# The Acidic and Basic Properties of Oxides

IV. The Thermal Decomposition of Dichromates

H. FLOOD and A. MUAN

*The Royal Norwegian Council for Scientific and Industrial Research, Institute of Silicate Science,
Technical University of Norway, Trondheim, Norway*

In previous communications [1-3] dealing with the acid-base properties of oxides, the influence of the cations on the stability of the polyacids was discussed. It was stated, as a general rule, that the stability of the oxygen bridges decreases with both decreasing ionic radius and increasing polarizing power of the cation.

A particularly simple type of reaction which clearly demonstrates this rule is the thermal decomposition of pyrosulphates which consists of a breaking of the oxygen bridge of the pyrosulphate ion:

$$[O_3S - O - SO_3]^{2-}_{(m)} = SO^{2-}_{4(m)} + SO_{3(g)}$$
(m = melt)
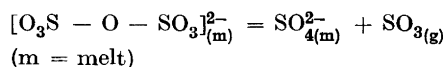
In a earlier communication [2], an account is given of the influence of various cations and their mixtures on the decomposition equilibrium at temperatures where the pyrosulphate and the sulphate form a homogeneous melt.

In the following, we are dealing with corresponding investigations on the thermal decomposition of the dichromates, according to the equilibrium:

$$O_3Cr - O - CrO^{2-}_{3(m)} = CrO^{2-}_{4(m)} + 1/2 \ Cr_2O_{3(s)} + 3/4 \ O_{2(g)} \tag{1a}$$
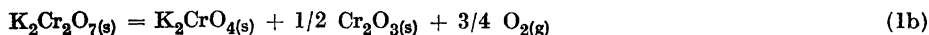$$(m = melt)$$
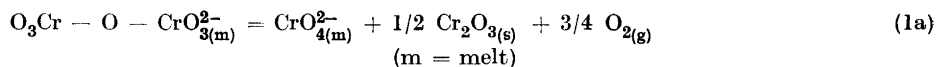
This reaction offers an interesting opportunity to compare the cation effect on two very similar equilibrium systems. In addition, values of the equilibrium constants can be estimated with a considerably greater degree of accuracy — and thus the influence of the cation can be examined in more detail.

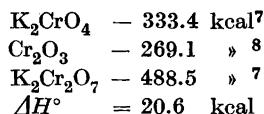The data on the dichromate decomposition in the literature are rather scarce.

Stanley [4] repost that $Na_2Cr_2O_7$ splits off gaseous oxygen forming Na_2CrO_4 and Cr_2O_3 when the temperature is raised to 400° C.

Groschulf [5] found considerable decomposition when $K_2Cr_2O_7$ was heated to 1 000° C, but Hempel and Schubert [6] state that the decomposition starts at 500° C and is complete at 1 500° C.

The heat of reaction of the $K_2Cr_2O_7$-decomposition according to

$$K_2Cr_2O_{7(s)} = K_2CrO_{4(s)} + 1/2\ Cr_2O_{3(s)} + 3/4\ O_{2(g)} \tag{1b}$$

follows from the heats of formation of the components:

$$\begin{aligned}
K_2CrO_4 &\quad - 333.4 \text{ kcal[7]} \\
Cr_2O_3 &\quad - 269.1 \quad \text{» [8]} \\
K_2Cr_2O_7 &\quad - 488.5 \quad \text{» [7]} \\
\Delta H^\circ &\quad = 20.6 \quad \text{kcal}
\end{aligned}$$

Data for the corresponding Na and Tl reactions are at present not available in the literature.

The following report is divided in to two parts. The first gives the results of the investigations on the decomposition of the pure K, Na, and Tl dichromates as a function of the temperature.

The second deals with the decomposition equilibria of mixed K-Na and K-Tl dichromates as a function of the composition.

I. THE DECOMPOSITION OF PURE DICHROMATES

A. Experiments

For the reaction (1a), we have:

$$K = \frac{a_{CrO_4^{2-}} \cdot p_{O_2}^{3/4}}{a_{Cr_2O_7^{2-}}} \tag{2a}$$

Values of:

$$K' = \frac{N_{CrO_4^{2-}} \cdot p_{O_2}^{3/4}}{N_{Cr_2O_7^{2-}}} \tag{2b}$$

(N = mole fraction) are found by determining the ratio $N_{CrO_4^{2-}}/N_{Cr_2O_7^{2-}}$ in melts in equilibrium with a known oxygen tension.

