Thermodynamic Aspects of the Flow of Sodium Vapor Through a Supersonic Nozzle

T. A. COULTAS
Research Department, Rocketdyne, A Division of North American Aviation, Inc., Canoga Park, Calif.

Data taken during the operation of a boiling sodium system have been analyzed to determine supersaturation and species equilibrium effects in vapor. These data strongly indicate that frozen equilibrium and supersaturated flow were obtained through the convergent section of the nozzle at 1200° to 1300° K. Further, these data along with theoretical thermodynamic calculations, indicate that the vapor pressure of sodium can be expressed adequately in this region by the Ditchburn–Gilmour equation and that the dimerization energy of sodium is between 16,000 and 17,000 calories per gram mole of Na_2.

AN EXPERIMENTAL and analytical investigation of the flow of sodium vapor through a converging-diverging nozzle was made. The experimental portion of the study was performed with a boiling sodium system. The sodium vapor entering the nozzle was essentially saturated at temperatures varied from 2250° to 2350° Rankine. Calculations have been made with the separate assumptions of (a) supersaturation, (b) vapor-liquid equilibrium, (c) frozen-chemical equilibrium and (d) shifting-chemical equilibrium. The experimental data show quite clearly (based upon the assumption that both species of sodium vapor are perfect gases) that the flow through the experimental nozzle was supersaturated, frozen-chemical equilibrium. In addition, an attempt was made to determine an appropriate vapor pressure equation and an enthalpy of dimerization with these data. In general, the experimental data were not of sufficient precision to determine these factors. However, thermodynamic consistency calculations of the type made by Makansi, Selke, and Bonilla (*7*) were made which essentially substantiate their conclusions that the Ditchburn-Gilmour vapor equation is adequate, and that the enthalpy of dimerization is about 16,800 cal/gram mole of Na_2. The methods used for thermodynamic and flow calculations as well as a discussion of the experimental program are contained herein.

With the suggestions (*3*, *5*) that alkali metals be used as working media in a closed-cycle power plant, there is renewed interest in the thermodynamic properties of sodium vapor. One of the major unknowns is the effective molecular weight of the vapor. Perhaps the most exhaustive analytical study made on this facet was by Thomson and Garelis (*9*). The major piece of experimental data used by these authors was the vapor pressure measurements made by Makansi, Muendel, and Selke (*6*). More recently Makansi, Selke, and Bonilla (*7*) reported on the thermodynamic properties of sodium. Their conclusions differ somewhat from those of both Thomson and Garelis (*9*) and from those of the present paper.

During the operation of an experimental boiling sodium system (*3*), data were obtained on sodium vapor flowrate through a converging-diverging nozzle. In these tests, the flowrate was measured in the liquid region, and vapor temperatures were measured upstream of the nozzle. From these measurements and previous results (*6*, *7*, *9*) it is possible to make conclusions regarding the thermodynamics and mechanics of sodium-vapor flow.

ANALYSIS

Most of the conclusions in this paper resulted from calculating the flow through a nozzle and comparing the results with the experimentally measured flowrate. However, certain assumptions are required to make the calculations. The most obvious is the requirement that both monatomic and diatomic sodium act as perfect gases. This assumption is probably justified because the highest pressure attained in the experimental study was 40 p.s.i.a. and the critical pressure of sodium has been variously estimated to be between 33 and 760 atm. (*7*). The present work was done at, or below, saturated vapor conditions,

