Thermochimica Acta, 55 (1982) 325–331
Elsevier Scientific Publishing Company, Amsterdam—Printed in The Netherlands

# CRYOSCOPIC STUDIES IN MOLTEN SALTS. DISSOCIATION STATE OF SOME ALKALI ISOPOLYMOLYBDATES AND SOME RELATED MOLYBDENUM(VI) COMPOUNDS IN MOLTEN $K_2Cr_2O_7$ AND $KNO_3$

M. HASSANEIN and N.S. YOUSSEF

*Department of Inorganic Chemistry, National Research Centre, Dokki, Cairo (Egypt)*

(Received 26 January 1982)

## ABSTRACT

The dissociation state of the solutes $M_2MoO_4$, $M_2Mo_3O_{10}$, $M_2Mo_4O_{13}$, $M_2Mo_5O_{16}$ (M = Rb or Cs), $Na_2CrO_4 \cdot MoO_3$, $K_2CrO_4 \cdot 2\ MoO_3$, $Cr_2Mo_3O_{12}$ and $V_2MoO_8$ was studied cryoscopically in molten $K_2Cr_2O_7$ and $KNO_3$ solvents. The freezing point depression, $\Delta T$, of the solvents was obtained by measuring the cooling curves of the binary salt mixtures over a limited range of solute concentration. The number of foreign ions obtained $\nu$, showed that the solutes were either simply dissociated in the melt into the probable stable species $(MoO_4)^{2-}$, $(Mo_3O_{10})^{2-}$, $(Mo_4O_{13})^{2-}$ and $(Mo_5O_{16})^{2-}$ or, in some cases after reactions and rearrangements, into $(CrMo_2O_{10})^{2-}$ heteropolyions The solute $V_2MoO_8$, on the other hand, was found to dissolve without any apparent dissociation. An agreement between the experimental and calculated values of activity, $a$, based on the Temkin and Random Mixing models and that of Van't Hoff's equation support the proposed simple dissociation scheme for $K_2Cr_2O_7$–$Cs_2MoO_4$ system.

## INTRODUCTION

It is a well known fact that the freezing point of a pure solvent is lowered provided the foreign ions or species, $\nu$, present are different from those of the dissociation products of that solvent. The factor, $\nu$, gives only the number of such foreign species formed, rather than the effects of the forces they exert, i.e., it expresses a molecular property of the solute. The evaluation of $\nu$ is performed by measuring the freezing point depression, $\Delta T$, of solvents induced by solutes, in very dilute solutions, where Raoult–Van 't Hoff's law of freezing point depression $\Delta T = T_1 - T = \nu\ x_2[RT_1^2/L_1]$ is obeyed. $T_1$ and $T$ are the crystallization temperatures in K of the pure solvent and the mixture, respectively. $L_1$ is the melt enthalpy of the solvent in cal mole$^{-1}$, $x_2$ is the mole fraction of the solute and $R$ is the ideal gas constant (1.986 cal deg$^{-1}$ mole$^{-1}$). The value of $[RT_1^2/L_1]$ is the molar depression of freezing point or cryoscopic constant, $K_0$, of the pure solvent ($K_0 = 101.1$ and 318 for $K_2Cr_2O_7$ and $KNO_3$, respectively).

## MATERIALS AND METHODS

The experimental technique used was the same as described earlier [1]. The working temperature was 450 and 350°C for $K_2Cr_2O_7$ and $KNO_3$ solvents, respectively. The solutes employed in the present investigation were prepared and identified as reported [2–4], while the solvents $K_2Cr_2O_7$ (p.a.) and $KNO_3$ (purest) were obtained from Merck.

## RESULTS AND DISCUSSION

I. The number of foreign ions produced by the solutes, $M_2MoO_4$, $M_2Mo_3O_{10}$, $M_2Mo_4O_{13}$ and $M_2Mo_5O_{16}$ ($M = Rb$ or Cs) in the two solvents turned out to be three, i.e., $\nu = 3$ as shown in Figs. 1 and 2. This showed that a simple dissociation scheme is followed in these melts. Accordingly, a general reaction may be given as

$$K_2Cr_2O_7 + M_2Mo_xO_y \rightarrow 2\,K^+ + (Cr_2O_7)^{2-} + 2\,M^+ + (Mo_xO_y)^{2-}$$

$$KNO_3 + M_2Mo_xO_y \rightarrow K^+ + (NO_3)^- + 2\,M^+ + (Mo_xO_y)^{2-}$$

where $M = Rb$ or Cs and $x/y = 1/4$, $3/10$, $4/13$ and $5/16$.