The composition of the melt was found by a simple gravimetric method. Starting with a weighed charge of dichromate + chromic oxide, the amount of oxygen expelled

during adjustment to equilibrium could be determined by weighing, after rapid cooling. During the experiments, pure O_2-gas or air of 1 atm was conveyed slowly upwards through a vertical furnace past a platinum crucible containing the weighed dichromate-chromic-oxide-charge. The arrangement was similar to that used in the pyrosulphate investigations.

The equilibrium was established in 2—6 hours in a pure O_2-atm. In an air atmosphere more time was required. By starting from the chromate side of the reaction, the melt consumed O_2, but the process was so slow that attempts to investigate the equilibrium from this side did not succeed.

The investigations in the Tl-system were complicated by the corrosive action of the melt on the platinum crucible.

In the experiments carried out at the highest temperatures [in the K-system 700°, in the Na-system and the K-Na-mixtures 660°], it was impossible to obtain absolutely constant weight. After a rather rapid decrease in weight during the first 2—3 hours, further heating resulted in a very small but continuous loss of weight, e. g. the weight as a function of time is shown for $Na_2Cr_2O_7$ at 662° in Table 1.

Table 1. The loss of weight of $Na_2Cr_2O_7$ at 662° C.

Starting with:

0.7716 g $Na_2Cr_2O_7$ + 0.0773 g Cr_2O_3
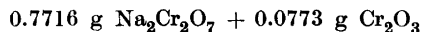
Time (min)	Weight (g)	dW/dt
		$g \cdot 10^{-4}$/min
0	0.8489	
90	0.8108	4.2
165	0.8101	0.09
225	0.8097	0.07
375	0.8089	0.05

Extrapolated ($t = 0$) 0.8110

Assuming that the slow loss of weight at these high temperatures is due to evaporation of some kind, the values of K' were calculated by using corrected values for the loss of weight found by extrapolating to zero time.

The materials used were $K_2Cr_2O_7$ and $Na_2Cr_2O_7 \cdot 2 H_2O$, "Baker's Analyzed". The sodium dichromate was dried at 170° C.

$Tl_2Cr_2O_7$ was prepared by precipitation of a Tl_2SO_4 solution with $K_2Cr_2O_7$ (in 2 N H_2SO_4). The analysis of the precipitate gave:

16.7 % Cr (theor. 16.64 %)

and

65.5 % Tl (theor. 65.43 %)

Cr_2O_3 was prepared by thermal decomposition of $(NH_4)_2Cr_2O_7$ (Merck reinst.).

It is of considerable importance in the following discussion that the Cr_2O_3 is practically insoluble in the dichromate-chromate melts. [The Na-K-meltphases which are completely soluble in water, gave no precipitate on addition of NH_3.]

In the Tl^I-dichromate-chromate melts there is a certain possibility of an oxidation reaction:

$$3\ Tl^I + 2\ Cr^{VI} = 3\ Tl^{III} + 2\ Cr^{III}$$
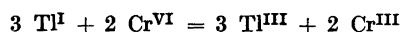
Attempts, however, to identify Tl^{III}, after dissolving the melt in diluted acid, was negative. The value of the red-ox-potential, in aqueous solutions containing chromate and dichromate ions in concentration of the same order of magnitude, also indicates that an oxidation of Tl^I will not take place to any appreciable extent.

Finally, it may be mentioned that it has been ascertained by X-ray examination that the higher Cr-oxides, already at temperatures below 400° C, are rapidly transformed in to the corund modification of Cr_2O_3. [In accordance with statements of Ryss and Siljanskaja[9].]

B. Discussion

The results of the equilibrium investigations are given in diagram 1.

A comparison of the experiments in oxygen and air atmospheres gives some information about the influence [compare (2b)] of the composition of the melt (cf. Table 3) on K'.

Table 3. K' as function of the chromate-dichromate ratio in the melt.

		$P_{O_2} = 1$ atm		$P_{O_2} = 0.21$ atm	
	$t°$ C	$N_{CrO_4^{2-}}$	log K	$N_{CrO_4^{2-}}$	log K
K	612	0.03	− 1.53	0.10	− 1.51
	650	0.04	− 1.35	0.16	− 1.33
Na	405	0.10	− 1.01	0.35	− 0.98
K : Na = 54 : 46	662	0.17	− 0.70	0.41	− 0.67

It is evident that the variation of log K' with the anion composition of the melt is very small. It scarcely exceeds the limit of experimental error.

