NAA-SR-141
PAGE 1 OF 36
COPY 88 OF 290
SERIES A

-1-

WO- 7585

THE THERMODYNAMIC PROPERTIES OF SODIUM VAPOR

WRITTEN BY:

T. H. INATOMI
A. BENTON

WORK DONE BY:

T. H. INATOMI
A. BENTON
J. DAVIS
B. LEMKE

M. M. MILLS, GROUP LEADER, THEORETICAL PHYSICS

S. SIEGEL—ASSOCIATE DIRECTOR
C. STARR—DIRECTOR

ATOMIC ENERGY RESEARCH DEPARTMENT
NORTH AMERICAN AVIATION, INC.
P. O. BOX 309
DOWNEY, CALIFORNIA

ISSUE DATE
OCTOBER 8, 1951

CONTRACT AT 40-1-GEN-1064

3749-2

This report is distributed according to the category "Chemistry" as listed in the "Distribution List for United States Atomic Energy Commission Non-Classified Research and Development Reports", July 15, 1951.

3749-3

TABLE OF CONTENTS

Appendices

3749-4

LIST OF TABLES

LIST OF FIGURES

3749-5

ABSTRACT

The free energy function $\frac{F^o - E_o^o}{T}$, the enthalpy function $\frac{H^o - E_o^o}{T}$, the entropy S^o, and the specific heat C_p^o for both the monatomic and diatomic sodium vapor, as well as entropies, enthalpies, and equilibrium constants K_p for equilibrium mixtures of the two species, are tabulated for the temperature range 100° K to 2600° K.. These values were obtained for a pressure of one atmosphere by the methods of statistical mechanics, assuming the vapors to be ideal gases.

For reasons stated in the text, the value of $\Delta E_o^o = 0.73$ ev was chosen for the ground state dissociation energy of diatomic sodium vapor, in preference to the value of $\Delta E_o^o = 0.76$ ev used by Gordon.[12]

This report was based on studies conducted for the Atomic Energy Commission under Contract AT-40-1-GEN-1064.

3749-6

I. INTRODUCTION

In a previous report (see NAA-SR-62)[1] on the construction of thermodynamic charts for sodium (e.g., temperature-entropy, and Mollier Chart), several simplifying assumptions were made. This was necessitated by the insufficiency of available data on the themodynamic properties of sodium vapor. These thermodynamic properties have now been calculated from spectroscopic data for sodium, and the results obtained are presented here. A further report is contemplated, which will revise the charts of report NAA-SR-62 in light of these new values.

The properties presented below are the calculated values of the free energy function $\frac{F^o - E_o^o}{T}$, the enthalpy function $\frac{H^o - E_o^o}{T}$, the entropy S^o, and the specific heat C_p^o for both monatomic and diatomic sodium vapor. In addition, entropies and enthalpies for the equilibrium mixture of the two species, together with the equilibrium constant K_p for the gaseous reaction

$$Na + Na = Na_2, \qquad \ldots(1)$$

are briefly recorded here.

These calculations were made for the vapors as ideal gases at a pressure of one atmosphere, and for the temperature range 100^o K to 2600^o K.

The method of Mayer and Mayer[2] was employed for the calculations, including their high temperature anharmonicity corrections to the rigid rotator-harmonic oscillator model.

For the ground state dissociation energy of Na_2 molecules, the value of $\Delta E_o^o = 0.73\text{ ev} = 16{,}836 \frac{\text{cal}}{\text{mole}}$ was used, rather than the value of $\Delta E_o^o = 0.76\text{ ev} = 17{,}515 \frac{\text{cal}}{\text{mole}}$ used earlier by Gordon, and others (see Appendix B).

Spectroscopic data were obtained from Herzberg's new book[3] on the "Spectra of Diatomic Molecules", while the physical constants used are those recently recommended by Dumond and Cohen.[4]

3749-1

II. THE FREE ENERGY FUNCTION $\frac{F^o - E_o^o}{T}$

The free energy F, of a mole of a perfect gas is related to its total partition function Q (see Appendix A) by the equation:

$$F = -R\,T \ln Q \qquad \ldots(2)$$

Substituting Eqs. (A-2), and (A-15) (see Appendix A) into Eq. (2), we have

$$F = -R\,T \ln \left(\frac{2\pi M kT}{h^2 N_o}\right)^{3/2} \frac{R\,T}{PN_o} - R\,T \ln Q_i \qquad \ldots(3)$$