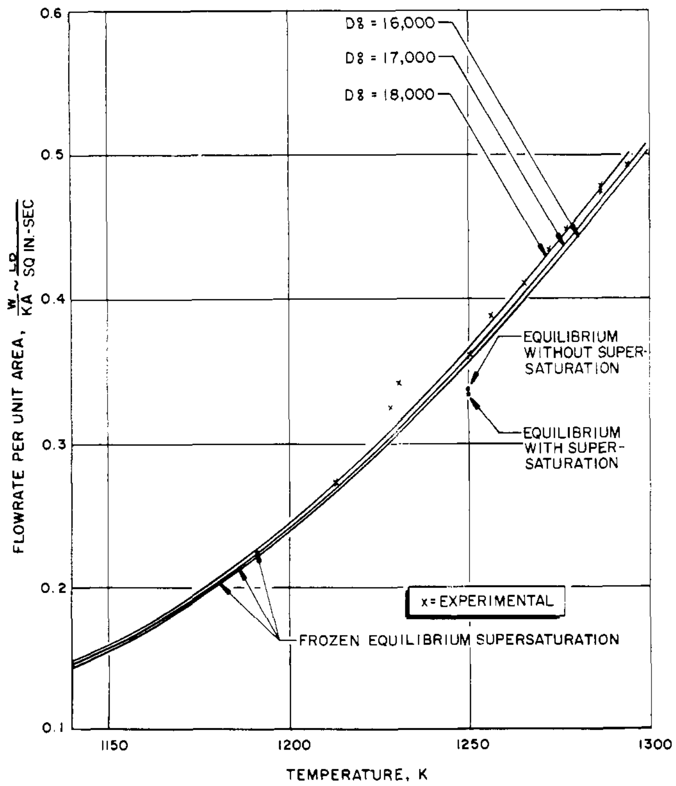

Figure 1. Calculated nozzle flowrate Ditchburn and Gilmour vapor pressure data

certainly weakening the assumption of a perfect gas. However, until further thermodynamic data become available, this assumption must be relied upon.

The flowrate of gases through a nozzle is most conveniently calculated by the assumption of frozen equilibrium, *i.e.*, it is assumed that the composition of the gas does not change as it flows through the nozzle. In the case of a vapor flowing through a nozzle, it is also convenient to assume that the quality of the vapor-liquid mixture does not change, but remains constant. Experiments with steam (*8*) and nitrogen (*10*), show that condensation of the vapor occurs as a shock in the divergent section of the nozzle, but not in the convergent section. (A similar experiment with alkali-metal vapors, although possible, would be quite difficult to perform because of the corrosion and high-temperature resistance required of a transparent nozzle test section.)

If the three assumptions discussed above (perfect gas, supersaturation, and frozen equilibrium) are used, the flowrate through a nozzle may be expressed by the simple equation:

$$w^{\circ} = \frac{K C_g A_o P_i}{(T_i R / M)^{1/2}} \tag{1}$$

where

w° = flowrate, lb./sec.
A_o = nozzle throat area, sq. in.
P_i = upstream pressure, p.s.i.a.
T_i = upstream temperature
M = effective molecular weight
R = universal gas constant
K = nozzle discharge coefficient
C_g = a constant involving the specific heat ratio, *i.e.*,

$$C_g = \left[\gamma \left(\frac{2}{\gamma + 1} \right)^{(\gamma+1)/(\gamma-1)} \right]^{1/2}$$

Even the utilization of this simple equation requires a knowledge of the vapor pressure and relative percentages of monomer and dimer in the vapor mixture at the nozzle inlet. For reasons given later, the Ditchburn-Gilmour vapor pressure equation was utilized, and the weight % dimer was calculated from free energy values reported by Benton and Inatomi (*4*). Figure 1 shows the results of Equation 1 for flowrate as a function of assumed values of dimerization enthalpy.