The fact, however, that the values of log K', in all three systems, are found to change in the same direction, increasing with increasing chromate content, is an argument favouring the view that the observed variation actually corresponds to a change in the activity coefficient with the anion composition.
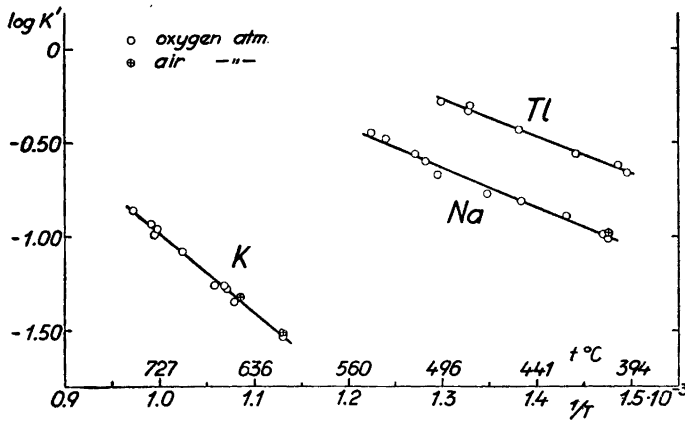
Fig. 1. The variation of $\log K' = \log N_{CrO_4^{2-}}/N_{Cr_2O_7^{2-}}$ *with* $1/T$.

Writing

$$\frac{a_{CrO_4^{2-}}}{a_{Cr_2O_7^{2-}}} = \frac{N_{CrO_4^{2-}} \cdot \gamma_{CrO_4^{2-}}}{N_{Cr_2O_7^{2-}} \cdot \gamma_{Cr_2O_7^{2-}}} \tag{3}$$

$(\gamma = $ activity coefficient$)$

and as a first approximation:

$$\log \gamma_{CrO_4^{2-}} = bN^2_{Cr_2O_7^{2-}}$$

$$\log \gamma_{Cr_2O_7^{2-}} = bN^2_{CrO_4^{2-}}$$

this gives a value of $b \leqq 0.1$, of the same order of magnitude both for the K-, Na- and the mixed K-Na-system.

It is evident that $\log K'$ can replace $\log K$ without appreciable error.

By plotting $\log K'$ against $\dfrac{1}{T}$ (Fig. 1) we get straight lines, within the limits of error, where:

$$- 2.303 \; R \; \frac{d \log K'}{d \left(\dfrac{1}{T}\right)}$$

represents the following approximate ΔH-values for the dichromate decomposition:

$$\begin{array}{lll} \text{K:} & 19.2 \text{ kcal} & (t = 611{-}750° \text{ C}) \\ \text{Na:} & 9.6 \text{ kcal} & (t = 400{-}550° \text{ C}) \\ \text{Tl:} & 9.0 \text{ kcal} & (t = 400{-}500° \text{ C}) \end{array}$$

It should be noticed that the value of K' for the Na and Tl systems at 662° C (Fig. 2) seems to indicate an increase in ΔH with increasing temperature. The composition of the melt at these high temperature, however, is so substantially different from the experiments at the lower temperatures that effects caused by deviations from ideal solutions (which also will tend to increase the value of K') have to be considered.

The ΔH-value for the K-system agrees fairly well with the previous mentioned calorimetric value for the reaction (1 b), where:

$$\Delta H° = 20.6 \text{ kcal}$$

It is evident from diagram 1 that the stability of the oxygen bridge of the dichromate ion decreases in the sequence

$$\text{K, Na, Tl}$$

the same as found in the investigations of the thermal decomposition of the pyrosulphates. The values of the change in free energy of the latter reactions involve considerably larger limits of error, but nevertheless it seems possible to draw some conclusions from them.

The difference $\Delta F_{\text{K}}{-}\Delta F_{\text{Na}}$ appears to be somewhat larger for the sulphate then for the chromate reaction ($7.0 > 5.8$ kcal at 660° C. Compare Fig. 1 with Fig. 1 in [3].) On the other hand, the difference $\Delta F_{\text{Na}}{-}\Delta F_{\text{Tl}}$ is evidently larger in the chromate than in the sulphate system. It seems, therefore, that the polarizing effect of the cation is a more important factor for the stability of the Cr—O—Cr than for the S—O—S bridge.