The free energy above the zero point energy E_o^o is then

$$\frac{F - E_o^o}{T} = R\left[\left({}^3/_2\right) \ln \left(\frac{h^2 N_o}{2\pi k}\right) - \left({}^3/_2\right) \ln M - \left({}^5/_2\right) \ln T + \ln \frac{PN_o}{R}\right] - R \ln Q_i \qquad \ldots(4)$$

Taking as the standard state the ideal gas at one atmosphere pressure, we have

$$\frac{F^o - E_o^o}{T} = R\left[\left({}^3/_2\right) \ln \left(\frac{h^2 N_o}{2\pi k}\right) - \left({}^3/_2\right) \ln M - \left({}^5/_2\right) \ln T + \ln \frac{N_o}{R}\right] - R \ln Q_i \qquad \ldots(5)$$

The internal partition function Q_i is related to the vibrational and rotational partition functions Q_v and Q_r through the equation (see Appendix A):

$$R \ln Q_i = R \ln Q_v + R \ln Q_r + R \ln Q_c \qquad \ldots(6)$$

where Q_c is the anharmonicity correction factor.

3749-8

Based on Eq. (2), we can rewrite Eq. (6) as

$$R \ln Q_i = -\left(\frac{F^o - E_o^o}{T}\right)_v - \left(\frac{F^o - E_o^o}{T}\right)_r + R \ln Q_c \qquad \ldots(7)$$

where $$\left(\frac{F^o - E_o^o}{T}\right)_v = -R \ln Q_v \qquad \ldots(8)$$

and $$\left(\frac{F^o - E_o^o}{T}\right)_r = -R \ln Q_r \qquad \ldots(9)$$

For homonuclear diatomic molecules, a symmetry term $R \ln 2$ must be added[5] to Eq. (9) so that we have:

$$\left(\frac{F^o - E_o^o}{T}\right)_r = -R \ln Q_r + R \ln 2 \qquad \ldots(10)$$

From Eqs. (A-10), and (A-8) we obtain (see Appendix A)

$$R \ln Q_r = -R \left[\ln B_o + \ln\left(\frac{hc}{k}\right) - \ln T - \frac{\sigma}{3}\right] \qquad \ldots(11)$$

so that Eq. (10) becomes

$$\left(\frac{F^o - E_o^o}{T}\right)_r = R \left[\ln B_o + \ln\left(\frac{hc}{k}\right) - \ln T - \frac{\sigma}{3}\right] + R \ln 2 \qquad \ldots(12)$$

Values for B_o and σ may be calculated from Eqs. (A-9) and (A-8) respectively (see Appendix A).

The anharmonicity correction term may be computed from Eqs. (A-11) and (A-5):

$$R \ln Q_c = R \left[{}^{A}/_{\theta} - B + C\theta - D\,\theta^2 - E\,\theta^3\right] \qquad \ldots(\text{A-11})$$

in which the constants A, B, C, D, and E may be obtained from Eqs. (A-12) and (A-13).

Combining Eqs. (A-11), (12), (7) with Eq. (5) gives us the final equation for the free energy function of a non-rigid rotator:

$$\left(\frac{F^o - E_o^o}{T}\right) = R\left[\frac{3}{2}\ \ln\left(\frac{h^2 N_o}{2\pi k}\right) - \frac{3}{2}\ \ln M - \frac{5}{2}\ \ln T + \ln\frac{N_o}{R}\right]$$

$$+ \left(\frac{F^o - E_o^o}{T}\right)_v + R\left[\ln B_o + \ln\left(\frac{hc}{k}\right) - \ln T - \frac{\sigma}{3}\right] + (R\ \ln 2)$$

$$- R\left[\frac{A}{\theta} - B + C\theta - D\theta^2 - E\theta^3\right] \qquad \ldots(13)$$

A considerable amount of work involved in the use of Eq. (13) may be eliminated by consulting the Rand Tables,[6] in which the vibrational contribution $\left(\frac{F^o - E_o^o}{T}\right)_v$ to the free energy function, is tabulated as a function of ν/T (where ν is the term value in cm^{-1}).

