THERMODYNAMIC AND TRANSPORT PROPERTIES OF FROZEN AND REACTING pH_2-oH_2 MIXTURES

H. G. Carter and R. E. Bullock
General Dynamics Corporation
Fort Worth, Texas

Abstract

Application of experimental state data and spectroscopic term values shows that the thermodynamic and transport properties of reacting pH_2-oH_2 mixtures are considerably different than those of chemically frozen pH_2 at temperatures below $300^{\circ}R$. Such differences will be significant from the standpoint of nuclear rocket design if it turns out that para- to ortho- hydrogen conversion can be catalyzed by radiation in the cold dense phase. Calculated H-S data also show that radiation-induced pH_2-oH_2 equilibration at constant enthalpy can produce a temperature drop of at least $28^{\circ}R$, corresponding to an ideal shaft work loss of 15% or more for a turbine operating downstream from the point of conversion. Aside from differences in thermodynamic and transport properties, frozen pH_2-oH_2 mixtures may differ from pure pH_2 on a purely hydrodynamical basis.

Significance of Possible Para-Orthohydrogen Conversion in Nuclear Rockets

Hydrogen is generally a mixture of two distinct H_2 components. A molecule of the component called "orthohydrogen" may assume quantized rotational energies that are not accessible to the component called "parahydrogen," and vice versa. The resulting disparities in energy-level populations at a given temperature imply differences in the thermodynamic and transport properties of the two types of hydrogen. Thus, for example, the enthalpies and thermal conductivities of pH_2-oH_2 mixtures differ appreciably from those of pure parahydrogen in the $36^{\circ}R$-$500^{\circ}R$ range, not only in absolute magnitude but also in temperature dependence. Aside from thermodynamic and transport properties, para- and orthohydrogen may differ on a purely hydrodynamical basis. The latter possibility, which has been given little attention, derives from the fact that the differences in accessible rotational energies for the two types of molecule are associated with differences in angular momenta.

The liquid hydrogen that is stored for use in nuclear rocket propulsion is usually over 99% pH_2. However, the high-temperature hydrogen gas that emerges from the nozzle of the nuclear rocket is invariably a mixture consisting of 75% oH_2 and 25% pH_2. This change in proportions results from the facts that (1) certain chemical or magnetic

reactions can convert parahydrogen to orthohydrogen when sufficient energy is available, and (2) in the presence of a suitable conversion catalyst, hydrogen tends to a pH_2/oH_2 ratio that is determined by the temperature. Catalysts which convert parahydrogen to its equilibrium proportions are available in the reactor core (in the form of H-atoms from thermal dissociation), if not elsewhere. When catalysts are present in large enough quantities that a shift in temperature is accompanied, practically instantaneously, by a shift in pH_2/oH_2 ratio to a value corresponding to the new temperature, the para-orthohydrogen mixture is called "reacting" or "equilibrating." When no such catalysts are available, the pH_2/oH_2 ratio is not affected by a temperature change, and the mixture is called "frozen." In the temperature range from 60°R to 300°R the specific heats of a given nominal pH_2/oH_2 mixture differ radically according to whether the hydrogen is frozen or reacting.

In nuclear rocket design, a question arises as to what type of hydrogen should be assumed to exist in the relatively cold regions between the propellant tank and the core inlet. If the hydrogen is chemically frozen throughout this region, then it obviously remains in almost pure pH_2 form, and thermodynamic and heat transfer calculations can be based on parahydrogen properties. If, on the other hand, the flowing hydrogen is catalysed by radiation or by paramagnetic surfaces, then the hydrogen may be chemically reacting over at least part of the region below the reactor core, and pure parahydrogen properties may not apply. From the standpoint of an overall design study, the effect of catalytic conversion is not limited to the values of thermodynamic and transport properties of hydrogen at a prescribed temperature and pressure. The sudden equilibration of hydrogen due to catalysis at a certain point in the flow-path can reduce the temperature by as much as 40°R, through a thermochemical process that is analogous to the cooling of paramagnetic salts in a decreasing magnetic field. Such "conversion-cooling" can reduce the available energy for a turbine operation or alter the dimensions of various orifices for an optimum design.