The present results for Rb and Cs orthomolybdates are analogous with those of Na and K orthomolybdates both in the same solvents [5]. However,

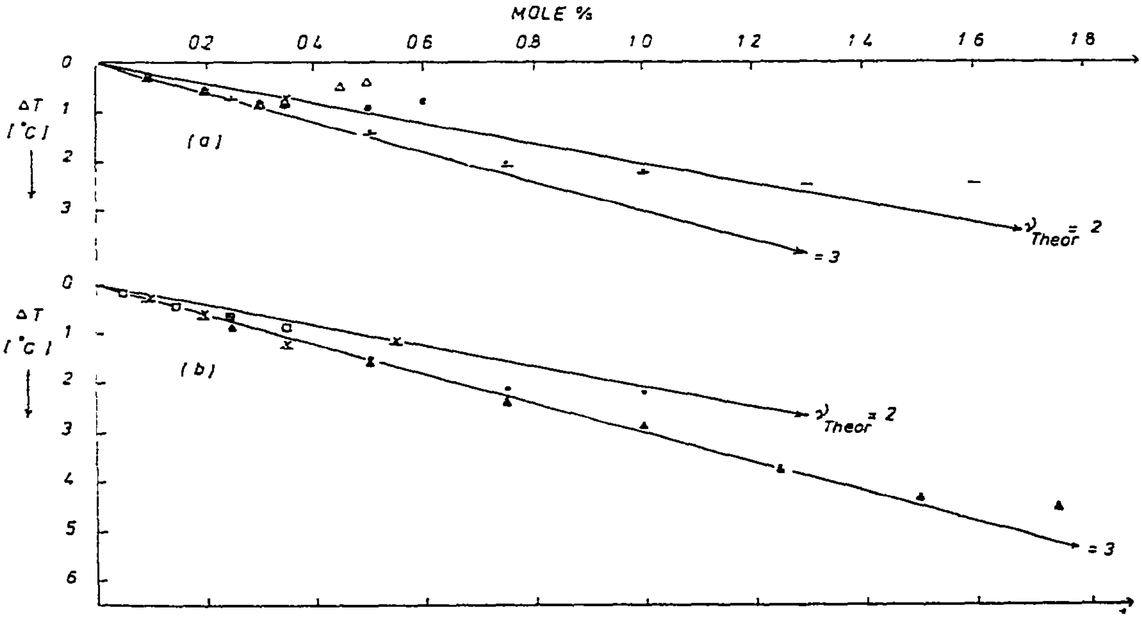

Fig. 1. Depression of the freezing point of molten $K_2Cr_2O_7$ by (a) ∸, $Rb_2MoO_4$; ●, $Rb_2Mo_3O_{10}$; △, $Rb_2Mo_4O_{13}$, ×, $Rb_2Mo_5O_{16}$; (b) ▲, $Cs_2MoO_4$; ○, $Cs_2Mo_3O_{10}$; $\underline{\times}$, $Cs_2Mo_4O_{13}$; □, $Cs_2Mo_5O_{16}$.