For a perfect monatomic gas, Eq. (13) reduces to

$$\left(\frac{F^o - E_o^o}{T}\right) = R\left[\left({}^3/_2\right)\ \ln\left(\frac{h^2 N_o}{2\pi k}\right) - \left({}^3/_2\right)\ \ln M - \left({}^5/_2\right)\ \ln T + \ln\frac{N_o}{R}\right] \qquad \ldots(14)$$

III. THE ENTHALPY FUNCTION $\frac{H^o - E_o^o}{T}$

The total enthalpy H^o, of a mole of an ideal gas is equal to the sum of the translational (H_k^o) and internal (H_i^o) enthalpies, i.e.

$$H^o = H_k^o + H_i^o \qquad \ldots(15)$$

For an ideal gas,

$$H_k^o = \left(5/2\right) R\,T \qquad \ldots(16)$$

The internal enthalpy is given by the expression

$$H_i^o - E_o^o = R\,T^2 \frac{d \ln Q_i}{dT} \qquad \ldots(17)$$

Upon substituting the expression for Q_i (see Appendix A), Eq. (17) can be written as:

$$\left(H_i^o - E_o^o\right) = R\,T^2 \frac{d \ln Q_v}{d\,T} + R\,T^2 \frac{d \ln Q_r}{dT} + R\,T^2 \frac{d \ln Q_c}{dT} \qquad \ldots(18)$$

Since

$$Q_v = \frac{1}{1 - e^{-\theta}} \qquad \ldots(\text{A-4})$$

where

$$\theta = \frac{hcw}{kT},$$

we have

$$H_v^o = R\,T^2 \frac{d \ln Q_v}{dT} = \frac{R\,T\,\theta\,e^{-\theta}}{1 - e^{-\theta}} \qquad \ldots(19)$$

From the relations

$$\ln Q_r = - \ln \sigma + \frac{\sigma}{3} \qquad \ldots(\text{A-10})$$

and

$$\sigma = \frac{B_o\,h\,c}{k\,T} \qquad \ldots(\text{A-8})$$

we can readily obtain the expression:

$$H_r^o = R\,T^2 \,\frac{d\,\ln Q_r}{d\,T} = R\,T - R\left(\frac{B_o\,h\,c}{3\,k}\right)$$

$$= R\,T\left(1 - \frac{\sigma}{3}\right) \qquad \ldots(20)$$

From the expression for $\ln Q_c$ as given by Eq. (A-11), we derive the expression for the anharmonicity correction factor H_c to the enthalpy:

$$H_c = R\,T^2\,\frac{d\,\ln Q_c}{d\,T} = R\,T\left[\frac{A}{\theta} - C\theta + 2\,D\,\theta^2 + 3\,E\,\theta^3\right] \qquad \ldots(21)$$

The constants A, C, D, and E are defined by Eqs. (A-12) and (A-13).

The final equation for the enthalpy function of an ideal gas as a non-rigid rotator is then equal to

$$\left(\frac{H^o - E_o^o}{T}\right) = \left({}^7\!/_2\right) R + \frac{R\,\theta\,e^{-\theta}}{1 - e^{-\theta}}\;\frac{R\sigma}{3} + R\left[\frac{A}{\theta} - C\theta + 2\,D\,\theta^2 + 3\,E\,\theta^3\right]$$

$$\ldots(22)$$

The Rand Tables[6] should be consulted, in which are tabulated the vibrational contribution

$$\left(\frac{H^o - E_o^o}{T}\right)_v = \frac{R\,\theta\,e^{-\theta}}{1 - e^{-\theta}}$$

to the enthalpy function.

For an ideal monatomic gas, Eq. 22 reduces to

$$\frac{H^o - E_o^o}{T} = \left({}^5\!/_2\right) R \qquad \ldots(23)$$

IV. THE SPECIFIC HEAT C_p^o

The translational specific heat of an ideal gas is given by the expression:

$$C_{p_k} = \left({}^5\!/_2\right) R \qquad \ldots(24)$$

37 49-12

The specific heat due to internal degrees of freedom is equal to

$$C_{p_i}^{o} = \frac{d}{dT}\left[R\,T^2 \frac{d}{dT} \ln Q_i\right] \qquad \ldots(25)$$

From Eq. (19), (20), and (21), we find respectively that

$$C_{p_v}^{o} = \frac{d}{dT}\left(\frac{R\,T\,\theta\,e^{-\theta}}{1 - e^{-\theta}}\right) = \frac{R\,\theta^2}{2\,(\cosh\,\theta - 1)} \qquad \ldots(26)$$

$$C_{p_r}^{o} = \frac{d}{dT}\left[R\,T\left(1 - \frac{\sigma}{3}\right)\right] = R \qquad \ldots(27)$$

$$C_{p_c}^{o} = \frac{d}{dT}\left[R\,T\left(\frac{A}{\theta} - C\theta + 2\,D\,\theta^2 + 3\,E\,\theta^3\right)\right] =$$

$$R\left[2\,{}^{A}/_{\theta} - 2\,D\theta^2 - 6\,E\,\theta^3\right] \qquad \ldots(28)$$