Whether hydrogen conversion in the sub-core region is of design significance depends on three questions. These are: (1) does an effective mechanism for conversion actually exist in relatively cold hydrogen

subject to irradiation and possible encounters with paramagnetic sites, and how much conversion can it produce? (2) What are the quantitative thermodynamic and transport properties of frozen and reacting pH_2/oH_2 mixtures? (3) What is the overall effect of conversion on a specific design? In regard to the first question, it will only be noted that data obtained during practical tests indicate that relatively cold parahydrogen can be converted by radiation, and that reasonable chemical models have been advanced to explain this effect. The third question is in the province of rocket designers. The results given here pertain only to the second question, viz., information on the basic properties of pH_2-oH_2 mixtures.

Equilibrium Orthohydrogen Fraction

The equilibrium orthohydrogen fraction at a given temperature is independent of pressure, at least for pressures in the range of nuclear rocket application and lower. For temperatures below 500°K (900°R) the equilibrium orthohydrogen fraction, ω_e, is given to an accuracy of 0.01% by

$$\omega_e = \sum_{j=1}^{7 \text{ (odd)}} g_j e^{-\theta_j/T} \Big/ \sum_{j=0}^{8} g_j e^{-\theta_j/T} \qquad (1)$$

where j is the number of a rotational level. Even and odd values of j correspond to pH_2 and oH_2 rotational levels, respectively. The parameter θ_j represents the molecular rotational energy of a particular level divided by Boltzmann's constant. Using the spectroscopic term values cited in the definitive work of Woolley, et al. at NBS (Ref. 1), it is found that a suitable approximation is

$$\theta_j(°K) = 85.3757 \, j(j+1) - 0.065769 \, j^2(j+1)^2$$
$$+ 0.0000712 \, j^3(j+1)^3 \qquad (2)$$

for values of j less than or equal to 8. This prescription ignores the role of vibrational excitation, which is negligible below 500°K. The parameter g_j in Equation (1) is a statistical weight given by

$$g_j = 3(2j+1), \quad j \text{ odd}$$
$$= (2j+1), \quad j \text{ even} \qquad (3)$$

At temperatures above T = 500°K, the equilibrium orthohydrogen fraction is $\omega_e = 0.750$.

Evaluation of Equation (1) yields the dependence of equilibrium orthohydrogen fraction on temperature shown in Figure 1. It is seen that the temperature range over which ω_e varies significantly is $30^{\circ}K$ to $220^{\circ}K$, or $54^{\circ}R$ to $396^{\circ}R$.
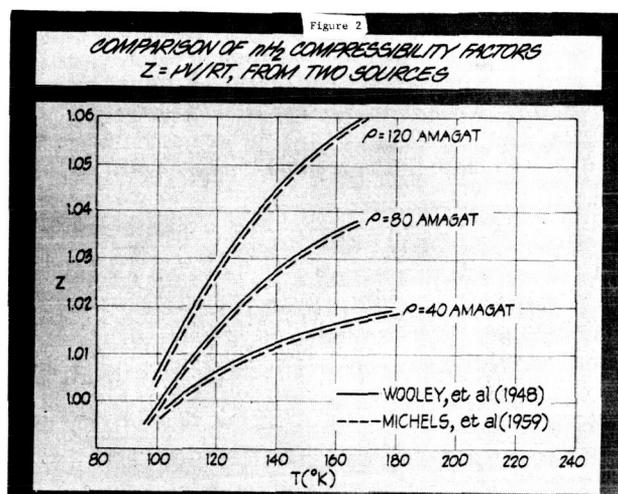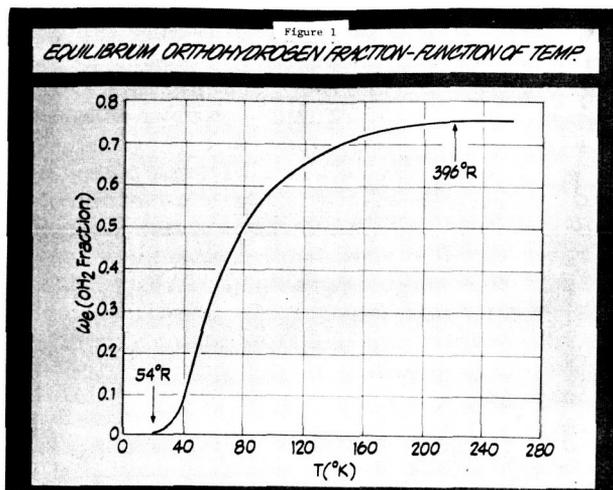
Calculation of Enthalpy and Entropy