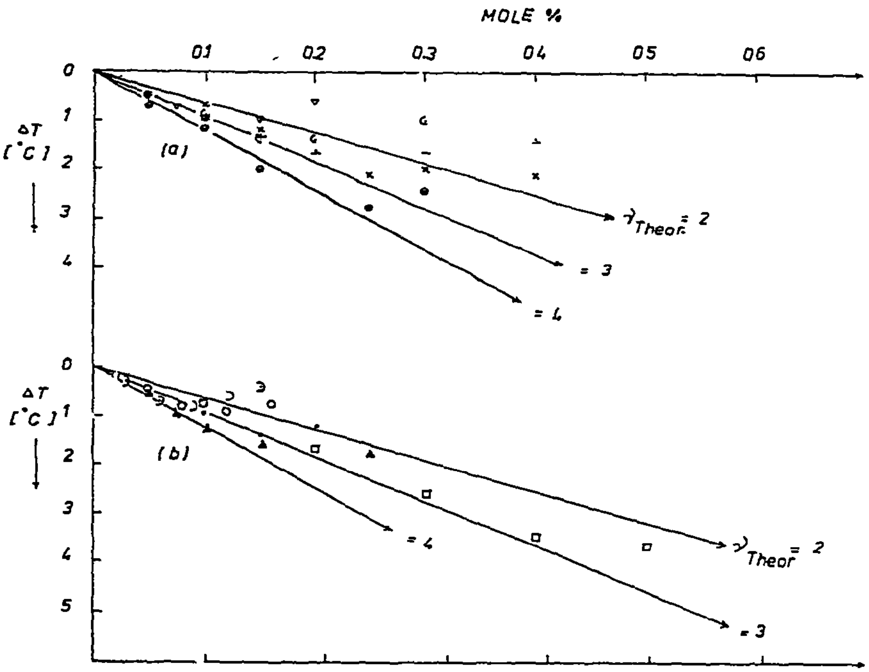

Fig. 2. Depression of the freezing point of molten $KNO_3$ by (a) ×, $Rb_2MoO_4$; ⊖, $Rb_2Mo_2O_7$; ∸, $Rb_2Mo_3O_{10}$ (·, $Rb_2Mo_4O_{13}$; ▽, $Rb_2Mo_5O_{16}$; (b) □, $Cs_2MoO_4$; ▲, $Cs_2Mo_2O_7$; ○, $Cs_2Mo_3O_{10}$; ○, $Cs_2Mo_4O_{13}$; ·), $Cs_2Mo_5O_{16}$.

neither $(MoO_4)^{2-}$ nor $(Mo_3O_{10})^{2-}$, $(Mo_4O_{13})^{2-}$ and $(Mo_5O_{16})^{2-}$ isopolymolybdate ions seem to undergo any reaction with those of the $(Cr_2O_7)^{2-}$ or $(NO_3)^-$ ions presumably because of their stability in the melt under the present experimental conditions. The formation and stability of one of the isopolymolybdate ions $(Mo_3O_{10})^{2-}$ in molten $KNO_3$ reported earlier [6] is

TABLE 1

Experimental and calculated values of $a$

| $x_1$ | $\nu_{exp}$ | $a_{1\,exp} = x_1^{\nu_{exp}}$ | Temkin $a_1 = x_1^3$ | Random Mixing $a_1 = x_1^2(\frac{2}{2+x_2})^2$ | Van't Hoff's equation $\ln a_1 = \frac{L_1}{R}(\frac{1}{T_1} - \frac{1}{T})$ |
|---|---|---|---|---|---|
| 0.9975 | 3.6 | 0.9826 | 0.9925 | 0.9925 | 0.9917 |
| 0.995 | 3.2 | 0.9831 | 0.9851 | 0.9851 | 0.9840 |
| 0.9925 | 3.2 | 0.9759 | 0.9777 | 0.9777 | 0.9780 |
| 0.9900 | 2.9 | 0.9709 | 0.9703 | 0.9704 | 0.9740 |
| 0.9875 | 3.0 | 0.9630 | 0.9630 | 0.9631 | 0.9623 |
| 0.985 | 2.9 | 0.9568 | 0.9557 | 0.9559 | 0.9570 |