The total specific heat for an ideal gas as a non-rigid rotator is then given by the equation:

$$C_p^{o} = \frac{7}{2}R + \frac{R\,\theta^2}{2\,(\cosh\,\theta - 1)} + R\left[2\,{}^{A}/_{\theta} - 2\,D\,\theta^2 - 6\,E\,\theta^3\right] \qquad \ldots(29)$$

In evaluating Eq. (29) for a gas, considerable labor may be saved by consulting the Rand Tables[6] for tabulated values of the vibrational contribution

$$C_{p_v}^{o} = \frac{R\,\theta^2}{2\,(\cosh\,\theta - 1)}$$

to the specific heat.

For an ideal monatomic gas, Eq. (29) reduces to Eq. (24).

V. THE ENTROPY S^o

The entropy of an ideal gas may be obtained from the relation

$$S^{o} = \left(\frac{H^{o} - E_{o}^{o}}{T}\right) - \left(\frac{F^{o} - E_{o}^{o}}{T}\right) \qquad \ldots(30)$$

The enthalpy function, and the free energy function for the gas in question, are calculated from equations presented in previous sections.

VI. THE EQUILIBRIUM CONSTANT K_p FOR THE DIMERIZATION OF SODIUM VAPOR

As mentioned previously, sodium vapor is in dynamic equilibrium between the monatomic and diatomic species:

$$2\ \mathrm{Na} \rightleftarrows \mathrm{Na}_2 , \qquad \Delta E_{o}^{o} = -16,836 \text{ cal/mole}$$

The equilibrium constant K_p (see Appendix C) for this reaction may be obtained from the equation:

$$-R \ln K_p = \frac{\Delta E_{o}^{o}}{T} + \left(\frac{F^{o} - E_{o}^{o}}{T}\right)_{Na_2} - 2\left(\frac{F^{o} - E_{o}^{o}}{T}\right)_{Na} \qquad \ldots(31)$$

where ΔE_{o}^{o} is the zero-point energy change.

For a dissociative equilibrium between a diatomic gas and the dissociated atoms, ΔE_{o}^{o} is simply equal to the heat of dissociation ΔH_{o}^{o} of that gas at the absolute zero.[7] (Herzberg[7] uses the symbol D_{o}^{o} for ΔE_{o}^{o}).

The numerical value of ΔE_{o}^{o} accepted here for the formation of sodium dimer is (see Appendix B):

$$\Delta E_{o}^{o} = \Delta H_{o}^{o} = -0.73 \text{ ev}$$

$$= -16,836 \text{ cal/mole}$$

3249-14

VII. ENTROPY AND ENTHALPY FOR EQUILIBRIUM SODIUM VAPOR MIXTURE

When ideal gases are mixed at constant temperature and pressure of the mixture, the entropy of the mixture is given by

$$S_M^o = \sum_i x_i \, S_i^o + \Delta S^o \qquad \ldots(32)$$

where S_i is the molar entropy, and x_i is the mole fraction of component i. ΔS^o is the entropy of mixing, and is given by

$$\Delta S^o = (-R \sum_i x_i \ln x_i) \text{ per mole of gas mixture,} \qquad \ldots(33)$$

where R is the gas constant, and x_i is the mole fraction of component i. The individual entropies S_i are found at the constant temperature and pressure of the mixture. The mole fractions x_i are found by the use of Eq. (C-5) of the Appendix, together with a knowledge of K_p as determined by Eq. (31).

When ideal gases are mixed at constant temperature, the enthalpy of the mixture is given by

$$H_M^o = \sum_i H_i^o \, x_i \qquad \ldots(34)$$

For ideal gases, the enthalpy of mixing is equal to zero. The enthalpy of the individual components H_i are taken at the pressure and temperature of the mixture.

