Analysis of the potentiometric data shows that the optimum hydrogenolysis conditions are achieved when the shift of the catalyst potential $(\Delta\varphi)$ from the potential of the reversible hydrogen electrode is approximately 200 mV. When $\Delta\varphi < 200$ mV, the reduction of the carbonyl group is accelerated; when $\Delta\varphi > 200$ mV, acid-formation reactions begin to occur at a high rate. In both cases the yields of glycerol and glycols fall. By varying the process conditions, it is possible to carry out the reaction under optimum conditions $(\Delta\varphi \simeq 200$ mV) and thereby increase the yields of the desired products. The activation energies for the hydrogenation of glucose to sorbitol and for the hydrogenolysis of glucose to glycerol were calculated. The process mechanism was examined on the basis of the results obtained.

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A Spectroscopic Study of Water-Monocarboxylic Acid-Heptane Liquid Systems

A.G.Kovaleva

Miscibility in the ternary liquid systems depends on the molecular state of the monocarboxylic acids in homogeneous saturated solutions of the systems[1]. The complete paper presents the results of a study of the infrared spectra of homogeneous saturated solutions of the system water−propionic acid−heptane, water−valeric acid−heptane, and water−oenanthic acid−heptane over a wide range of concentrations in the region of the stretching vibrations of the carbonyl group.

The presence of a single intense band in the spectrum of an equimolecular propionic acid−water solution is evidence of the formation in the solution of 1:1 complexes. This conclusion is confirmed also by data for the viscosity of the binary solutions[2]. The simultaneous presence in the spectra of the test systems of several bands can be accounted for by an equilibrium between various forms of the complexes. The observed differences in the spectra of the solutions can be explained by different structures of the hydrates.

The decrease of the integral intensities of the C=O bands with increase of the concentrations of the acid and water and also with increase of the densities of the solutions can be accounted for by the formation of a non-linear hydrogen bond in the monocarboxylic acid hydrates.

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# The Krypton Difluoride-Bromine Pentafluoride Binary System

V.N.Prusakov and V.B.Sokolov

The present study deals with the possibility of using bromine pentafluoride for the synthesis of KrF_2 complexes. The $KrF_2 - BrF_5$ binary system, the phase diagram of which is shown in the Figure, was investigated by differential thermal analysis. The miscibility of the system components is limited. The solubility of krypton difluoride in bromine pentafluoride does not exceed 16.5 moles per 1000 g of BrF_5. The incongruently melting solvates $KrF_2 \cdot 9BrF_5$ and $KrF_2 \cdot 2BrF_5$ and the congruently melting solvate $KrF_2 \cdot BrF_5$ (the distectic point is at $-17°C$) are formed in the system. When $c_{KrF_2} > 0.75$ mole fraction, two layers are observed. The marked exothermic effect at 77°C can be accounted for by the fusion of KrF_2 with decomposition into the elements.
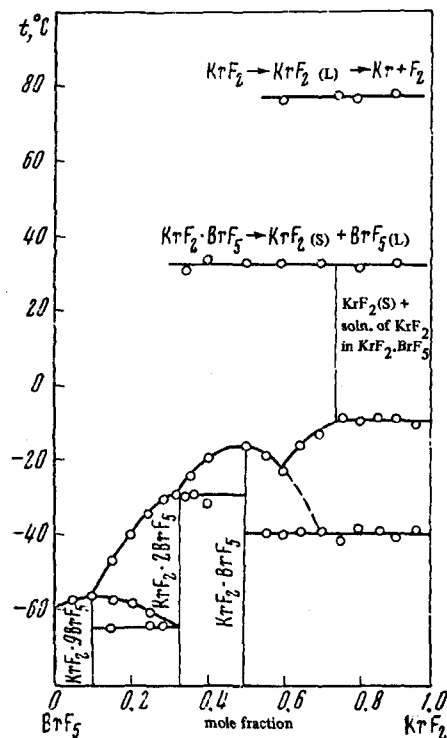
Phase diagram for the $KrF_2 - BrF_5$ system [S = solid, L = liquid (Ed. of Translation)].

