CONFRONTATION OF COMPLEX ANIONIC POTENTIALS AND COMPOUND POTENTIALS WITH THERMOCHEMICAL DATA

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The complex anionic potentials and the compound potentials calculable from atomic data have been widely used so far to interpret geochemical processes even in the absence of thermochemical data. The present paper mentions some of the correlations of the above-mentioned potential values and thermochemical data that is correlations between anionic potentials and heat of hydration and that between the compound potentials and heat of formation. So beside the extension of the field of application of these potentials we may approach a more precise physical interpretation of the aforesaid potentials.

Introduction

The compound potential introduced by SZÁDECZKY-KARDOSS (1954, 1955) may be considered as the arithmetic mean of the potentials of the ions (cations and simple or complex anions) constituting a compound. Compound potentials are readily calculated from atomic data (ionic radius and charge) taking into consideration the coordination number of the cations, the ionic distances within the complex anions and — in the case of silicates — the degree of silification as discussed by SZÁDECZKY-KARDOSS and GRASSELLY (1965). These compound potentials proved useful in characterizing the properties and behaviour of diverse compounds even if no thermochemical data are available for the compounds in question. Therefore, the compound potentials may be widely used to interpret geochemical processes.

The introduction of the concept "compound potential" is thought of as justified not only by mineralogists and geochemists but also by physicochemists — although the latters still consider the compound potential as a rather arbitrarily defined, empirical value — because several remarkable and plausible correlations were shown up in the papers dealing with atomic and compound potentials. Furthermore should it be possible to interpret the correlations stated by the geochemical potential concept based on the ionic, atomic and compound potentials, respectively, a more profound insight would be gained into geochemical processes since in contrast to thermodynamics correlations revealed by the potential concept offer also some conclusions regarding the mechanism of the processes.

It seems to be evident that the more correlations there are discovered between termochemical data and the corresponding potential values, the more closely one can approach the unequivocal definition of the compound potential also from the physical point of view, the more completely the physical meaning of this concept will be revealed.

While CARTLEDGE (1951) dealt in his paper published in 1951 with the problem of the correlation between the heat of formation of given compounds and the corresponding cationic potentials, this paper represents the first effort to establish correlations between complex anionic and compound potentials and thermochemical data.

Correlation between the heat of hydration and the anionic potential of some complex anions

In one of his previous papers (1959) the author proposed a simple method to determine the effective radius of the complex anions bearing in mind that the tetrahedral complex anions in the crystal lattice can hypothetically be substituted by a spherical ion, i.e. by a sphere, the surface and volume of which are nearest to the volume and effective surface of the tetrahedral oxyanion (from the point of view of the bond and isomorphy relations, respectively). The radius of this sphere can be considered as the effective radius of the complex anion. The anionic potentials calculated with these radii differ from the potential values used at present.

It is known that the heat of hydration of ions is a function of the radius of the ions:

$$L = z^2 \cdot f(r).$$

In his work dealing with the thermochemistry of complex compounds, JAZIMIRSKY (1956) illustrated diagrammatically the correlation between that heat of hydration and the radii of the anions and cations, respectively, plotting the L/z^2 values in kcal against the radii given in Å.

The correlation between the heat of hydration and the complex anionic potential is obvious in Fig. 1. The once-, twice and trice-charged complex anions are separated from each other and the correlation within the individual groups is fairly linear. Moreover, some connection with the position of the central cations in the periodic table is also recognized. The points corresponding to the BO_3—CO_3—NO_3 anions are arranged along a fairly straight line. It would be expected that the points corresponding to the PO_4—SO_4—ClO_4 anions will also be arranged along a straight line. The lines connecting the points of BO_3—CO_3 and those of PO_4—SO_4 and AsO_4—SeO_4, respectively, intersect in one point. The point corresponding to the ClO_4 anion should be expect to fall