For the heat of formation of monatomic sodium gas at 0° K, the Bureau of Standards[8] gives the following value:

$$Na_{(solid)} \rightleftarrows Na_{(gas)} \; , \quad \left(\Delta E_o^o\right)_f = 26,050 \; \frac{\text{cal}}{\text{mole}} \qquad \ldots(35)$$

(NOTE: At 0° K, $H_o^o = E_o^o$)

Combining Eq. (35) with Eq. (1),

$$2Na_{(gas)} \rightleftarrows Na_{2_{(gas)}} \; , \quad \Delta E_o^o = -16,836 \; \frac{\text{cal}}{\text{mole}}, \qquad \ldots(1)$$

3749-15

we obtain the heat of formation of the diatomic sodium gas:

$$2Na_{(solid)} \rightleftharpoons Na_{2(gas)}, \quad \left(\Delta E_o^o\right)_f = 35,260 \frac{cal}{mole} \qquad \ldots(36)$$

Since the heat of formation of the crystalline sodium is equal to zero by definition, we obtain from Eqs. (35) and (36) respectively, the following zero point energy values for the monatomic and diatomic sodium gas respectively,

$$\left(E_o^o\right)_{Na} = 26,050 \frac{cal}{mole}$$

$$\left(E_o^o\right)_{Na_2} = 35,260 \frac{cal}{mole}$$

3749-16

TABLE I

NOMENCLATURE

B_o	Rotational constant for the lowest vibrational state	
c	Velocity of light (see Table II)	
C_p^o	Specific heat of an ideal gas	$\frac{\text{cal}}{\text{mole}\ ^o\text{K}}$
E_o^o	Zero point energy (energy at the absolute zero)	$\frac{\text{cal}}{\text{mole}}$
ΔE_o^o	Heat of reaction at 0 ^{o}K (e.g., energy of dissociation)	$\frac{\text{cal}}{\text{mole}}$
F^o	Free energy per mole in the ideal state	$\frac{\text{cal}}{\text{mole}}$
$\left(\frac{F^o - E_o^o}{T}\right)$	Free energy function	$\frac{\text{cal}}{\text{mole}\ ^o\text{K}}$
h	Planck constant (see Table II)	
H^o	Enthalpy of an ideal gas	$\frac{\text{cal}}{\text{mole}}$
H_M^o	Enthalpy of an equilibrium mixture of Na and Na_2 molecules	$\frac{\text{cal}}{\text{mole of mixture}}$
H_m^o	Enthalpy of an equilibrium mixture of Na and Na_2 molecules	$\frac{\text{cal}}{22.997\ \text{gm}}$
$\left(\frac{H^o - E_o^o}{T}\right)$	Enthalpy function	$\frac{\text{cal}}{\text{mole}\ ^o\text{K}}$
K_p	Equilibrium constant for the formation of Na_2 vapor from Na vapor	atm^{-1}
k	Boltzman constant (see Table II)	

3749-17

m	Mass per molecule	$\frac{\text{gm}}{\text{molecule}}$
M	Molecular weight	$\frac{\text{gm}}{\text{mole}}$
N_o	Avogadros' Number (see Table II)	
n_1, n_2	Moles of monatomic and diatomic sodium vapor molecules at equilibrium, respectively	moles
n_t	Total moles $(n_1 + n_2)$ of sodium vapor at equilibrium	moles
P	Pressure	atm
P_t	Total pressure $(P_1 + P_2)$	atm
Q	Partition function	
R	Gas constant (see Table II)	
S^o	Entropy of the ideal gas at 1 atm, pressure	$\frac{\text{cal}}{\text{mole }^o\text{K}}$
$S_M{}^o$	Entropy of an equilibrium mixture of Na and Na_2 molecules	$\frac{\text{cal}}{(\text{mole of mix.})\ ^o\text{K}}$
$S_m{}^o$	Entropy of an equilibrium mixture of Na and Na_2 molecules	$\frac{\text{cal}}{(22.997\text{ gm})\ ^o\text{K}}$
T	Absolute temperature	^{o}K
V	Molar volume	cm^3/mole
w	Wave number	cm^{-1}
W	Molecular weight of equilibrium mixtures of Na and Na_2 vapor	$\frac{\text{gm}}{\text{mole of mix.}}$
x_1	Mole fraction of monatomic sodium vapor	
x_2	Mole fraction of diatomic sodium vapor	
θ	$\frac{hcw}{kT}$	
Σ	Symbol for summation	

