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 followed by a sharp increase to about 85 kcal per mole of O_2 around $PrO_{1.78}$. No difference in partial molar enthalpy is observed between the oxidation and reduction paths within experimental error, even though different equilibrium pressures are observed depending on the path. The slight increase in the partial molar enthalpy in the "two-phase" region is attributed to the interaction term of the different domains using the same regular solution model as has been used to account for the hysteresis observed previously. The sharp change in $-\Delta\bar{H}_{O_2}$ around $PrO_{1.78}$ is believed associated with the phase change from the coherently intergrown ordered phases to the disordered alpha phase. The difference between the partial molar entropy on oxidation and reduction is explained by both the regular solution model and the usual thermodynamic treatment using the data of isothermal hysteresis.

Quasi-Chemical Treatment of Intermediate Phase Appearing in Nonstoichiometric Compounds. JUN TATENO, Japan Atomic Energy Research Institute, Tokai-mur, Naka-gun, Ibaraki-ken, Japan. A quasi-chemical treatment of the superlattice formation model is applied to intermediate phases appearing in nonstoichiometric compounds. Two kinds of interaction energy are introduced and both intermediate phase and two-phase separation are described in a single formula. The order parameter and the free energy are obtained as a function of temperature and of composition. The boundaries of phases are determined by the common tangent method.

The System $BaO–SnO_2–Fe_2O_3$ with less than 50 mole% BaO at 1200°C in Air, a Crystallographic Study. M. C. CADÉE* AND D. J. W. IJDO, Section of Solid State Chemistry, Gorlaeus Laboratories, Leiden State University, P.O. Box 9502, 2300 RA Leiden, The Netherlands. The $BaO–SnO_2–Fe_2O_3$ system has been investigated after heating at 1200°C in air. The mole percentage BaO was less than 50%. In the part of the system examined five quaternary compounds were determined: $BaSn_2Fe_4O_{11}$, $Ba_3SnFe_{10}O_{20}$, $Ba_{0.69}Sn_{2.62}Fe_{1.38}O_8$, $BaSn_{0.90}Fe_{5.47}O_{11}$, and a compound of still unknown composition; the best approximation is $BaSn_{1.70}Fe_{2.75}O_{8.52}$. The compounds were recognized by their X-ray diffraction patterns. All X-ray powder diffraction patterns could be indexed. No indication was found for reduction of Fe^{3+} to Fe^{2+} at 1200°C. A solid solution of perovskite compounds was found in the system $Ba_2Fe_2O_5–BaSnO_3$, caused by oxidation of Fe^{3+} to Fe^{4+}. This oxidation was observed also in the area $Ba_2Fe_2O_5–BaFe_2O_4–BaSnO_3$. The triangulation found in the $BaO–SnO_2–Fe_2O_3$ system is discussed and the system is compared with the $BaO–TiO_2–Al_2O_3$ system.

Crystal Structure and Pyroelectric Coefficient of $Co(IO_3)_2$ and Structural Relationships among the Anhydrous Noncentrosymmetric 3d-Transition Metal Iodates. C. SVENSSON, S. C. ABRAHAMS,* AND J. L. BERNSTEIN, Bell Laboratories, Murray Hill, New Jersey 07974. Cobalt iodate, $Co(IO_3)_2$ is pyroelectric at room temperature and crystallizes in the trigonal space group $P3$ with four formulas in the unit cell. The pyroelectric coefficient $p_3 = 5.1(5) \times 10^{-5}$ C m^{-2} K^{-1}, and the lattice constants at 298 K are $a = 10.9597(1)$ and $c = 5.0774(1)$ Å. The crystal structure was solved from the Patterson function and a consideration of the structural similarities among the anhydrous 3*d*-transition metal iodates. Refinement was by the method of least squares using 1825 observed reflections measured with a four-circle diffractometer. The final agreement factor $R = 0.050$. Two of the three independent octahedrally coordinated cobalt atoms are disordered. The absolute orientation of the polar axis was determined with respect to the crystal morphology. The iodine atoms in the trigonal pyramidal iodate ions point toward the morphologically undeveloped end of the crystals, as does the positive sense of the spontaneous polarization: It is this end that develops a positive polarization on heating. The spontaneous polarization is estimated at about 22×10^{-2}C m^{-2}. The iodate ion arrangement is very similar to that in α-$LiIO_3$. The anhydrous noncentrosymmetric 3*d*-iodates may be classified into three isomorphous sets, with space group $P6_3$ and corresponding maximal subgroups $P3$ and $P2_1$. All three sets are isostructural with α-$LiIO_3$ except for the cation distribution. The ability of the iodate ion framework to accept a range of cations of different valences is discussed in terms of the tricapped trigonal-prismatic environment about the iodine atoms.

Solid Solutions of $Pb_8M_2(XO_4)_6$ Lead Alkali Apatites. I. MAYER,* S. COHEN, AND J. R. MATALON, Department of Inorganic and Analytical Chemistry, Hebrew University, Jerusalem, Israel. The $Pb_8Na_{2-x}K_x(PO_4)_6$, $Pb_8Na_{2-x}K_x(AsO_4)_6$, $Pb_8Na_{2-x}Rb_x(PO_4)_6$, and $Pb_8K_{2-x}Rb_x(PO_4)_6$ systems were studied. The compounds crystallize at all compositions in the $P6_3/m$ hexagonal apatite structure and