Table 1

Complex anion	Thermochemical radius Å	Effective radius Å	Anionic potential	L	L/z^2
				kcal	
NO_3^-	1.89	1.76	0.56	71	71
ClO_4^-	2.36	2.09	0.47	50	50
MnO_4^-	2.40	2.16*	0.46	49	49
JO_4^-	2.49	2.24	0.44	40	40
CO_3^{2-}	1.85	1·81	1.10	317	79
SO_4^{2-}	2.30	2.12	0.94	241	60
CrO_2^{4-}	2.40	2.16	0.92	229	57
SeO_4^{2-}	2.43	2.18*	0.91	224	56
MoO_4^{2-}	2.54	2.28*	0.87	216	54
TeO_4^{2-}	2.54	2.28*	0.87	216	54
WO_4^{2-}	2.57	2.31*	0.86	202	50
BO_3^{3-}	1.91	1.96	1.53	760	84
PO_4^{3-}	2.38	2.14*	1.40	550	61
AsO_4^{3-}	2.48	2.27	1.32	530	54

* The effective radii marked (*) were derived from the corresponding thermochemical radii on the basis of the relationship $R_{effective}/R_{thermochemical} = 0.9 \pm 0.02$. The L/z^2 values calculated by JAZIMIRSKY are shown vs. the complex anionic potentials computed from the effective radii in Fig. 1.

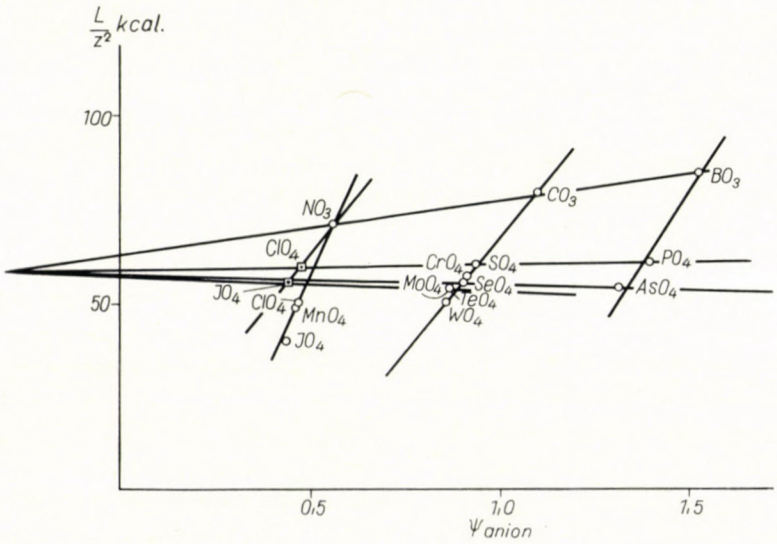

Fig. 1. Heat of hydration of some complex anions vs. complex anionic potential

on the line connecting the points of SO_4—PO_4. However, this would require a heat of hydration of 59—60 kcal. for ClO_4 instead of the 50 kcal. given by JAZIMIRSKY (1956). The point corresponding to the JO_4^- anion would fall on the line connecting the point of TeO_4 with the common intersection point only, if the heat of hydration of JO_4^- were 54 kcal instead of the 40 kcal. given by JAZIMIRSKY.

It is to be noted, however, that the heat of hydration of the JO_4^- anion as given in the paper referred to, is an uncertain value on the other hand the heat of hydration of the ClO_4^- anion as given in another paper by JAZIMIRSKY amounts to 55 kcal., much closer to the 59 kcal. estimated from the relationships outlined above.

The complex anionic potentials — as it is known — can be calculated from atomic data, from the ionic distances determined by X-rays. By means of the relationship between the heats of hydration and the complex anionic potentials as outlined above, it seems possible to estimate or to correct some missing or uncertain heats of hydration of complex anions in the possession of a few accurate heats of hydration on the basis of the exactly calculable complex anionic potentials. Further investigations into this problem are in progress.

Correlation between heat of formation and compound potential of some oxysalts

Dealing with the relationships between the heat of formation of alkali and alkali earth oxysalts on the one hand and the acidity and basicity of the oxides involved on the other, RAMBERG (1952 a) discussed some of the links between the thermochemical properties of these oxysalts and the position of their cations in the periodic table. In Fig. 2 the heats of formation per two gram equivalents of salt formed from acidic and basic oxides are illustrated after RAMBERG.