3749-18

Superscript

o	Refers to the hypothetical reference state of unit fugacity

Subscripts

1	Refers to monatomic sodium vapor
2	Refers to diatomic sodium vapor
i	Refers to internal degrees of freedom
k	Refers to translational degrees of freedom
v	Refers to vibrational degrees of freedom
r	Refers to rotational degrees of freedom
c	Refers to anharmonicity correction

TABLE II

PHYSICAL CONSTANTS

h	Planck Constant	6.623773×10^{-27} erg sec
c	Velocity of light	$2.9979022 \times 10^{10} \frac{\text{cm}}{\text{sec}}$
R	Gas constant	$1.98719 \frac{\text{cal}}{\text{gm mole } ^{\circ}\text{K}}$
	or	$82.0790 \frac{\text{cm}^3 \text{ atm}}{\text{gm mol } ^{\circ}\text{K}}$
N_o	Avogadro's Number	$6.025438 \times 10^{23} \frac{\text{molec.}}{\text{mole}}$
k	Boltzmann Constant	$1.3802565 \times 10^{-16} \frac{\text{ergs}}{\text{deg}}$
$\frac{hc}{k}$		1.438675 cm deg

3749.20

TABLE III

BASIC DATA FOR SODIUM

Atomic Weight (Physical scale)	22.99618
Melting Point	371° K
Boiling Point	1155° K

Spectroscopic data for Gaseous Sodium Atom:[9]

Term value, cm^{-1}	Degeneracy
0	2
16956.183	2
16973.379	4
25739.86	2
29172.855	6
29172.904	4
:	:

Spectroscopic Constants for the Electronic States[3] of Diatomic Sodium Molecule Na_2^{23}:

	Te, cm^{-1}	w_e, cm^{-1}	$w_e x_e$, cm^{-1}	$w_e y_e$, cm^{-1}	B_e, cm^{-1}	α_e, cm^{-1}
$^1\Sigma_g^+$	0	159.23	0.726	-0.0027	0.15471	0.00079
$^1\Sigma_u^+$	14680.4	117.6	0.38	- - -	0.1107	0.00054
$^1\pi_u$	20320.2	123.79	0.6303	-0.00936	0.12588	0.00094

$$\Delta E_o^o = 0.73 \text{ ev} = 16,836 \frac{\text{cal}}{\text{mol}}$$

3749-21

TABLE IV

Thermodynamic Functions for Monatomic and Diatomic Sodium Vapor as Perfect Gases, in Their Standard State of One Atmosphere Pressure.*

T, °K	$-\left(\frac{F^o - E_o^o}{T}\right)_1$ $\frac{cal}{mole\ ^oK}$	$-\left(\frac{F^o - E_o^o}{T}\right)_2$ $\frac{cal}{mole\ ^oK}$	K_p	$\left(\frac{H^o - E_o^o}{T}\right)_1$ $\frac{cal}{mole\ ^oK}$	$\left(\frac{H^o - E_o^o}{T}\right)_2$ $\frac{cal}{mole\ ^oK}$	S_1^o $\frac{cal}{mole\ ^oK}$	S_2^o $\frac{cal}{mole\ ^oK}$	$C_{p_1}^o$ $\frac{cal}{mole\ ^oK}$	$C_{p_2}^o$ $\frac{cal}{mole\ ^oK}$
100	26.318	37.996	3.9362×10^{33}	4.9680	7.4871	31.286	45.483	4.9680	8.2982
298.1	31.744	46.659	4.6236×10^{8}	4.9680	8.3331	36.712	54.992	4.9680	8.9623
371	32.831	48.496	1.4664×10^{6}	4.9680	8.4630	37.799	56.959	4.9680	9.0233
500	34.313	51.045	3.2853×10^{3}	4.9680	8.6181	39.281	59.663	4.9680	9.1005
800	36.648	55.146	4.2905	4.9680	8.8255	41.616	63.971	4.9680	9.2369
1000	37.757	57.125	0.45780	4.9680	8.9160	42.7250	66.041	4.9680	9.3188
1155	38.473	58.414	0.13688	4.9680	8.9742	43.441	67.389	4.9680	9.3807
1200	38.663	58.758	0.10193	4.9680	8.9898	43.631	67.748	4.9680	9.3985
1400	39.429	60.148	0.034630	4.9680	9.0538	44.397	69.202	4.9680	9.4771
1600	40.092	61.361	0.015346	4.9680	9.1116	45.060	70.473	4.9680	9.5552
1800	40.677	62.438	0.0081268	4.9680	9.1652	45.645	71.603	4.9680	9.6329
2000	41.201	63.406	0.0048796	4.9680	9.2159	46.169	72.622	4.9680	9.7104
2200	41.674	64.287	0.0032108	4.9680	9.2643	46.642	73.551	4.9680	9.7879
2273	41.836	64.589	0.0028065	4.9680	9.2816	46.804	73.871	4.9680	9.8161
2400	42.106	65.095	0.0022641	4.9680	9.3112	47.074	74.406	4.9680	9.8652
2600	42.504	65.842	0.0016844	4.9680	9.3568	47.472	75.199	4.9680	9.9424