The calculation of enthalpies and entropies is obviated by expressing the results as ideal gas values, augmented by "real-gas" terms that arise from intermolecular reactions. The latter are obtained from an equation of state, which is usually written in the form of a temperature and density dependent for the compressibility factor $Z = pv/RT$. In obtaining the present results it has been assumed that the equation of state
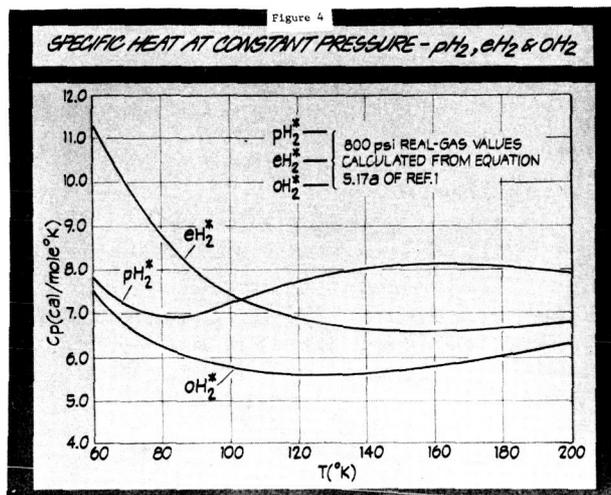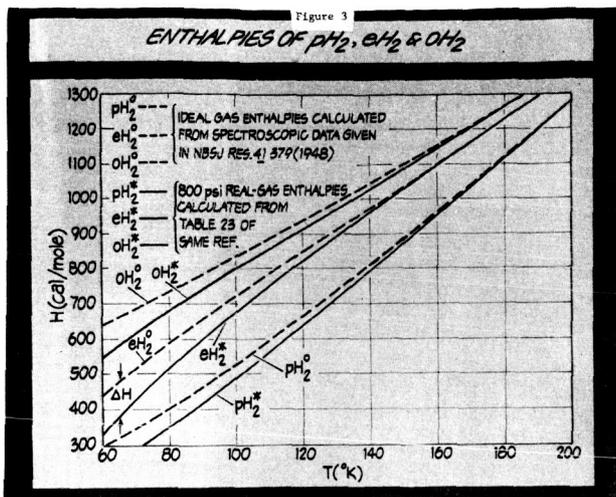
$$Z = Z(T,\rho) \qquad (4)$$

is the same for either para- or ortho-hydrogen. The state equation used is that given by Wooley et al. for normal hydrogen (75% ortho). This state equation, which was based on rather old normal hydrogen data, has been compared with data reported more recently by Michels et al. (Ref. 2). Typical comparisons are shown in Figure 2. An analysis of the difference between the old and new data, which is taken as a measure of the present uncertainty in the state equation for normal hydrogen, shows that the corresponding uncertainties in enthalpy and energy of normal hydrogen are respectively only about 1 Btu/lb and 0.002 Btu/lb $^{\circ}R$. Furthermore, recent data by Hermans et al. (Ref. 3), on the difference between the second virial coefficients of para- and normal hydrogen, indicate that the use of a normal hydrogen state equation on pH_2-oH_2 mixtures will not lead to an error greater than that corresponding to the present uncertainty in the normal-hydrogen state data.

The real-gas enthalpies and entropies of a number of mixtures have been calculated using tabular data given by Woolley et al. to obtain the integrals involving Z. Ideal-gas values of the enthalpy and entropy for both frozen and reacting pH_2-oH_2 mixtures have been obtained from the θ_j and g_j defined in Equations (2) and (3).

Figure 1

EQUILIBRIUM ORTHOHYDROGEN FRACTION-FUNCTION OF TEMP.