Fig. 2. was constructed by RAMBERG as follows: the ΔH values of all sulfates were plotted on a line which made an arbitrary angle with the abscissa. The alkali and alkaline earth metals were spaced along the vertical axis. Then horizontal lines were drawn through the points of the sulfate line, each line belonging to a given metal. The heats of formation of the perchlorates, nitrates, etc. were plotted on the line of the corresponding metal. The points representing the ΔH values fell close to straight inclined lines, each line connecting the ΔH points of the salt of a given acid.

From Fig. 2 it can be clearly stated that 1. the heat of formation of a salt of a basic oxide is the lower, the stronger the acidity of the acidic oxide, and 2. the heat of formation of a salt of an acidic oxide is the lower, the stronger the basicity of the metal oxide. Thus as summarized by RAMBERG (1952 a)

the heat of formation of oxysalts from the constituent oxides is a measure of the strength of the acids — when comparing the salts of the same metal — and a measure on the strength of the bases when comparing the salts of the same acids.

From Fig. 2 a further fact can also be derived, namely that most of the lines except the nitrates relative to the sulfates converge toward the upper right-hand corner, showing that base exchange reactions between two solid salts are exothermic if the most acidic anion combines with the most basic

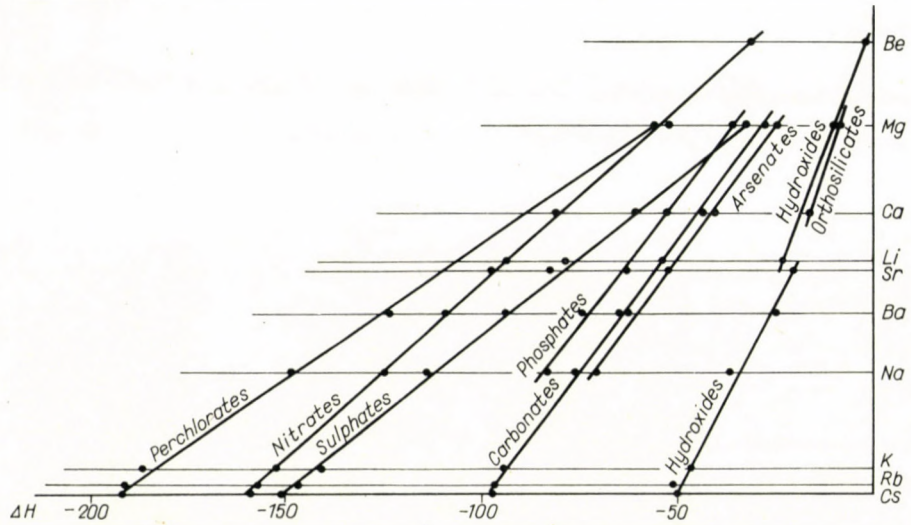

Fig. 2. ΔH of formation of some oxysalts from their basic and acidic oxides; given in kcal per two equivalents according to RAMBERG

metal oxide and the less acidic anion with the less basic metal, as was pointed out by RAMBERG.

In our opinion, should the compound potentials be considered as true indicators of the properties and behaviour of the compounds, the same relationships must hold between the compound potentials, too. To clear up the problem the reciprocal values of the compound potentials of alkali and alkaline earth perchlorates, sulfates, nitrates, etc., were plotted the way RAMBERG plotted the heats of formation. The reciprocal values were employed for the reason that the compound potential decreases with the increase of the negative value of the heat of formation, and the reciprocal value of the compound potential and the heat of formation change in the same direction.