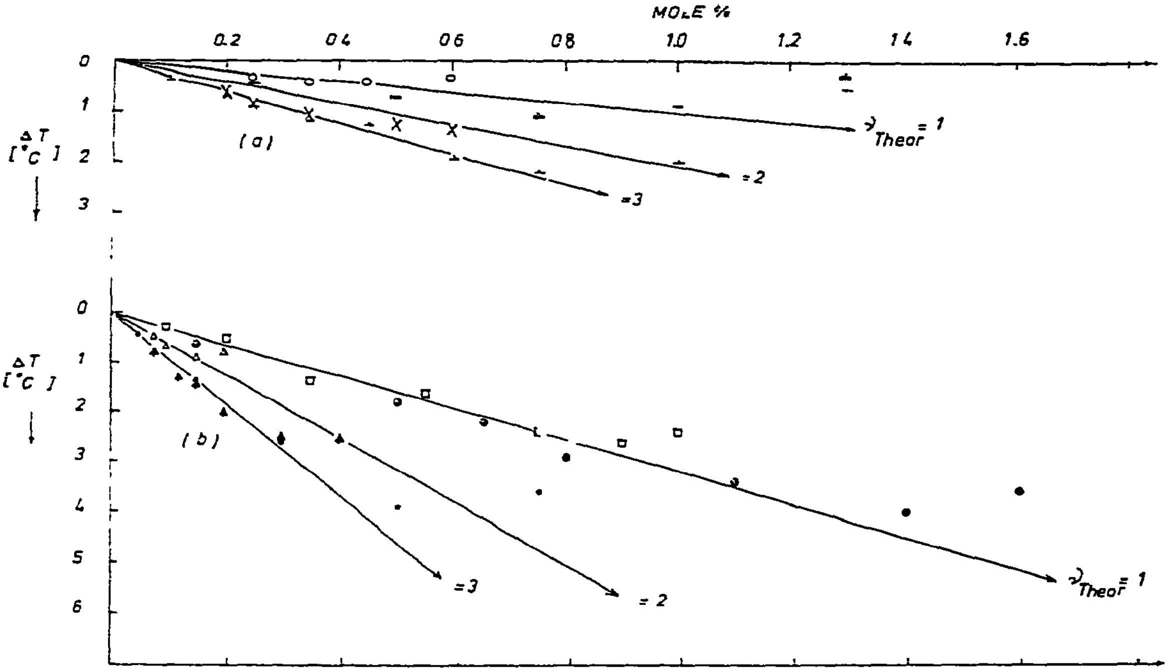

Fig. 3 (a) Depression of the freezing point of molten $K_2Cr_2O_7$ by ×, $Na_2CrO_4 \cdot MoO_3$; ○, $K_2CrO_4$ 2 $MoO_3$, ∸, $Cr_2Mo_3O_{12}$; =, $V_2MoO_8$; (b) Depression of the freezing point of molten $KNO_3$ by ●, $Na_2CrO_4 \cdot MoO_3$, ⊘, $K_2CrO_4 \cdot 2$ $MoO_3$; ↑, $Cr_2Mo_3O_{12}$; □, $V_2MoO_8$; △, $Cr_2O_3$.

based on a different method. The $Cs_2MoO_4$-rich (1.5 mole%) mixture of $K_2Cr_2O_7$ was chosen, as an example of this group of solutes, to calculate its activity using Temkin [7] and Random Mixing [8] models as well as Van 't Hoff's equation. The experimental and calculated activities, $a$, are given in Table 1.

Table 1 demonstrates an excellent agreement between the values of $a_{exp}$ and $a_{calc}$ thus supporting the proposed dissociation scheme. However, the choice of a specific model is not possible, since such an agreement depends on the same ideality criteria used rather than the model chosen [8].

II-1. Although the solutes $K_2CrO_4 \cdot 2\ MoO_3$ and $V_2MoO_8$ gave the same number of foreign ions, $\nu = 1$, in both the solvents (Fig. 3), they showed an obviously different behaviour in the melt. The solute $K_2CrO_4 \cdot 2\,MoO_3$ appears to be dissociated, while $V_2MoO_8$ presumably dissolves without dissociation. The corresponding reactions may consequently be represented as

$$K_2Cr_2O_7 + K_2CrO_4 \cdot 2\ MoO_3 \rightarrow 4\ K^+ + (Cr_2O_7)^{2-} + (CrMo_2O_{10})^{2-}$$

$$KNO_3 + K_2CrO_4 \cdot 2\ MoO_3 \rightarrow 3\ K^+ + (NO_3)^- + (CrMo_2O_{10})^{2-}$$

$$K_2Cr_2O_7 + V_2MoO_8 \rightarrow 2\ K^+ + (Cr_2O_7)^{2-} + V_2MoO_8$$

$$KNO_3 + V_2MoO_8 \rightarrow K^+ + (NO_3)^- + V_2MoO_8$$

The above scheme for the dissociation of $K_2CrO_4 \cdot 2\ MoO_3$ and that for the dissolution of $V_2MoO_8$ is, however, supported by the fact that the value obtained of $\nu = 1$, is smaller than that required for their constituents: $K_2CrO_4$, $MoO_3$ and $V_2O_5$ studied separately in the same solvents as reported earlier [1,5,9].