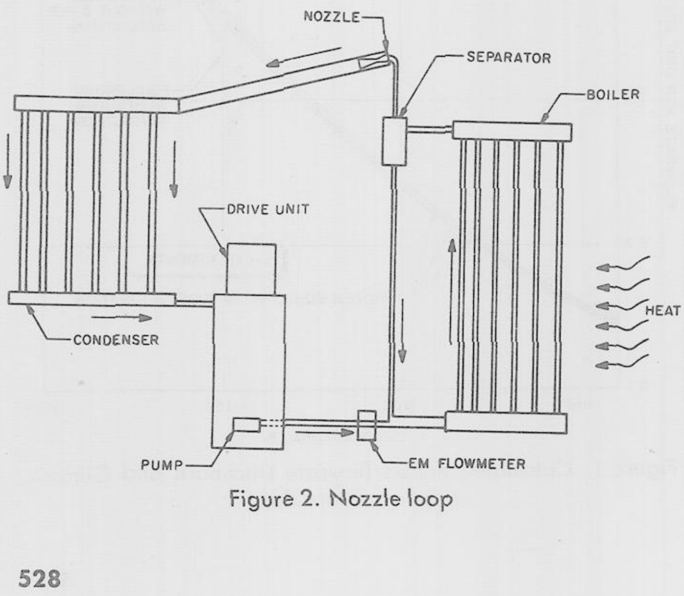

Figure 2. Nozzle loop

It can be seen in Figure 1 that the difference between the values of 16,000 and 18,000 cal./gm. mole for dimerization energy only affects the flowrate approximately 2%. Similar calculations were made using vapor pressure data from (*6*) and from a vapor pressure equation determined experimentally at Rocketdyne (*1*). Again, the difference in flowrate with different dimerization values was only 2%. Further, the difference between the individual vapor pressure equations was also approximately 2%.

Superimposed upon Figure 1 are the points determined experimentally. Although the accuracy of the experimental points is not sufficiently precise to rigorously determine the value of dimerization energy, it can be seen that the data are very near the calculated value of flowrate for frozen equilibrium supersaturated flow. Similar results were obtained using the other vapor pressure equations.

Several iterative calculations were made with the assumption of chemical equilibrium. These points are generally 5 to 6% below the flowrate for frozen equilibrium. One of these points is shown in Figure 1 for the case of the Ditchburn-Gilmour vapor pressure equation and a dimerization enthalpy of 18,000 cal./gm. mole. Also plotted in Figure 1 is a flowrate calculation without supersaturation. Again, the flowrate is approximately 5% less than observed experimentally.

Chemical equilibrium calculations were made by taking small increments of temperature and solving for new values of dimer weight per cent from equilibrium considerations, specific volume from the perfect gas equation, pressure from the energy equation, and velocity from the momentum equation. The ratio of velocity to specific volume was then plotted as a function of temperature to find a maximum. From the continuity equation, this gave a maximum weight flow per unit area. This value was taken as the nozzle flowrate. The thermodynamic equilibrium calculations involved a similar technique except that values of enthalpy, entropy, and specific volume were calculated from simultaneous solution of the Clausius-Clapeyron and Ditchburn-Gilmour equations.

