THERMODYNAMIC PROPERTIES OF HYDROGEN PEROXIDE

The H_2O_2 properties which define energy changes in the physical transitions through the various solid, liquid, and gas states, as in chemical changes, have been listed under thermodynamic properties.

Heat of Formation

The heats of formation (ΔHF) of propellant-grade H_2O_2 solutions were calculated in this study from heat of dissociation data given in Ref. 1. Heat of fusion, heat of vaporization, heat of mixing, and heat capacity data used to characterize the heat of formation over & range of temperatures, phases, and concentrations are given in subsequent sections. Data for the aqueous solutions are presented as heats of formation of the solution (which includes the heat of formation contributions of both H_2O and H_2O_2, and the heat of mixing).

The ΔHF data for the liquid and solid phases of propellant-grade H_2O_2 solutions are given in Tables 2.3 through 2.8 and Fig. 2.12 and 2.12a. Figures 2.13 and 2.13a illustrate the ΔHF of the liquid at 25 C (77 F) as a function of composition. The heats of formation of the vapor of propellant-grade H_2O_2-H_2O solutions are given in Tables 2.9 through 2.14.

Heat of Fusion

The heats of fusion of propellant-grade H_2O_2 solutions were taken from the experimental studies of Ref. 2; these data are shown in Tables 2.3 through 2.8 as the change in enthalpy at the freezing point.

Heat of Vaporization

The experimental data, of Ref. 3 were used to plot the heats of vaporization of H_2O_2-H_2O solutions as a function of temperature; curve-fits of the data at 0, 25, 45, and 60 C (32, 77, 113, and 140 F) are shown in. Fig. 2.14 and 2.14a. Heats of vaporization of propellant-grade H_2O_2 solutions at other temperatures can be obtained by computing the difference in the heats of formation of the liquid (Tables 2.3 through 2.8) and vapor (Tables 2.9 through 2.14) phases of the H_2O_2-H_2O solutions at the corresponding temperatures and H_2O_2 concentrations.

Heat of Sublimation

The heat of sublimation of 100 w/o H_2O_2 has been calculated (Ref. 4) from the heats of fusion and vaporization as 457.8 cal/gm (824 Btu/lb).

Heat of Mixing

Graphical representations of the heats of mixing propellant-grade H_2O_2-H_2O solutions, shown in Fig. 2.15 and 2.15a, were plotted from smoothed data given in Ref. 3. These data represent experimental data of the referenced work, previous experimental studies (Ref. 1), and their extrapolation to higher temperatures for comparison with the experimental data of Ref. 5. Excellent agreement is noted between the data of Ref. 3 and Ref. 5 except in the 20 to 30 w/o H_2O_2 concentration range.

Heat of Decomposition

The heats of decomposition, graphically represented in Fig. 2.16 and 2.16a, were converted from smoothed data from the experimental studies of Ref. 1. The figures illustrate the heats of decomposition of propellant-grade H_2O_2-H_2O solutions with decomposition to either liquid water or water vapor.

Heat Capacity

The heat capacities of solid and liquid propellant-grade H_2O_2-H_2O solutions are shown in Tables 2.8 through 2.13 and Fig. 2.17 and 2.17a from 0 to 400 K (0 to 720 R). The heat capacities of solid H_2O_2 were taken from the data of Ref. 6. Since solid solutions of H_2O_2 and H_2O are not formed in the concentration region of interest, the heat capacities of the solid phases of propellant-grade H_2O_2-H_2O solutions were assumed to be the sum of the individual heat capacity contributions of solid H_2O and solid H_2O_2.

The liquid heat capacities were curve-fitted from the experimental data of Ref. 1 and 3; these studies indicated that the change in heat capacity of an H_2O_2-H_2O solution of constant composition over the indicated temperature range was of the order of the accuracy of the experimental data. Experimental measurements of liquid heat capacity were not conducted below 0 C (32 F); therefore, the heat capacity was estimated in this region using the heat capacity of supercooled H_2O and the extrapolated heat capacity contribution of the H_2O_2.

During experimental heat transfer studies at relatively high temperatures (Ref. 7), the heat capacities of 90 w/o H2O2 were indirectly determined from heat transfer data over a temperature range of 240 to 380 F. An equation was developed for the data which indicated an increasing deviation of the experimental data from the curve fit of the data with increasing temperature. The differences in these data from extrapolations of the data presented in Fig. 2.17 and 2.17a, which are ≤ 0.0l Btu/lb-F (cal/gm-C), are assumed to be the result of H2O2 decomposition in the experimental study.

The heat capacities of the vapor phase of propellant-grade H2O2 solutions are given in Tables 2.9 through 2.14. The origin of these data is discussed in Section 2.2.3.9.

Entropy and Enthalpy

The entropy and enthalpy of the solid and liquid phases of propellant-grade H2O2 solutions were calculated from the other thermodynamic functions given in Tables 2.3 through 2.8. The basis for the vapor-phase entropy and enthalpy data on propellant-grade H2O2 solutions, given in Tables 2.9 through 2.14 is discussed in Section 2.2.3.9.

Vapor-Phase Thermodynamic Properties

The thermodynamic properties of hydrogen peroxide vapor were calculated (Ref. 8) from structural data. These data, which replaced earlier reported data (Ref. 9), were based on new spectroscopic measurements (Ref. 10) and new calorimetric data (Ref. 6 and 1). The primary difference in the presently accepted values and those reported earlier are in the internal rotation values.

The structural values used by Ref. 8 in the computation of the vapor-phase thermodynamic properties, given in Tables 2.9 through 2.14, are:

r O-H = 0.965Å	υ1 = 3610 cm-1
r O-O = 1.49Å	υ2 = 1350 cm-1
α OOH = 100 degrees	υ3 = 880 cm-1

φ = 95 degrees	υ4 = 520 cm-1
IA = 2.785 x 10-40gm-cm2	υ5 = 3610 cm-1
IB = 34.0 x 10-40gm-cm2	υ6 =1266 cm-1
IC = 33.8 x 10-40gm-cm2	o = 2
IRed = 0.696 x 10-40gm-cm2	

Source : http://www.diyspaceexploration.com/thermodynamic-properties-of-hydrogen-peroxide/