II-2. The dissociation of $Na_2CrO_4 \cdot MoO_3$ gave $\nu = 3$ in both the molten solvents (Fig. 3), suggesting that the reactions take place through dissociation and simultaneous rearrangement of ions as shown.

$$K_2Cr_2O_7 + 2\ Na_2CrO_4 \cdot MoO_3 \rightarrow 2\ K^+ + 4\ Na^+ + 2\ (CrMoO_7)^{2-} + (Cr_2O_7)^{2-}$$
$$2(CrMoO_7)^{2-} \rightarrow (CrMo_2O_{10})^{2-} + (CrO_4)^{2-}$$

---

$$K_2Cr_2O_7 + 2\ Na_2CrO_4 \cdot MoO_3 \rightarrow 2\ K^+ + 4\ Na^+ + (CrMo_2O_{10})^{2-} + (CrO_4)^{2-} + (Cr_2O_7)^{2-}$$

Similarly

$$KNO_3 + 2\ Na_2CrO_4 \cdot MoO_3 \rightarrow K^+ + (NO_3)^- + 4\ Na^+ + (CrMo_2O_{10})^{2-} + (CrO_4)^{2-}$$

It can be seen that the number of foreign ions, $\nu = 3$, does not change after rearrangement of the heteroions $2(CrMoO_7)^{2-}$. However, such a rearrangement seems to be probable because the continuence of $(CrMoO_7)^{2-}$ ions as such in the melt will lead to a lower and a higher value of $\nu$ in the cases of molten $K_2Cr_2O_7$ and $KNO_3$ solvents, respectively. This assumption can be explained by considering the heteroions $2(CrMoO_7)^{2-}$ as a mixed crystal of $(Cr_2O_7)^{2-}$–$(Mo_2O_7)^{2-}$, then the $(Mo_2O_7)^{2-}$ group has the tendency to form an isomorphous substitution within the $K_2Cr_2O_7$-lattice [5], thus leading to $\nu < 3$, and also the same heteroions may dissociate in $KNO_3$-solvent giving $2(CrO_4)^{2-}$ and $2(MoO_4)^{2-}$ groups, leading to $\nu > 3$, which is not the case here. The behaviour of dimolybdate anion $(Mo_2O_7)^{2-}$ of Rb and Cs salts was, therefore, studied in molten $KNO_3$ ($\nu = 4$, Fig. 2). The resulting species were found to be unstable giving rise to two basic monomolybdate anions analogous to the reactions of $K_2Cr_2O_7$ and $K_2Mo_2O_7$ in molten $KNO_3$ [5]. These solutes were found to behave as Lux-acids and took their oxide-ions from the nitrate base electrolyte, leading to the formation of the more basic $CrO_4^{2-}$ and $MoO_4^{2-}$ ions, respectively. Accordingly, the reaction may be written as

$$2\ KNO_3 + M_2Mo_2O_7 \rightarrow 2\ M^+ + 2\ K^+ + 2(MoO_4)^{2-} + 2\ NO_2 + \tfrac{1}{2}\ O_2$$

$(M = Rb \text{ or } Cs)$

The results obtained by investigating the ions, $(Cr_2O_7)^{2-}$ and $(Mo_2O_7)^{2-}$ separately in the two solvents support the above mechanism for the heteroions rearrangement process.

II-3. The mechanism of dissociation of $Cr_2Mo_3O_{12}$ in the two solvents seems to be obviously different, though the same number of foreign ions, $\nu = 3$, has been found (Fig. 3) as in the above cases of II-1 and II-2. Consequently, the proposed mechanism for the dissociation of $Cr_2Mo_3O_{12}$ in molten $K_2Cr_2O_7$ may be given as follows

$$\begin{array}{l}
\text{(a) } Cr_2Mo_3O_{12} \rightarrow Cr_2O_3 + Mo_3O_9 \\
\text{(b) } K_2Cr_2O_7 + Mo_3O_9 \rightarrow 2\ K^+ + (Mo_3O_{10})^{2-} + 2\ CrO_3 \\
\text{(c) } 2\ K_2Cr_2O_7 + 2\ CrO_3 \rightarrow 4\ K^+ + 2(Cr_3O_{10})^{2-} \\
\hline
3\ K_2Cr_2O_7 + Cr_2Mo_3O_{12} \rightarrow 6\ K^+ + Cr_2O_3 + (Mo_3O_{10})^{2-} + 2(Cr_3O_{10})^{2-}
\end{array}$$