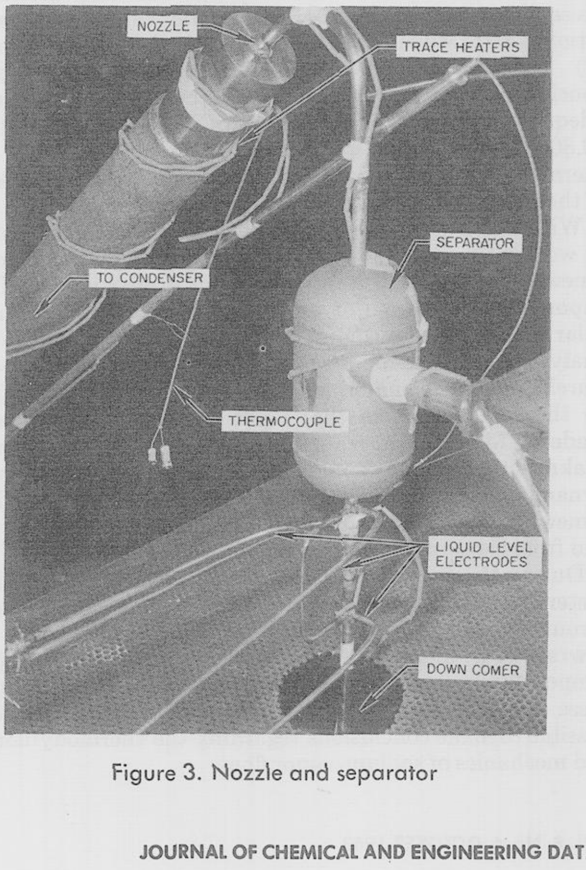

Figure 3. Nozzle and separator

EXPERIMENTAL

The experimental points in Figure 1 indicate a dimerization enthalpy of about 18,000 cal./gm. mole of Na_2. The difference is only about 2% between 16,000 and 18,000 cal./gm. mole. This is less than the limit of accuracy of the experimental data. Perhaps the greatest uncertainty in the experimental data is the vapor quality entering the nozzle.

Figure 2 shows a schematic of the system used to obtain the data. Figure 3 is a photograph of the plumbing details between the boiler and the nozzle. The vapor quality entering the nozzle was calculated by assuming saturated vapor leaving the boiling and measuring the heat losses between boiler and nozzle. Because electric trace heaters on the line between boiler and nozzle were not quite adequate to supply the heat loss, superheating was impossible. A measurement of liquid flow from the separator drain indicated that less than 0.8% of the flowrate was being returned as liquid. Based upon this measurement and known heat losses, the vapor quality was estimated at 99.4%.

Temperature was measured with Chromel-Alumel thermocouples made of wire compared with platinum-platinum-13% rhodium thermocouples calibrated by the National Bureau of Standards. The maximum calibration error of 3° F. makes an insignificant difference in the effect of temperature upon flowrate. The effect of temperature error on vapor pressure, however, amounts to approximately 1%.

The flowrate was measured with a calibrated electromagnetic flowmeter (*2*). The maximum error obtainable with this meter was less than 2%. Other sources of error involve the measurement of nozzle throat area and the nozzle discharge coefficient. The nozzle area was calculated from optical measurements of diameter and published coefficients of expansion of Type 321 stainless steel. The nozzle discharge coefficient was taken at 99% in the calculations. The nozzle was calibrated by the flow of cold nitrogen. Even so, the calibration may be in error by 1 to 2%. Assuming that all experimental errors were directly additive, the precision of these data is about 5%.

THERMODYNAMIC CALCULATIONS

The value of enthalpy of dimerization, D_0°, of 18,000 had been determined from the present work prior to the publication of Makansi, Selke, and Bonilla (*7*). This value was essentially in agreement with the work of Thomson and Garelis (*9*). Makansi, Selke, and Bonilla (*7*) offered a very powerful thermodynamic tool to check the consistency of vapor pressure, specific heat, and spectroscopic measurements. In essence they present the means of an energy balance around the saturation region at a particular temperature. The balance is expressed as a function of enthalpy of dimerization and temperature, $f(D_0^\circ, T)$. Ideally, this function should be zero at every temperature if the correct value for D_0° is chosen. Further details can be found in (*7*).

Makansi's method of checking thermodynamic consistency seemed to establish the value of D_0° definitely at 16,840. This prompted the checking of Makansi's calculations. At first this checking was done by hand, and the agreement between the two calculations was only fair. Correspondence from Dr. Makansi indicated that although the absolute numbers did not agree, there was really very little difference between the conclusions arrived at and his own. Also pointed out was the difficulty in obtaining sufficient precision with hand calculations, particularly for values of the partial derivatives $\partial x/\partial T$. As a result, these calculations were programmed on an IBM 7090 computer, and once the program was in hand, it became very easy to utilize various vapor pressure equations.

Three vapor pressure equations were used:

Makansi, Muendel, and Selke (*6*):

$$\log_{10} P_{\text{atm}} = \frac{-5220}{T_{^\circ K}} + 4.521$$

Ditchburn and Gilmore (*7*):

$$\text{Log}_{10} P_{\text{atm}} = \frac{-5567}{T_{^\circ K}} - 0.5 \log_{10} T_{^\circ K} + 6.354$$

Burge (*1*):

$$\text{Log}_{10} P_{\text{atm}} = \frac{-5178.5}{T_{^\circ K}} + 4.474$$

The latter equation was obtained in the course of developing a pressure transducer suitable for use in liquid sodium.