II. THE THERMAL DECOMPOSITION OF MIXED DICHROMATES

The systems investigated were the mixtures of K-Na and K-Tl-dichromates. The experiments were carried out in the same way as for the pure systems except that the temperature was kept constant [662° C] for the whole range of cation compositions. The results are shown in Fig. 2, where log K' is plotted against the mole fraction of Na and Tl, respectively, in the melt.
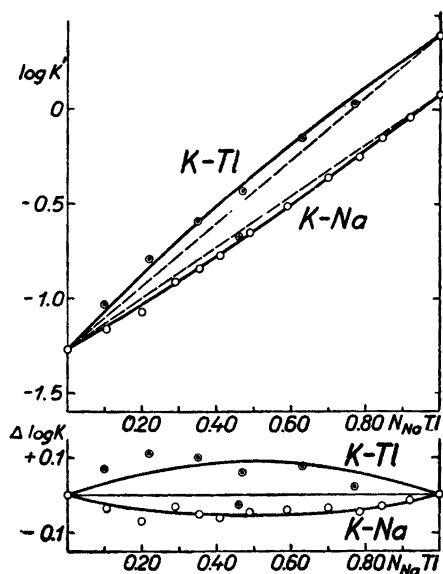
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Fig. 2. The variation of log $K' =$ log $N_{CrO_4^{2-}}/N_{Cr_2O_7^{2-}}$ with the cation composition of the melt. (N = mole fraction.)

It is striking that log K', in the mixtures, does not differ very much from the straight line between the values of the pure components of the systems.

The K-Na mixtures show a small negative deviation, whereas the K-Tl-mixtures show a more appreciable positive deviation.

As a first approximation log K' can be calculated by the simple formula:

$$\log K' = N_1 \log K'_1 + N_2 \log K'_2 + b\, N_1 N_2$$

where N_1 and N_2 are the mole fractions of the cations Na, (Tl), and K in the melt, and b is a constant

$$b_{K-Na} = -0.20 \quad (t = 662° \text{C})$$
$$b_{K-Tl} = +0.35 \quad (t = 662° \text{C})$$

This approximation is in fairly good agreement with the experiments in the Na-K-system. In the K-Tl-system, however, it is evident that the deviations from linearity are not as symmetrical as represented by the simple term $b\, N_1 N_2$.

The thermodynamic relation between K', K'_1, and K'_2 (compare the foregoing paper) is the following:

$$\log K' = N_1 \log K'_1 + N_2 \log K'_2 \tag{4}$$
$$+ (N_1 \log \gamma Y(A)/\gamma X(A) + N_2 \log \gamma Y(B)/\gamma X(B) - \log \gamma Y(AB)/\gamma X(AB))$$
$$+ (N_1 \log \gamma A(X) + N_2 \log \gamma B(X)) - (N_1 \log \gamma A(Y) + N_2 \log \gamma B(Y))$$

The activity coefficients correspond to deviations from idealty in the following 5 binary mixtures:

	Components	Subscript of	
	$Na_2Cr_2O_7 - Na_2CrO_4$	X(A),	Y(A)
	$K_2Cr_2O_7 - K_2CrO_4$	X(B)	Y(B)
	$Na_2CrO_4 - K_2CrO_4$	A(Y),	B(Y)
	$Na_2Cr_2O_7 - K_2Cr_2O_7$	A(X),	B(X)
	$(Na,K)_2Cr_2O_7 - (K,Na)_2CrO_4$	X(A,B),	Y(A,B)

[In the Tl-K-system, Na has to be replaced by Tl.]

The deviation from linearity of $\log K' = f(N)$ evidently is caused by the activity coefficient including terms.

As already pointed out (p. 368), the three $\gamma Y/\gamma X$ quotients [corresponding to the (Na), (K), and (Na,K) systems] seem to be comparatively small.

In addition, they are of opposite signs in eq. 4.

It therefore appears as if cancelling the second term causes no great error.

There also is reason to believe that this condition will be fulfilled in the Tl-K mixtures. Hence, the deviations from linearity in the first order must be connected with the γ_A and γ_B including terms.

Regarding the importance of the γ_A terms compared with the γ_B terms it is at present difficult to decide which are the most important.

There should be some reason to believe that the $\gamma_{A(Y)}$ and $\gamma_{B(Y)}$ (chromate) terms are more important than the $\gamma_{A(X)}$ and $\gamma_{B(X)}$ (dichromate) terms.

