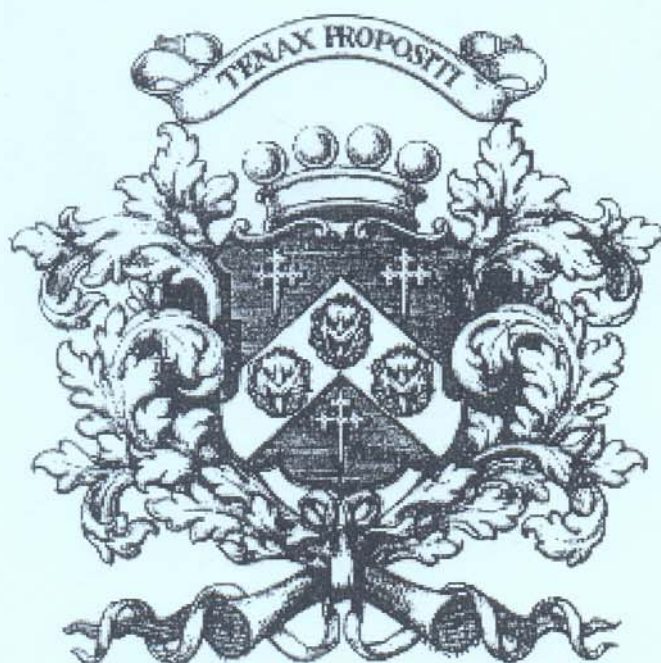


ANGLO-RUSSIAN CONFERENCE

ON NOVEL MATERIALS

12<sup>TH</sup> - 14<sup>TH</sup> JULY 2004



*Cavendish Laboratory*  
*Cambridge*

THE MOLLER CENTRE,  
STOREY'S WAY  
CAMBRIDGE, UNITED KINGDOM

JULY 2004 DOCUMENT SP1146

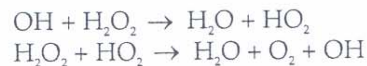
## Thermochemistry of Concentrated Aqueous Solutions of Hydrogen Peroxide

*Frolov S. M. and Kuznetsov N.M.*

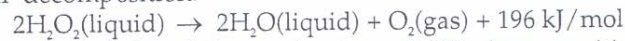
N. N. Semenov Institute of Chemical Physics  
Moscow, Russia

Hydrogen peroxide (HP) and its aqueous solutions are very complex energetic substances in terms of physical and chemical properties, in particular, chemical kinetics. Aqueous solutions of HP exhibit electrolytic properties. Apart from neutral molecules and radicals, aqueous solutions of HP contain solvated ions. There are still many unresolved problems related to chemical kinetics and thermodynamics, especially at temperatures considerably exceeding normal temperature.

Chemical bonds in the HP molecule are very strong therefore thermal dissociation of the molecule in the gas phase is negligibly small even at 1000 K. Decomposition of HP in aqueous solutions is closely connected with chain reactions involving active radicals. One of possible chain reaction mechanisms is :



The rate of HP decomposition according to this mechanism depends on the rate constants of both reactions and radical concentrations. The latter are dependent of the competition between the processes of radical formation and removal in other reactions. The combination of these two reactions results in exothermic reaction of HP decomposition:



Based on the analysis of the chain mechanism of HP decomposition, two estimates of the characteristic decomposition times have been obtained. The first estimate is based on the hypothesis of radical formation in the dissociation reaction of HP with no effect of impurities. The second, more realistic, estimate is based on the radical formation due to charge exchange reactions between iron ions and solvated ions of radicals. It is shown that available experimental data for HP decomposition time under conditions when impurities are present in trace amounts agree satisfactorily with the second estimate at temperatures up to 100 °C.

Total pressure  $P(x, T)$  of the binary two-phase system HP – water is modeled based on the expression:

$$\begin{aligned} P(x, T) &= \left[ (T / \alpha(x))^{1/8} - A(x) \right]^8 \\ \alpha(x) &= 3.4679 \cdot 10^{-7} (1 - x) + 3.7642 \cdot 10^{-7} x \\ A(x) &= 12.4575(1 - x) + 12.5302x \end{aligned}$$

where  $T$  is temperature (in K),  $x$  and  $1-x$  are the molar fractions of HP and water in solution, respectively, and  $P$  is in atm. This expression does not incorporate the ideal-gas approximation and is applicable within the entire temperature range where each of the solution components exists in both liquid and gas phases. Based on this expression and the solution of Duhem's equation, equilibrium gas-phase composition in the two-phase system was obtained for temperatures less than 520 K. Given the chemical potential of the gas-phase components as a function of  $T$ ,  $P$ , and composition, the approach can be readily used for estimating the equilibrium gas-phase composition up to the critical curve. The predictions are compared with available experimental data on the boiling temperature of overheated aqueous solutions of HP, and satisfactory agreement between the results is obtained.

The results can be used for estimating the potential of HP containing systems as to various applications including propulsion.