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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, $Bi_3Ti_2O_8F$ and $PbBi_3Ti_3O_{11}F$, 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, Bi_2NbO_5F and $Bi_2TiO_4F_2$, 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: $TbO_{1.5+x} + (3/28 - x/2)O_2 \rightarrow \frac{1}{7}Tb_7O_{12}$. 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 $TbO_{1.5+x} + (3/28 - x/2)O_2 \rightarrow \frac{1}{7}Tb_7O_{12}$ 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 $TbO_{1.5+x}$ region which can be described in terms of a point defect model and strong interaction between neighboring excess oxygen atoms. Second, the region between $TbO_{1.54}$ and $TbO_{1.61}$ is interpreted as the intrinsic hysteresis region and discussed in terms of the regular solution model. Third, the region between $TbO_{1.61}$ and $TbO_{1.70}$ 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 $CeO_{1.714}$, $PrO_{1.714}$, and $TbO_{1.714}$. 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 $2BaC_2O_4 \cdot H_2O$. 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. $2BaC_2O_4 \cdot H_2O$ ($M = 468.73$) is triclinic space group $P\,\bar{1}$, with $a = 9.312(1)$ Å, $b = 9.649(1)$ Å, $c = 6.188(1)$ Å, $\alpha = 90.13(2)°$, $\beta = 95.36(2)°$, $\gamma = 125.18(2)°$, $Z = 2$, $D_m = 3.48$; $D_x = 3.51$ g $\cdot$ 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 Mo$K\alpha$ 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 $(C_2O_4)^{2-}$ ions. The first are planar, the second are notably separated from the plane configuration (deviation = 30°); 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 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_mO_n. Tetsurō' Nakamura, Research Laboratory of Engineering Materials, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Yokohama 227, Japan. The standard entropy change $\Delta S°$ for the reduction of nonmagnetic, nonconducting oxides, $M_mO_n(s) = mM(s) + (n/2)O_2(g)$, 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 $\Delta S°_{calc} = a\ m + b\ n$ with constant a and b based on effective Debye temperatures, $\theta_M = 165$ K for M and $\theta_{OX} = 540$ K for M_mO_n, agrees well with the observed $\Delta S°_{obs}$ for M_2O, MO, M_2O_3, MO_2, M_2O_5, and MO_3 in the temperature range $T = 300$–1300 K. Possible electronic entropy corrections are applied to $\Delta S°_{calc}$ for M_2O_7 and MO_4.

Thermodynamics of Double Oxides. III. Study of the CaO–Ga_2O_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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Chemical Thermodynamics, Chemical Faculty, Moscow Lomonossov State University, Moscow 117234, USSR. Using the methods of X-ray and differential thermal analysis, four compounds $Ca_3Ga_2O_6$, $Ca_3Ga_4O_9$, $CaGa_2O_4$, and $CaGa_4O_7$ have been found in the subsolidus region of the phase diagram of the $CaO–Ga_2O_3$ system. The existence of the gallate $Ca_3Ga_4O_9$ discovered for the first time is confirmed by experiments on measuring the emf's of galvanic cells. Changes in Gibbs energy, enthalpy, and entropy for the reactions of formation of all four calcium gallates from oxides and elements have been determined by the emf method with a solid $|F^-|$-ionic electrolyte in the range 1100–1400 K. On the basis of the data obtained the relative stability of the compounds is analyzed and the activity of calcium oxide in the system under study is calculated.