In calculating the compound potentials the coordination numbers of the cations were also taken into consideration, as far as there were appropriate data available, that is, the ionic potentials of the cations were calculated with

Table 2

Compound	1.	2.	3.	4.	Compound	1.	2.	3.	4.
$Mg(ClO_4)_2$	1.32	0.75			$MgCO_3$	2.06	0.48		
$Ba(ClO_4)_2$	0.81	1.23			$CaCO_3$	1.56	0.64	1.51[9]	0.66
$NaClO_4$	0.75	1.33			$SrCO_3$	1.44	0.69	1.40[9]	0.71
$KClO_4$	0.61	1.63			$BaCO_3$	1.29	0.77	1.26[9]	0.79
$RbClO_4$	0.57	1.75			Li_2CO_3	1.34	0.74		
$CsClO_4$	0.53	1.88			Na_2CO_3	1.05	0.95		
$Mg(NO_3)_2$	1.38	0.72			K_2CO_3	0.86	1.16		
$Ca(NO_3)_2$	1.04	0.96	1.02[8]	0.98	Rb_2CO_3	0.82	1.21		
$Sr(NO_3)_2$	0.96	1.04	0.95[8]	1.05	Cs_2CO_3	0.76	1.31		
$Ba(NO_3)_2$	0.87	1.14	0.85[8]	1.17	$Mg_3(AsO_4)_2$	2.34	0.42		
$LiNO_3$	1.01	0·99			$Ca_3(AsO_4)_2$	1.73	0.57		
$NaNO_3$	0.79	1.26			$Sr_3(AsO_4)_2$	1.59	0.62		
KNO_3	0.65	1.53	0.63[9]	1.58	$Ba_3(AsO_4)_2$	1.42	0.70		
$RbNO_3$	0.62	1.61	0.60[9]	1.66	Na_3AsO_4	1.10	0.90		
$CsNO_3$	0.57	1.75	0.56[9]	1.78	$Mg_3(PO_4)_2$	2.38	0.42		
$BeSO_4$	3.32	0.30			$Ca_3(PO_4)_2$	1.77	0.56		
$MgSO_4$	1.98	0.50			$Sr_3(PO_4)_2$	1.63	0.61		
$CaSO_4$	1.48	0.67	1.45[8]	0.68	$Ba_3(PO_4)_2$	1.45	0.68		
$SrSO_4$	1.36	0.73	1.29[12]	0.77	Na_3PO_4	1.12	0.89		
$BaSO_4$	1.21	0.82	1.16[12]	0.86	Mg_2SiO_4	2.62	0.38		
Li_2SO_4	1.29	0.77			Ca_2SiO_4	1.95	0.51		
Na_2SO_4	1.00	1.00							
K_2SO_4	0.81	1.23	0.78[9]	1.28					
Rb_2SO_4	0.76	1.31	0.74[9]	1.35					
Cs_2SO_4	0.70	1.42	0.69[9]	1.44					

Plotting the data of Table 2 according to RAMBERG's method, one obtains Fig. 3.

the radius valid in the given structure. Failing such data, however, the cationic potentials were taken in related sixfold-coordination. The complex anionic potentials were calculated with the effective radii computed by the author (GRASSELLY 1959). The compound potentials are listed in Table 2. Column 1 comprises the compound potentials with the cations in sixfold-coordination, column 2 shows their reciprocal values, column 3 lists the compound potentials calculated by taking into consideration the coordination number of the cations in the given structure; finally column 4 comprises the reciprocal values of column 3.

It can be stated that the diagram of the compound potentials gives the same result as the plotting of the heats of formation. The points corresponding

to the compound potentials of the alkaline and alkali earth perchlorates, sulfates, nitrates, etc., fall along inclined straight lines and the lines converge just like those in Fig. 2. The sequence of the metals on the vertical axis is the same and the metals are arranged in the order of decreasing cationic potential from Be toward Cs. The compound potentials of the different Li salts are not plotted on Fig. 3. They would, however, fall along a horizontal line closely beneath the line of Sr.