The computer results are plotted in Figure 4. Similar curves were drawn for the Makansi and Burge vapor pressure equations. It is seen that the vapor pressure equation used has a greater effect upon the thermodynamic consistency than the value of D_0°. Superimposed upon the computer results in Figure 4 are values interpolated from Makansi, Selke, and Bonilla (*7*). In general, the agreement is good except for the D_0° value of 16,840. The disagreement is probably the result of small errors in the previous hand calculations by Dr. Makansi. As Dr. Makansi pointed out, the conclusions are essentially the same.

CONCLUSIONS

It is shown that the Ditchburn-Gilmour vapor pressure equation and a heat of dimerization of about 16,840 cal./gm. mole Na_2 give good thermodynamic consistency, and this conclusion is verified experimentally. This represents no change from the calculations and Mollier diagram presented by Makansi, Selke, and Bonilla (*7*). The present study confirms their calculations because there is so little difference noted in either the experimental or analytical results of this study between their preferred heat of dimerization value of 16,840 and the 16,000 to 17,000 range determined herein. Values of D_0° determined spectroscopic-

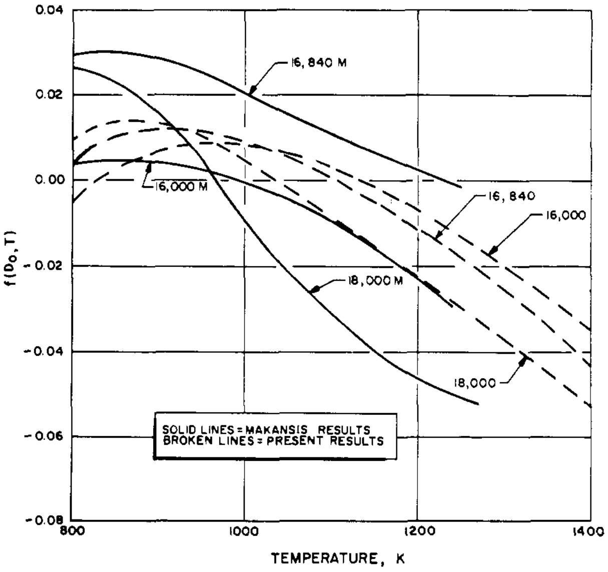

Figure 4. Thermodynamic consistency Ditchburn and Gilmour vapor pressure

ally (*7*) are somewhat higher than this, but based upon the assumptions used, the thermodynamic consistency is better at the lower values.

The theoretical calculations clearly indicate the very large effect that even small differences in vapor pressure have in attaining thermodynamic consistency of data. This shows that future experiments should devote considerable effort toward minimizing errors in vapor pressure data for sodium and other alkali metals.

The present study has shown rather definitely that sodium vapor acts very much as other vapors with regard to supersaturation. It also has shown, at least for the convergent section of this small nozzle, that chemical equilibrium between species is not attained. Again, it should be remembered that all of these results would be negated should it be proved that sodium does not act as a perfect gas near the saturated vapor conditions.

ACKNOWLEDGMENT

Computer calculations of thermodynamic values were programmed by Edwin Rabin.

