

## Abstracts of Forthcoming Articles

*New Members of a Family of Layered Bismuth Compounds.* HIROSHI KODAMA,\* FUJIO IZUMI, AND AKITERU WATANABE, National Institute for Researches in Inorganic Materials, 1-1 Namiki, Sakura-Mura, Niihari-Gun, Ibaraka-Ken, 305, Japan. Two new compounds,  $\text{Bi}_2\text{Ti}_2\text{O}_8\text{F}$  and  $\text{PbBi}_2\text{Ti}_2\text{O}_{11}\text{F}$ , are prepared and identified by X-ray diffraction analysis. These compounds are members of the family called layered bismuth compounds. Thermal properties of the new compounds are also studied. Besides the preparation and identification of these new compounds, a new method for preparing already known members,  $\text{Bi}_2\text{NbO}_5\text{F}$  and  $\text{Bi}_2\text{TiO}_4\text{F}_2$ , is reported. Moreover, the possibility of the existence of other new members belonging to the family is discussed.

*A Thermochemical Study of the Phase Reaction:  $\text{TbO}_{1.5+x} + (3/28 - x/2)\text{O}_2 \rightarrow \frac{1}{2}\text{Tb}_7\text{O}_{12}$ .* HIDEAKI INABA, ALEXANDRA NAVROTSKY, AND LEROY EYRING,\* Department of Chemistry, Arizona State University, Tempe, Arizona 85281. The heat of reaction and equilibrium pressure for the oxidation reaction  $\text{TbO}_{1.5+x} + (3/28 - x/2)\text{O}_2 \rightarrow \frac{1}{2}\text{Tb}_7\text{O}_{12}$  have been measured by means of a Tian-Calvert type of calorimeter and a thermal balance. The results of the weight measurement show a reproducible hysteresis loop. The heat of reaction has been measured along the oxidation branch of the hysteresis loop. The partial molar enthalpy indicates four distinct compositional regions. First, the  $\text{TbO}_{1.5+x}$  region which can be described in terms of a point defect model and strong interaction between neighboring excess oxygen atoms. Second, the region between  $\text{TbO}_{1.54}$  and  $\text{TbO}_{1.61}$  is interpreted as the intrinsic hysteresis region and discussed in terms of the regular solution model. Third, the region between  $\text{TbO}_{1.61}$  and  $\text{TbO}_{1.70}$  is recognized as a pseudophase region. Fourth, a region of *iota* phase exists in which the partial thermodynamic quantities can be compared with those of  $\text{CeO}_{1.714}$ ,  $\text{PrO}_{1.714}$ , and  $\text{TbO}_{1.714}$ . The partial molar enthalpy was also measured for a scanning loop which is also interpreted in terms of the four regimes.

*Structure Cristalline de l'Oxalate de Baryum  $2\text{BaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ .* J. C. MUTIN,\* Y. DUSAUSOY, AND J. PROTAS, Laboratoire de Recherches sur la Réactivité des Solides, Faculté des Sciences Mirande, B.P. 138, 21004 Dijon Cédex, France.  $2\text{BaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  ( $M = 468.73$ ) is triclinic space group  $P \bar{1}$ , with  $a = 9.312(1) \text{ \AA}$ ,  $b = 9.649(1) \text{ \AA}$ ,  $c = 6.188(1) \text{ \AA}$ ,  $\alpha = 90.13(2)^\circ$ ,  $\beta = 95.36(2)^\circ$ ,  $\gamma = 125.18(2)^\circ$ ,  $Z = 2$ ,  $D_m = 3.48$ ;  $D_x = 3.51 \text{ g} \cdot \text{cm}^{-3}$ . The position of the Ba atom was determined from a Patterson function. A subsequent Fourier synthesis clearly revealed the position of all C and O atoms in the structure. Refinement of the MoK $\alpha$  diffractometer data by a least-squares method using full matrix gave  $R = 0.065$ . The structure presents two remarkable characteristics: (a) We distinguish two types of  $(\text{C}_2\text{O}_4)^{2-}$  ions. The first are planar, the second are notably separated from the plane configuration (deviation =  $30^\circ$ ); this deformation is of a steric origin. (b) The water molecules are located in channels parallel to  $[001]$ . They enter in the coordination of one of the  $\text{Ba}^{2+}$  ions but do not exchange any strong hydrogen bond with oxygen atoms which surround them.

*Estimation of the Standard Entropy Change on Complete Reduction of Oxide  $M_m\text{O}_n$ .* TETSURŌ NAKAMURA, Research Laboratory of Engineering Materials, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Yokohama 227, Japan. The standard entropy change  $\Delta S^\circ$  for the reduction of nonmagnetic, nonconducting oxides,  $M_m\text{O}_n(\text{s}) = m\text{M}(\text{s}) + (n/2)\text{O}_2(\text{g})$ , has been estimated as a function of  $m$ ,  $n$ , and temperature  $T$  from motional entropies of oxygen molecules and vibrational entropies of solid phases. An available formula of  $\Delta S_{\text{calc}}^\circ = a m + b n$  with constant  $a$  and  $b$  based on effective Debye temperatures,  $\theta_M = 165 \text{ K}$  for  $M$  and  $\theta_{\text{O}_2} = 540 \text{ K}$  for  $M_m\text{O}_n$ , agrees well with the observed  $\Delta S_{\text{obs}}^\circ$  for  $M_2\text{O}$ ,  $\text{MO}$ ,  $M_2\text{O}_3$ ,  $\text{MO}_2$ ,  $M_2\text{O}_5$ , and  $\text{MO}_3$  in the temperature range  $T = 300\text{--}1300 \text{ K}$ . Possible electronic entropy corrections are applied to  $\Delta S_{\text{calc}}^\circ$  for  $M_2\text{O}_7$  and  $\text{MO}_4$ .

*Thermodynamics of Double Oxides. III. Study of the  $\text{CaO}\text{--}\text{Ga}_2\text{O}_3$  System by the emf Method and X-Ray Analysis.* YU. YASCOLIS, V. A. LEVITSKII,\* L. N. LYKOVA, AND T. A. KALININA, Laboratory of

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