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SUMMARY OF RESEARCH PROGRESS MEETING OF NOVEMBER 6, 1952

Sergey Shewchuck

December 24, 1952

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Berkeley, California

SUMMARY OF RESEARCH PROGRESS MEETING OF NOVEMBER 6, 1952

Sergey Shewchuck

Radiation Laboratory, Department of Physics
University of California, Berkeley, California

December 24, 1952

I. Stable Gas Molecules at Star Temperatures. L. Brewer.

At star temperatures of 2000° - 7000°K it is very difficult to get direct laboratory information and so stellar observations are the principal source of information as to which molecules are stable in that region. These data are then correlated with whatever laboratory information may be available, mostly from spectral studies of sparks, discharges, etc.; whose temperatures, however, tend to be too high ~ 10,000°K. Because of dire lack of thermal equilibrium in the laboratory at this temperature range the results may not be exactly comparable.

One is able to compute the concentrations of various molecules from general thermodynamic data. But comparison with stellar observations discloses discrepancies which definitely show that something is wrong with the calculations. The difficulty arises from not taking into account all species of molecules that may be present. It had been assumed that there were no complex molecules at high temperatures. Now it appears from studies on stars that some polyatomic molecules have strong bonding and really do exist at high temperatures. Their spectra are complex and not discrete; hence, they are easily overlooked unless specifically looked for in the spectra.

In the Daniel's pile where Be and H_2O were heated to high temperatures it was discovered that Be disappeared, contrary to calculations. $Be(OH)_2$(gas) was found to be very stable at 2000°K. The stability actually increases with temperature in this case. The CuCl system on which good spectroscopic data was available was studied in order to look for complex stable molecules at high temperatures. An experiment was conducted by testing the vapor pressure of CuCl in the reaction:

$$x\ Cu\ (s) + y\ HCl\ (g) \longrightarrow Cu_xCl_y + \frac{y}{2} H_2$$

By varying H_2 and HCl it was found at 1800° - 1900°K surprisingly that y = 3; i.e., the reaction results in

$$\longrightarrow Cu_3Cl_3 + \frac{3}{2} H_2$$

Further reduction to $Cu_3Cl_3 \rightarrow CuCl$ was possible only at very high temperatures.

There are other evidences which indicate that many complex molecules will need to be taken into account in caluclations. Examples are K_2I^+ and Ba_2O^+ where it appears that complex ions certainly exist if not the whole molecule. Among the oxides UO_3, MoO_3, and P_4O_{10} appear to be stable as gaseous molecules. For the reaction

$$UO_2\ (s) + Y_2O_2 \rightarrow UO_3\ (g)$$

at 2000°K there is .1 mm partial pressure due to UO_3; for P_4O_{10} it becomes appreciable at 3000°K. When Pt is heated in O_2 up to 2000° - 2500°K molecules are formed of the type

$$Pt\ (s) + O_2\ (g) \longrightarrow PtO_2\ (g)$$

For these molecules the entropies are $\Delta S > O$ and $\Delta H > O$. The reaction is endothermic, so it becomes more improtant at higher temperatures. $\Delta S > O$ and $\Delta F = \Delta H - T\Delta S$. Therefore ΔF can equal zero at high temperature; hence, there is a great deal of reaction at higher temperature until one reaches the temperature at which O_2 breaks up and solid Pt becomes gaseous.

Some gaseous hydroxides have been studied since they are easy to handle be passing steam over various substances. The following molecules were found:

$B_e \cdot H_2O$	$WO_3 \cdot H_2O$	FeOH
$SiO_2 \cdot H\ O$	$MoO_3 \cdot H\ O$	

Another difficulty is that certain molecules are found to exist in the stars but the star data for them do not correspond to the chemical data of the true ground states of the molecules. The ratio of ground state to excited state may be several thousand to one, therefore, the calculations could be greatly in error. For MgO, SiO, CaO, and AlO there is a greater concentration indicated than that calculated from spectroscopic data. The true situation has not been discovered. From star data one would conclude for $AlO \longrightarrow Al + O$ that $\Delta H \sim 30$ k cal. However, from chemical data one finds $\Delta H \sim 130$ k cal. One might say that the ground state has not been observed spectroscopically. With singlet and triplet band systems it can not be said which is the ground state. Most calculations assume the singlet state to be the ground state. If this isn't true a serious discrepancy results.

The situation in stars must be more complex than originally thought. All types of experiments will need to be conducted in the future to help determine the actual molecules that are present. More careful and complete spectral studies can be made of the sun and stars. Molecular beam experiments might be able to separate singlet and triplet states (a difficult method). One may be able to study a system at thermal equilibrium by heating in a furnace up to the emission temperature of bands as, for example, with C_2 and studying the function of H to prove ground states and their relative order. Vaporization experiments often can determine which molecules are important in a system as

$$\begin{aligned} CaO\ (s) &\longrightarrow Ca\ (g) + O\ (g) \\ &\longrightarrow CaO\ (g) \\ &\longrightarrow Ca_2O_2\ (g) \end{aligned}$$

The extent of vaporization is calculated for each product and then compared with experiment. Some oxides show higher volatility than can be expected from dissociation to the elements. The CO to PbO series was successful and corresponded to the second step; others were not, indicating perhaps some other gaseous reaction. One still has to resort to guesses on the nature of the molecule and the free energy. Much of the difficulty lies in being able to hold the species in a system where the variables are controllable at equilibrium.

There is a possibility of doing absorption spectra studies on a system where an appreciable quantity of the molecules in question is present. A difficulty is encountered here of getting a sufficiently intense light source above black body radiation. Identifiable information may be gained from the continuous spectrum. By varying the pressures of the constituents the importance of specific molecules could be traced by the variance in absorption. Even though feeble discrete spectra may possibly be resolved, the complexity of the problem still remains great.