Figure 2

COMPARISON OF nH_2 COMPRESSIBILITY FACTORS
$Z = pV/RT$, FROM TWO SOURCES

The enthalpies of frozen pH_2, frozen oH_2 and equilibrating hydrogen at 0 and 800 psi are shown in Figure 3. The corresponding specific heats, obtained by differentiation of H with respect to temperature, are shown in Figure 4. It is seen that EH_2 behaves as a mixture with an intermediate specific heat only above $100^{\circ}K$; at lower temperatures the specific heat of reacting hydrogen is appreciably higher than that of either frozen component. By contrast, the specific heat of a frozen mixture is obtained by simply calculating the average of the frozen pH_2 and oH_2 values, weighted by their respective concentrations in the mixture.

478

Figure 3
ENTHALPIES OF pH₂, eH₂ & OH₂

Figure 4
SPECIFIC HEAT AT CONSTANT PRESSURE - pH₂, eH₂ & OH₂

Figure 5
THERMAL CONDUCTIVITY - pH₂, eH₂ & OH₂

Transport Properties

The viscosity of a pH_2-oH_2 mixture is determined by transport of momentum alone, and is therefore independent of the pH_2-oH_2 composition insofar as pH_2 and oH_2 conform to the same equation of state. On the other hand, the thermal conductivity of an ideal-gas mixture of para- and ortho-hydrogen is related to the viscosity, η, by Eucken's relation

$$K_o = (9\gamma-5)C_v^o \eta/(4M) \tag{5}$$

where C_v^o is the specific heat of the ideal gas, γ is the ratio of specific heats, and M is the molecular weight. The real-gas thermal conductivity K is related to K_o by the following Enskog relation:

$$K/K_o = 1 + 0.575E + 0.5017E^2 - 0.204E^3 \tag{6}$$

where E is given by

$$E = Z - 1 + T \left(\frac{\partial Z}{\partial T}\right)_\rho \tag{7}$$

Figure 5 shows the thermal conductivity for pH_2, oH_2 and a reacting mixture at 0 psi and 800 psi. As in the case of specific heat, the thermal conductivity depends strongly on whether a given mixture is frozen or reacting.
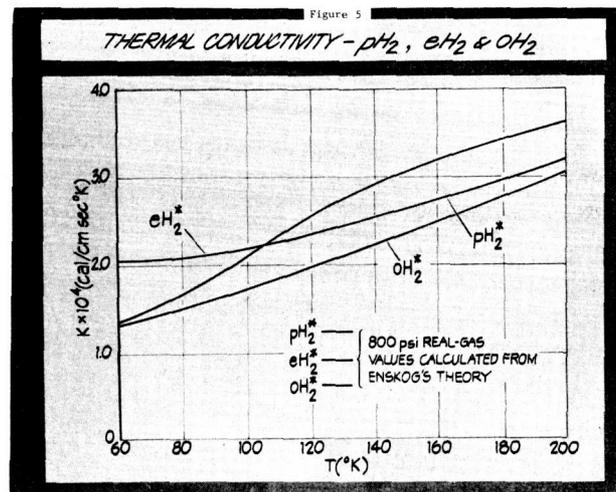
Cooling Due to Conversion

If a chemically frozen parahydrogen gas is suddenly exposed to a conversion-catalyst such as radiation or a paramagnetic surface, the resulting equilibration to a pH_2-oH_2 mixture is an irreversible process. Hence, the reaction cannot be isentropic even if it happens to be adiabatic. In general, the enthalpy change due to a differential conversion process is

$$dH = TdS + Vdp + \mu_1 dx_1 + \mu_2 dx_2 \tag{8}$$

where x_1 and x_2 are the pH_2 and oH_2 mole fractions, respectively, and where μ_1 and μ_2 are the chemical potentials. In the case where no heat enters or leaves the system and the pressure is kept at a constant value, Equation (8) simplifies to