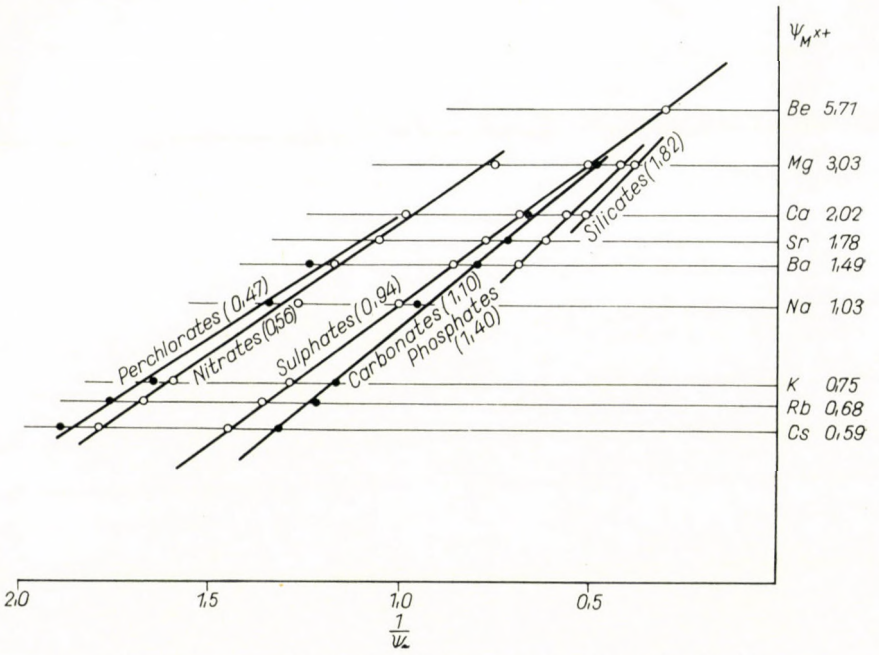

Fig. 3. Compound potential of the same oxysalts as in Fig. 2

Comparing the two figures (Fig. 2 and 3) the following differences can be established:

a) The lines representing the different perchlorates, nitrates, etc., on the basis of the reciprocal compound potential values follow each other on the order of the decreasing strength of the oxyacids: perchlorates — nitrates — sulfates, whereas the sequence obtained on the basis of the heats of formation is perchlorates — sulfates — nitrates. The correct sequence seems to be given by the compound potentials.

b) In the case of carbonates — arsenates — phosphates, the sequence obtained on the basis of the compound potentials corresponds to the order of increasing strength of the oxyacids whereas the heats of formation of these oxysalts, show no correlation with the strength of the oxyacids, since the sequence is: phosphates — carbonates — arsenates. It is to be noted that in Fig.

3, the arsenates are not plotted, since the line representing the arsenates would almost coincide with the line of the phosphates.

c) The inclined lines converge in both figures. However, in Fig. 3 compounds arranged according to their compound potential values do not show such irregularities as the ΔH values of the different oxysalts, mentioned also by RAMBERG.

In Fig. 3 the numbers beside the cations are the cationic potentials, whereas the numbers in parentheses beside the individual compounds are the corresponding complex anionic potentials. As it may be seen, the different Be-, Mg-, Ca-, etc., salts are arranged vertically in the order of decreasing cationic potential and the compound potential increases (its reciprocal value decreases) from the Cs-salts toward the Mg-salts for salts of the same acid, whereas for salts of the same metal the succession of the salts: perchlorates — nitrates — sulfates — carbonates — phosphates — orthosilicates is characterized by the increase of the complex anionic potentials and the increase of the compound potential from the perchlorates toward the silicates.

Now the question may arise as to what connection is there between the heats of formation and corresponding compound potentials (reciprocal values).