The larger size of the dichromate ion makes the average distance of the cations larger. Secondly, the oxygen atoms of the chromate ion are less polarized by the central chromium ion, and therefore are more exposed to attraction from the cations in the melt. If this is true the term $[N \log \gamma_{A(Y)} + N_2 \log \gamma_{B(Y)}]$ is chiefly responsible for the deviation of $\log K'$ from the straight line between $\log K'_1$ and $\log K'_2$.

The empirical formula is derived by putting

$$\log \gamma_{A(Y)} = b\ N^2_{B(Y)} \text{ and } \log \gamma_{B(Y)} = b\ N^2_{A(Y}$$

According to this assumption the negative deviation of log K' from linearity in the Na-K-melts corresponds to a *positive* deviation from Raoults law in the Na-K-chromate mixtures, and, in the same way, the positive deviation of log K' in the Tl-K-melts results from a *negative* deviation from Raoults law in the Tl-K-chromate mixtures. It seems reasonable that this negative deviation may be connected with a tendency to complex formation between Tl^+ and CrO_4^2 . This may also, perhaps, explain the unsymmetrical deviations observed on this system. The effect of a complex formation is expected to be more important in the Tl-poor than in the Tl-rich range of the system.

On the other hand there is also some evidence for the opiniom that a salt mixture of a noble gas ion and a transition element ion shows less negative deviation from ideality than corresponding mixtures of noble gas ions of the same size (compare the silver-alkali bromide melts investigated of Hildebrand and Salstrom [10])

In our systems the conditions would be analogous if the γ_X (dichromate) terms were the dominating in the expression of log K'.

SUMMARY

The equilibrium between CrO_4^{2-}-$Cr_2O_7^{2-}$ melts and O_2-gas shows that the stability of the dichromates on thermal decomposition, according to the equation:

$$Cr_2O_{7(m)}^{2-} = CrO_{4(m)}^{2-} + 1/2\ Cr_2O_{3(s)} + 3/4\ O_{2(g)}$$

[m = melt, s = solid, g = gas]
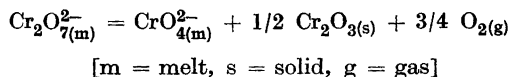
increases in the order Tl, Na, K.

It appears that the stability of the oxygen bridge Cr—O—Cr depends on the size and the polarizing power of the cation.

The results are compared with those obtained in the $S_2O_7^{2-}$-SO_4^{2-}-system.

The equilibrium constant:

$$K' = \frac{N_{CrO_4^{2-}} \cdot p_{O_2}^{3/4}}{N_{Cr_2O_7^{2-}}}$$

[N = mole fraction in the melt, p = gas pressure] is determined at two different O_2-tensions, and the activity coefficients in the melts are discussed.

Equilibrium investigations were made in mixtures of K-Na resp. K-Tl-dichromates by varying the cation composition at a constant temperature. The variation of log K' is found to be expressed by the equation

$$\log\ K' = N'_1\ \log\ K'_1 + N_2\ \log\ K'_2 + b\ N_1 N_2$$

where N_1 and N_2 are the mole fractions of Na(Tl) and K, and K'_1, K'_2 are the equilibrium constants in the melts with single cations.

The equation is verified by thermodynamic calculations. The activity coefficients in the melts are discussed.

REFERENCES

1. Flood, H., and Förland, T. *Acta Chem. Scand.* 1 (1947) 592.
2. Flood, H., and Förland, T. *Acta Chem. Scand.* 1 (1947) 781.
3. Flood, H., Förland, T., and Roald B. *Acta Chem. Scand.* 1 (1947) 790.
4. Stanley, A. *Chem. N.* 54 (1886) 194.
5. Groschuff, E. *Z. anorg. Chem.* 58 (1908) 102.
6. Hempel, W., and Schubert, C. *Z. Elektrochem.* 18 (1912) 729.
7. Bichowsky, C. F., and Rossini, F. D. *Thermochemistry of chemical substances.* New York (1936).
8. Grube, G., and Flad, M. *Z. Elektrochem.* 48 (1942) 377.
9. Ryss, J. G., and Seljanskaja, A. I. *Acta Physicochimica U. R. S. S.* VIII (1938) 623.
10. Hildebrand, J. H., and Salstrom, L. *J. Am. Chem. Soc.* 54 4257 (1932).