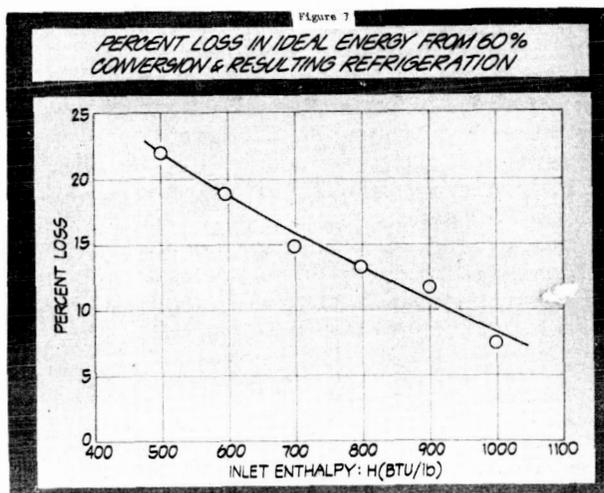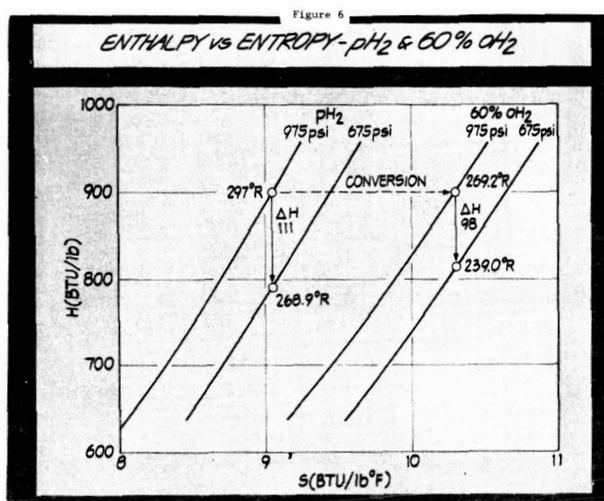$$TdS = (\mu_1-\mu_2)dx_2 \tag{9}$$

This increase in entropy is accompanied by a decrease in temperature, which can, for example, subsequently reduce the amount of available energy from a turbine operating between two prescribed pressures. The possible effect of such cooling is seen from the approximate H-S chart shown in Figure 6, which has been constructed from Figure 3 and calculated entropy data. When parahydrogen at 297°R is converted to 60% oH_2 at constant enthalpy and constant pressure, the temperature decreases from 297°R to 269°R. If conversion had not occurred, the energy available to a turbine operating between 975 psi and 675 psi would be 111 Btu/lb. However, it is seen that 60% conversion would reduce the available energy to 98 Btu/lb. The magnitudes of such losses depend upon the inlet enthalpy and, of course, the amount of conversion that is assumed. Figure 7 shows the percent loss in ideal energy for an assumed conversion of 60% as a function of inlet enthalpy.

Possible Hydrodynamic Differences Between pH_2 and oH_2

The difference between the thermodynamic and transport properties of parahydrogen and those of orthohydrogen are completely specified by the rotational energy levels accessible to each, at least insofar as the two modifications conform to the same equation of state. However, from the hydrodynamical standpoint, another type of difference might be worth exploring.

Parahydrogen molecules may take intrinsic angular momenta of 0, $2\hbar$, $4\hbar$, etc.; whereas orthohydrogen molecules may take intrinsic angular momenta of $\hbar$, $3\hbar$, $5\hbar$, etc. At temperatures below 180°R, over 97% of all parahydrogen molecules are in a state of zero angular momentum. For practical purposes one may say that, at these temperatures, parahydrogen is a fluid composed of molecules with no intrinsic angular momentum, whereas orthohydrogen is a fluid whose molecules have an intrinsic angular momentum of $\hbar$. Hence, on a rigorous hydrodynamical basis (Ref. 4), the equations for energy and momentum conservation, which are sufficient to describe the behavior of a parahydrogen fluid, must be augmented by an equation of angular momentum in the case of orthohydrogen. In the language of transport theory, collisions between orthohydrogen molecules involve an extra summational invariant. It is therefore conceivable that the details

of such phenomena as the transition from laminar to turbulent flow might differ in the two types of fluids, independently of any effects associated with thermodynamic and transport properties.

Figure 6

ENTHALPY vs ENTROPY - pH_2 & 60% oH_2

Figure 7

PERCENT LOSS IN IDEAL ENERGY FROM 60% CONVERSION & RESULTING REFRIGERATION

References

1. Woolley, H. W., Scott, R. B., and Brickwedde, F. G., NBS Research Paper RP1932, Volume 41, November 1948, pp. 379-475.

2. Michels, A., et al., Physica 25, 1959, pp. 25-42.

3. Hermans, L. J. F., et al., Physica 31, 1965, pp. 1567-1574.

4. Chapman, S., and Cowling, T. G., The Mathematical Theory of Non-Uniform Gases (Cambridge), 1953, p. 202.