Etude, par RMN Large Bande du Proton, d'Hydrogénophosphates et -Arséniates d'un Métal Trivalent (Al, Ga) et de Sodium. M. PINTARD-SCRÉPEL, C. DORÉMIEUX-MORIN, AND F. D'YVOIRE,* Laboratoire de Chimie Appliquée, Université Paris-Sud, 91405 Orsay, France. Eleven aluminum–sodium or gallium–sodium hydrogenophosphates or -arsenates and an aluminum hydrogenarsenate have been studied. The preparation and characteristic properties of the new compounds are described. The wide-band proton NMR powder spectra have been interpreted by shape function calculation. The models used imply two types of magnetic configuration: one with two spins, the other with three spins located at the apices of an isosceles triangle. The hydrogen distribution between water molecules and OH groups has been determined and the constitution of the salts has thus been deduced. The constitution of the hydroxyhydrogen salts $Na_3Al(OH)(HXO_4)(XO_4)$ (X = P, As) is confirmed but two compounds previously considered as orthoarsenates probably contain condensed anions as expressed by the formula $NaM^{III}H_3As_3O_{11} \cdot 2H_2O$. The method for interpreting NMR spectra is discussed.

A Kinetic Study of the Oxidation and Reduction of Praseodymium Oxides: $(1/7)Pr_7O_{12} + (1/7 - x/2)O_2 \rightleftarrows PrO_{2-x}$. HIDEAKI INABA, SHENG H. LIN, AND LEROY EYRING,* Department of Chemistry, Arizona State University, Tempe, Arizona 85281. Kinetic and thermodynamic studies between the ordered iota ($n = 7$ in Pr_nO_{2n-2}) and the disordered alpha (PrO_{2-x}) phases have been carried out as a function of oxygen pressure at 655, 675, 695, and 715°C using a sample of small single crystals. The existence of a reproducible hysteresis loop, which depends on the temperature and pressure, having an inflection point around a composition $PrO_{1.75}$ is shown. The inflection point is interpreted as a phase of $n = 8$ in Pr_nO_{2n-2} (eta) coherently intergrown with $n = 7$, 9, and 10, giving an average composition of $PrO_{1.75}$. In order to interpret the kinetic data, various theoretical models are examined, for example, oxygen diffusion, a phase-boundary reaction control, or nucleation and growth. None of these models, however, is capable of correlating the experimental data. It was found that a plot of the reaction rate versus the ambient pressure extrapolates linearly to a finite pressure at zero rate, as was previously observed in the oxidation reaction between iota and zeta phases of the same system. The model developed for the oxidation reaction between the iota and the zeta phases has been modified by taking into account the intermediate phases around $PrO_{1.75}$, through which the reaction passes. The modified rate law has two reaction constants: the rate constant from the reactant transforming to the intermediate phase (k_1) and for the transformation from the intermediate to the product phase (k_2). The fit to the experimental curve is satisfactory for both the oxidation and reduction reaction. From the temperature dependence of the observed rate constants, the activation energy for the oxidation and reduction was determined to be 75.0 and 60.9 kcal/mole, respectively.

A Thermochemical Study of the Phase Reaction: $(1/7)Pr_7O_{12} + (1/7 - x/2)O_2 = PrO_{2-x}$. HIDEAKI INABA, ALEXANDRA NAVROTSKY, AND LEROY EYRING,* Department of Chemistry, Arizona, State University, Tempe, Arizona 85281. The heat of reaction and equilibrium pressure for both the oxidation and reduction reactions $(1/7)Pr_7O_{12} + (1/7 - x/2)O_2 = PrO_{2-x}$ have been measured by means of a Tian–Calvert type of calorimeter and thermal balance. The results of equilibrium pressure measurements under isothermal conditions show a reproducible and unsymmetrical hysteresis loop. The loop is interpreted as due to a different pattern of intergrowth formed during oxidation and reduction. The ordered intermediate phases (Pr_nO_{2n-2}) are intergrown coherently at the unit cell level with each other but not with the disordered alpha phase (PrO_{2-x}). The role of coherent intergrowth in both symmetric and unsymmetric hysteresis loops has been discussed. The partial molar enthalpy ($-\Delta\bar{H}_{O_2}$) is about 58 kcal per mole of O_2 in the Pr_7O_{12} phase; it increases slightly as O/Pr increases