LITERATURE CITED

(1) Burge, H.L., Rocketdyne Research Rept. **59-19** (April 6, 1959).
(2) Burge, H.L., Rocketdyne Research Memo **490/91** (April 21, 1959).
(3) Coultas, T.A., Burge, H.L., Rocketdyne Research Rept. **59-44** (1959).
(4) Inatomi, T.H., Benton, A.J., *J. Chem. Phys.* **20**, 1946 (1952).
(5) Mackay, D., Paper **230**, Soc. Auto. Engrs., National Aeronautic Meeting, Los Angeles, Calif. (October 1960).
(6) Makansi, M.M., Muendel, C.H., Selke, W.A., *J. Phys. Chem.* **59**, 40 (1955).
(7) Makansi, M.M., Selke, W.A., Bonilla, C.F., J. CHEM. ENG. DATA **5**, 441 (1960).
(8) Stodola, A., "Steam and Gas Turbines," Vol. **I**, McGraw-Hill, New York (1927).
(9) Thomson, G.W., Garelis, E., Rept. PR **19**, Ethyl Corp. Research Laboratories, Detroit, Mich (November 25, 1955).
(10) Yellott, W., Holland, W., *Engineering* **143**, 647 (1937).

RECEIVED for review February 2, 1963. Accepted June 19, 1963.

Changes in Enthalpy During the Heating of $CaHPO_4 \cdot 2H_2O$

R. E. MESMER and R. R. IRANI
Monsanto Chemical Co., St. Louis, Mo.

The changes in enthalpy which occur when $CaHPO_4 \cdot 2H_2O$ is heated up to 1300° C. have been determined in a humid atmosphere by the DTA method. The heats were determined for the following reactions: dehydration of $CaHPO_4 \cdot 2H_2O$ to give two moles of water vapor at 135° C., 21.1 kcal./mole; intermolecular dehydration of $CaHPO_4$ to give γ-$Ca_2P_2O_7$ at 430° C., 7.2 kcal./mole; transitions form γ to β at 850° C., 0.20 kcal./mole, and β to α-$Ca_2P_2O_7$ at 1220° C., 0.76 kcal./mole respectively. (All heats are based on one mole of $CaHPO_4 \cdot 2H_2O$.) The stability of γ –$Ca_2P_2O_7$ is discussed on the basis of these data.

THE DEHYDRATION of $CaHPO_4 \cdot 2H_2O$ has been studied by Vol'fkovich and Urusov (*12*), Boullé and du Pont (*3*) and Rabatin, *et al.*, (*10*) since 1950. All of these authors concur on the importance of the humidity above the sample on the rate of the dehydration process which occurs. In humid air, the reaction proceeds more rapidly than in dry air or vacuum, and only crystalline products are formed. In 1960, Rabatin, *et al.*, (*10*) demonstrated by differential thermal analysis (DTA), thermogravimetric analysis (TGA), and x-ray diffraction techniques that in humid air single peaks occurred for the transition of $CaHPO_4 \cdot 2H_2O$ to the anhydrous salt and from the anhydrous salt to $Ca_2P_2O_7$. In dry air, they obtained several additional peaks which were attributed to amorphous phases and $CaHPO_4$ with unknown hydrate content. The behavior above 600° C. was not previously reported.

These observations by DTA in both humid air and dry air have been confirmed. Because the complex behavior in dry air or vacuum does not lend itself to straightforward interpretation, humid atmosphere was used for measurement of the heats of reactions which occur when $CaHPO_4 \cdot 2H_2O$ is heated to 1300° C. The heats were determined by the DTA method using the internal standard technique described by Barshad (*2*); however, the additional refinement of including heat capacities of the solids has been made.

EXPERIMENTAL

Materials. The $CaHPO_4 \cdot 2H_2O$ used as the starting material for the DTA curves had a surface area of 0.7 $m.^2$/gm. and was prepared by the method of Aia, *et al.*, (*1*). An ammoniacal solution of $CaCl_2$ was added to a solution of $NH_4H_2PO_4$ at room temperature. The precipitate was washed with dilute phosphoric acid solution and then with acetone before allowing to dry. The γ-$Ca_2P_2O_7$ was prepared by heating $CaHPO_4 \cdot 2H_2O$ at 400° C. for 48 hours.

The $CaCO_3$ used was reagent grade material produced by Baker and Adamson and dried at 110° C. The DTA reference material was γ-alumina prepared for high temperature combustions by Fisher Scientific Company.