A study was also made of the solid products in the 1:2 $BrF_5 - SbF_5$, 1:2 $KrF_2 - SbF_5$, and $KrF_2 - SbF_5 - BrF_5$ systems by chemical analysis and infrared spectroscopy. This made it possible to characterise krypton difluoride as a more powerful donor of fluoride ions than BrF_5: the only compound formed in the $KrF_2 - SbF_5 - BrF_5$ system is a complex of krypton difluoride—$KrF_2 \cdot 2SbF_5$.

The data obtained lead to the conclusion that bromine pentafluoride can be employed (together with anhydrous HF) as a non-aqueous solvent in the study of the complex formation reactions of KrF_2 and also for its stabilisation. Bromine and chlorine trifluorides and iodine pentafluoride are fluorinated by krypton difluoride at room temperature to higher fluorides. Krypton difluoride is almost insoluble in chlorine pentafluoride.

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The Probability of the Escape of Molecules From an Effusion Chamber with Evaporation from the Bottom

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In order to determine the probability of the escape of molecules from a straight circular-cylindrical Knudsen chamber, use was made of a direct method for the solution of the integral equations describing the distribution of molecular fluxes in the system taking into account the repeated re-evaporation and reflection of the molecules from the bottom, lateral walls, and the lid of the chamber in accordance with the cosine law. It was assumed that the lid and the lateral walls are indifferent with respect to the test substance, which completely covers the bottom of the chamber. Vapour effuses through an ideal central circular opening in the lid. The integral equations were solved on a Setun' computer. The integral equations were reduced to a system of linear algebraic equations by replacing the integrals by finite sums. The system parameters were varied in the following ranges: $0.1 \leqslant \alpha \leqslant 1$, $0.1 \leqslant r/R \leqslant 1$, and $0.1 \leqslant H/R \leqslant 3$, where α is the evaporation coefficient, r the radius of the effusion aperture, and H and R are respectively the height and the cross-sectional radius of the chamber. The results of the calculation, presented in tabular form, were compared with the literature data [1]. The study showed that the previously derived formulae [1] describe the state of the system fairly satisfactorily only when $H \simeq R$. For cells with $H \ll R$, these formulae are quite unsuitable.

The complete article has been deposited at the All-Union Institute of Scientific and Technical Information (VINITI) (No. 3144-71 Dep. from 23rd July, 1971).

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Measurements of the Activity Coefficients of Sodium Chloride at 25°C in the Sodium Chloride-Sodium Nitrate-Water and Sodium Chloride-Sodium Perchlorate-Water Systems by an Electromotive Force Method Using Glass Electrodes

N.Sh.Gokhman, G.P.Lepnev, and M.M.Shul'ts

A development of the method involving the use of glass electrodes reversible with respect to cations in studies of the thermodynamics of solutions at concentrations lower than in Lanier's work [1] (see Figure) is described. The electromotive force of a glass electrode–silver, silver chloride electrode cell without transport (eight glass and six silver, silver chloride electrodes) was measured by a compensation method using an R-307 potentiometer and an LPU-01 pH-meter in conjunction with an M-95 galvanometer. Before the experiments, the apparatus with the cell and isomolal solutions (which could be interchanged by remote control) was kept in an air thermostat for 12 h.
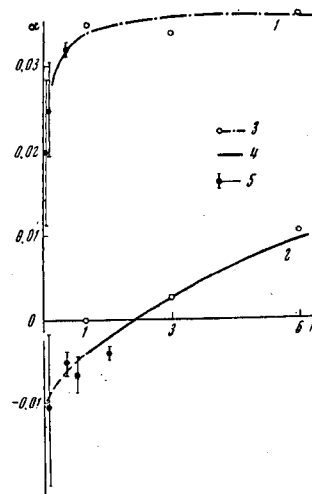
Variation of α_{NaCl} with concentration for different systems:
1) $NaCl-NaNO_3$; 2) $NaCl-NaClO_4$; 3) Lanier's data [1]; 4) data of Scatchard and Yoest; 5) this work.

The results were interpreted on a Promin' M computer according to a program based on the formula

$$\delta E = \theta \lg \frac{m'\gamma_{\pm}'^{\prime}}{m\gamma_{\pm}'} - \theta \lg \frac{m'}{m} = 2\theta(\lg \gamma_{\pm}' - \lg \gamma_{\pm}),$$

where $\theta = 2.3 RT/F$, $\gamma_{\pm}$ is the mean activity coefficient of sodium chloride in a binary solution at a molality m, and