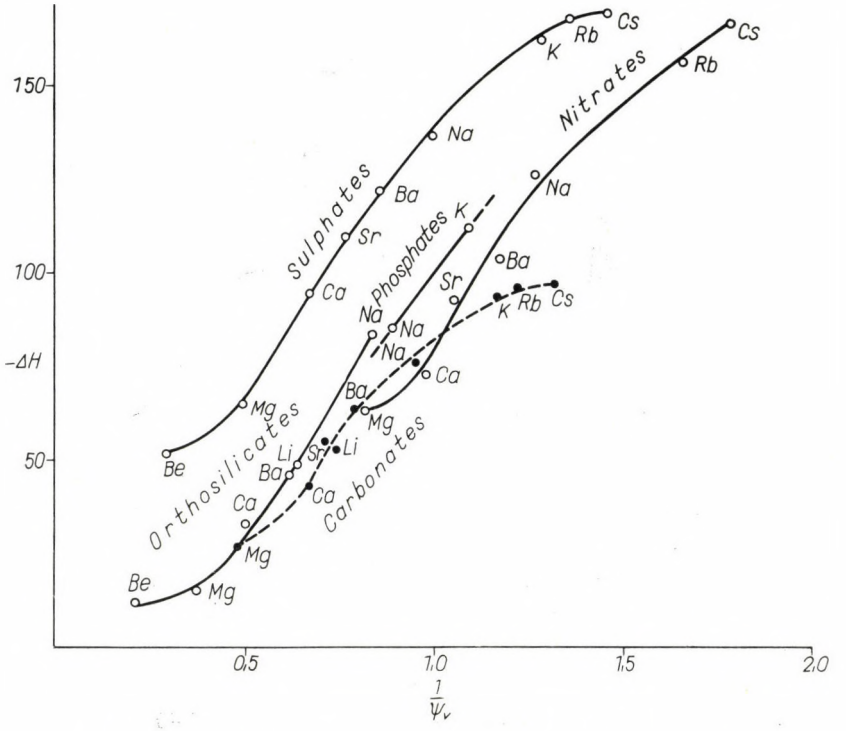

Fig. 4. ΔH of formation vs. compound potential of oxysalts

The heats of formation taken from RAMBERG's work (1952 b) are comprised in Table 3, whereas the $1/\psi$ values are taken from Table 2.

In Fig. 4 the correlation of the heats of formation with the compound potentials is just as evident as in Fig. 2 and 3. Without intending to go into details of Fig. 4, we wish to point out once more that the compound potentials can be accurately calculated from atomic data knowing the coordination num-

Table 3

	Heat of formation kcal/mol				
	M_2CO_3	$2MNO_3$	M_2SO_4	$\frac{2}{3}M_3PO_4$	M_4SiO_4
Li	53.35	89.00	106.15		49.0 ±5
Na	75.99	124.59	137.13	85.22	83.7
K	93.81	150.58	162.56	112.7	87.5 ±7
Rb	96.31	156.18	167.68		
Cs	96.21	160.70	168.85		
	MCO_3	$M(NO_3)_2$	MSO_4		M_2SiO_4
Be	—	—	52.1		12.0 ±5
Mg	27.45	63.11	64.95		15.1 ±1
Ca	43.35	72.97	95.1		32.8 ±0,5
Sr	55.15	93.0	110.6		
Ba	63.45	104.5	122.5		46.0 ± 7

ber of the cations and the 0—0 distances within the complex anion in the compound investigated, whereas the heats of formation are sometimes uncertain as is indeed the case with alkali and alkaline earth silicates.

It is hoped that by pointing out the correlations mentioned above, the purpose of giving a physical interpretation to the compound potentials whose empirical values have proved suitable to interpret geochemical processes, is to some extent approached.

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О НАСТОЯЩЕМ ПОЛОЖЕНИИ РАЗВИТИЯ КОНЦЕПЦИИ ПОТЕНЦИАЛОВ В ГЕОХИМИИ

ДЬ. ГРАССЕЛЛИ

Р е з ю м е

Величины комплексных анионных потенциалов или потенциалов соединений, подсчитываемых из атомных констант, использовались и до сих пор широко для интерпретации геохимических процессов, несмотря на отсутствие термохимических данных. Автор настоящей работы указывает на несколько закономерных зависимостей между величинами вышеупомянутых потенциалов и термохимическими данными, а именно между величинами комплексного анионного потенциала и гидратационного тепла, с одной стороны, и потенциалов соединений и выделяющейся теплоте, с другой. Таким образом, наряду с расширением области применения потенциалов, раскрытие закономерностей позволит додойти ближе к более точной физической интерпретации величин упомянутых потенциалов.