.15 |

* Values are calculated combining enthalpy of sublimation and the ionization energy of the element [29].

Following the schema 2, I, the ionic strength in the Glasser equation, is equal to 10. Values of $U_{POT2}$ using both approaches are reported in table I column 5 and 6.

Whatever the path of the decomposition, one can notice that results obtained from the BHF cycle differ considerably from those determined by the formula of Glasser. This difference shows that the equation made by Glasser does not suit in alkaline diphosphate. This gap underlines the partially ionic character of the series $M_4P_2O_7$.

## STANDARD MOLAR ENTHALPY OF FORMATION OF $K_4P_2O_{7(S)}$

Formally these compounds differ only by the nature of the alkali cation; therefore it was interesting to search a correlation between $U_{POT}$ and the molar energy of formation of the cation. The BHF approach lead to enough results allowing the drawing of $U_{POT}$ *versus* the standard energy of formation of the cation $M^+_{(g)}$ [29] (table II). One can notice the straight line shape with a value of $R^2$ close to one (figure 1).

**Table III**: Enthalpy of formation, absolute entropy, entropy of formation and free energy of formation of the series $M_4P_2O_7$

| Compound | $Li_4P_2O_{7(s)}$ | $Na_4P_2O_{7(s)}$ | $K_4P_2O_{7(s)}$ | $Rb_4P_2O_{7(s)}$ | $Cs_4P_2O_{7(s)}$ |
|---|---|---|---|---|---|
| $\Delta_fH°$ (kJ $mol^{-1}$) | -3147<br>[22] | -3210.5<br>[21] | -3212 | -3183.7<br>[23] | -3252.04<br>[11] |
| S°(J $mol^{-1}$ $K^{-1}$) | 192.2 | 227.6 | 283.0 | 304* | 325* |
| $\Delta_fS°$ (J $mol^{-1}$ $K^{-1}$) | -725.1 | -778.6 | -776.7 | -804.2 | -816.8 |
| $\Delta_fG°$ (kJ $mol^{-1}$) | -2930.8 | -2978.3 | -2980.4 | -2944 | -3008 |

(*) Values determined by linear extrapolation

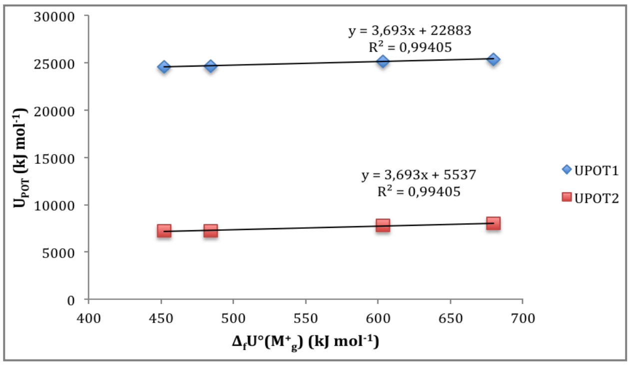

**Figure 1** : $U_{POT}$ *versus* $\Delta_fU°(M^+_g)$ for $M_4P_2O_7$ (M = Li, Na, Rb and Cs)

As $\Delta_fU°(K^+_g) = 507.75$ kJ mol$^{-1}$ is situated between that of $Na^+$ and $Rb^+$, the lattice energy of $K_4P_2O_7$ can be calculated by interpolation according to the two paths of decomposition (Table I). So on the standard molar energy of formation of this compound can be determined according to one or the other schema following equations (III) and (IV).

The standard molar enthalpy of formation of potassium diphosphate $\Delta_fH^°(K_4P_2O_7)_s$ is -3212 kJ mol$^{-1}$. It has already been determined in 1979 by B. Luff [32]. It equals -3232.4 kJ mol$^{-1}$. These values differ only by 0.6%.

## FREE ENERGY OF FORMATION OF $M_4P_2O_{7(S)}$

The thermodynamic stability of the series $M_4P_2O_7$, is also studied in this work by determination of the free energy of formation and for that, values of the absolute entropy of these compounds are required. Jenkins and Glasser [33], proposed an empirical relationship between entropy and the molar volume in the form:

$$S°_{298}/\text{J K}^{-1}\text{ mol}^{-1} = 1262\ (V/\text{nm}^3) + 13 \qquad \text{(VII)}$$

The absolute entropy of $Rb_4P_2O_{7(s)}$ and $Cs_4P_2O_{7(s)}$ were not determined through this formula because of the lack of their crystallographic data. However the drawing of the calculated absolute entropy of $Li_4P_2O_{7(s)}$, $Na_4P_2O_{7(s)}$ and $K_4P_2O_{7(s)}$ as a function of the absolute entropy of the element M [29], figure 2, gave a straight line suggesting a linear correlation between these quantities. Results are given in table III.

By linear extrapolation to S°(Rb) = 76.8 J mol$^{-1}$K$^{-1}$ and S°(Cs)= 85.2 J mol$^{-1}$K$^{-1}$ one can derive the absolute entropy of $Rb_4P_2O_{7(s)}$ and $Cs_4P_2O_{7(s)}$ as 304 and 325 J mol$^{-1}$ K$^{-1}$ respectively.

The free energy of formation $\Delta_fG°$, at 298 K, is then estimated according to the expression:

$$\Delta_fG° = \Delta_fH° - T\,\Delta_fS° \qquad \text{(VIII)}$$

Results displayed in table III.

## DISCUSSION AND CONCLUSION

Values of lattice energy estimated according the BHF cycle and the Glasser equation are different. The gap between these results highlights the partially ionic character of the series $M_4P_2O_7$ as glasser's equation was extended to complex ionic solids. $U_{POT}$ evolve in a same sense for the series and lithium diphosphapte has the highest lattice energy. This is not the case for the free energy of formation. Indeed, this magnitude ($\Delta_fG°$) is determined in order to inform about the thermodynamic stability. ΔG° is the sum of the enthalpic and entropic terms. The latter take into account of the crystalline structure and positions of the atoms. This could explain the non linear values of $D_fG°$ obtained for the series of alkaline diphosphate as they don't have the same crystalline structures.

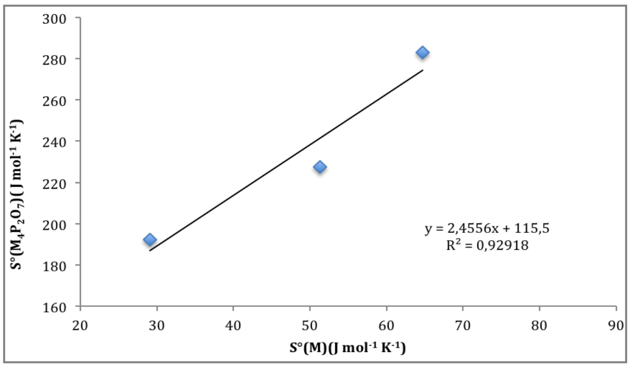

**Figure 2** : $S°(M_4P_2O_7)$ *versus* S°(M) for $M_4P_2O_7$ (M = Li, Na and K)

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