The mechanism of these reactions can be understood by supposing that $Cr_2Mo_3O_{12}$ is first dissociated into [step (a)] two oxides, $Cr_2O_3$ and $Mo_3O_9$, without undergoing further dissociation of the latter oxide. It has already been pointed out that the first dissociation product, $Cr_2O_3$, is stable and insoluble in molten $K_2Cr_2O_7$ [5], and hence it does not contribute to the freezing point depression. The second dissociation product may then react with the solvent [step (b)] by taking its oxide-ion from the $(Cr_2O_7)^{2-}$ group, to form the trimolybdate anion $(Mo_3O_{10})^{2-}$ and the 2 $CrO_3$ molecules. The stability of $(Mo_3O_{10})^{2-}$ ion in molten $K_2Cr_2O_7$ has already been demonstrated in the present work (Fig. 1). Finally, a reaction may occur between the [step (c)] $CrO_3$ molecules and the $(Cr_2O_7)^{2-}$ group to form the well-known stable $(Cr_3O_{10})^{2-}$ ion in such a solvent [5].

In the case of the $KNO_3$ melt, one of the dissociation products of $Cr_2Mo_3O_{12}$, namely, $Mo_3O_9$ may also give rise to the relatively more basic ion $(Mo_3O_{10})^{2-}$, by taking its oxide-ion from the nitrate melt. Such an ion $(Mo_3O_{10})^{2-}$ has already been prepared in the solid phase, studied in molten $KNO_3$, and has been found to be stable (Fig. 2). The other dissociation product, $Cr_2O_3$, seemed to react with the nitrate melt to give $2(CrO_4)^{2-}$ ions, probably via the formation of $(Cr_2O_7)^{2-}$ ions. The resulting three foreign ions, $\nu = 3$, may consequently be identified as $2(CrO_4)^{2-}$ and $(Mo_3O_{10})^{2-}$ [Fig. 3(b)].

In addition to the above studies, the behaviour of $Cr_2O_3$ oxide has also been investigated in molten $KNO_3$ to support the formation of the chromate ion. Thus the experimentally determined [Fig. 3(b)] value of $\nu$ as 2 may suggest the following sequence of reactions

$$\begin{array}{l}
\text{(a) } 2\ KNO_3 + Cr_2O_3 \rightarrow 2\ K^+ + (Cr_2O_7)^{2-} + 2\ NO \\
\text{(b) } 4\ KNO_3 + (Cr_2O_7)^{2-} \rightarrow 4\ K^+ + 2(CrO_4)^{2-} + 4\ NO_2 + \tfrac{3}{2}\ O_2
\end{array}$$

Moreover, the yellow solution obtained as a result of the reaction of $Cr_2O_3$ as well as that of $Cr_2Mo_3O_{12}$ in molten $KNO_3$ showed an absorption maximum at 27100 $cm^{-1}$, thus confirming the formation of $(CrO_4)^{2-}$ ions.

Similar results were also obtained for the reaction of $Cr_2O_3$ in molten lithium-potassium nitrate eutectic [10].

## REFERENCES

1 M. Hassanein and N.S. Youssef, Z. Anorg. Allg. Chem., 422 (1978) 216.
2 R. Salmon and P. Caillet, Bull. Soc. Chim. Fr., 5 (1969) 1569.
3 W.P. Doyle, G. McGuire and C.M. Clark, J. Inorg. Nucl. Chem., 28 (1966) 1185.
4 M.V. Mokhosoev, E.I. Getman, V L. Butukhanov, V.G. Pitsuga and I.F., Kokot, Zh Neorg. Khim., 18 (1973) 1011.
5 M Hassanein and E. Kordes, Z. Anorg. Allg. Chem , 387 (1972) 1.
6 A.M. Shams el Din and A.A. el Hosary, J. Electroanal. Chem., 9 (1965) 349.
7 M. Temkin, Acta Physikochim. U.R.S.S., 20 (1945) 411.
8 C. Sinistri, J. Chem. Educ., 48 (1971) 753.
9 M. Hassanein, Z. Anorg Allg. Chem , 399 (1973) 125.
10 B.J. Brough, D.H. Kerridge and S.A. Tariq, Inorg Chim Acta, 1 (1967) 267.