* Subscript 1 refers to monatomic sodium vapor.
Subscript 2 refers to diatomic sodium vapor.

TABLE V

The Composition and Molecular Weight of the Equilibrium Mixture of Monatomic and Diatomic Sodium Vapor (Total Pressure = 1 Atmosphere).

T, °K	K_p	X_1	X_2	W $\frac{gm}{mole}$
100	3.9362×10^{33}	1.5939×10^{-17}	1.0000	45.994
298.1	4.6236×10^{8}	4.6505×10^{-5}	0.99995	45.993
371	1.4664×10^{6}	8.2546×10^{-4}	0.99917	45.975
500	3.2853×10^{3}	0.017295	0.98271	45.596
800	4.2905	0.38011	0.61990	37.253
1000	0.45780	0.74554	0.25446	28.849
1155	0.13668	0.89139	0.10861	25.495
1200	0.10193	0.91471	0.085286	24.958
1400	0.034630	0.96758	0.032421	23.743
1600	0.015346	0.98511	0.014893	23.340
1800	0.0081268	0.99200	0.007997	23.181
2000	0.0048796	0.99517	0.004833	23.108
2200	0.0032108	0.99681	0.003190	23.070
2273	0.0028065	0.99721	0.002791	23.061
2400	0.0022641	0.99775	0.002254	23.049
2600	0.0016844	0.99832	0.001679	23.036

3749-23

TABLE VI

The Entropy of the Equilibrium Mixture of Monatomic and Diatomic Sodium Vapor (Total Pressure = 1 Atmosphere).

T, °K	S_M^o $\frac{\text{cal}}{\text{mole }^\circ\text{K}}$	S_m^o $\frac{\text{cal}}{(22.997\text{ gm})^\circ\text{K}}$
100	45.483	22.742
298.1	54.992	27.497
371	56.957	28.490
500	59.484	30.002
800	56.794	35.060
1000	49.785	39.687
1155	46.725	42.147
1200	46.267	42.631
1400	45.485	44.057
1600	45.592	44.923
1800	45.945	45.581
2000	46.357	46.134
2200	46.771	46.622
2273	46.918	46.787
2400	47.168	47.062
2600	47.543	47.463

TABLE VII

The Enthalpy of Monatomic and Diatomic Sodium Vapor, and of the Equilibrium Mixture (Total Pressure = 1 Atmosphere). *

T, ^oK	$(H^o-E_o^o)_1$ cal/mole	$(H^o-E_o^o)_2$ cal/mole	$(H^o)_1$ cal/mole	$(H^o)_2$ cal/mole	H_M^o cal/mole	H_m^o cal/(22.997 gm)
100	496.80	748.71	26,547	36,009	36,009	18,004
298.1	1481.0	2484.1	27,531	37,744	37,744	18,872
371	1843.1	3139.8	27,893	38,400	38,391	19,204
500	2484.0	4309.0	28,534	39,569	39,378	19,861
800	3974.4	7060.4	30,024	42,320	37,647	23,240
1000	4968.0	8916.0	31,018	44,176	34,366	27,395
1155	5738.0	10365.	31,788	45,625	33,291	30,029
1200	5961.6	10788	32,012	46,048	33,209	30,599
1400	6955.2	12675	33,005	47,935	33,489	32,438
1600	7948.8	14579	33,999	49,839	34,235	33,732
1800	8942.4	16497	34,992	51,757	35,126	34,848
2000	9936.0	18432	35,986	53,692	36,072	35,898
2200	10930.	20382	36,980	55,642	37,039	36,921
2273	11292.	21097	37,342	56,357	37,395	37,291
2400	11923.	22347	37,973	57,607	38,017	37,932
2600	12917.	24328	38,967	59,588	39,001	38,936

* Subscript 1 refers to monatomic sodium Vapor.
Subscript 2 referes to diatomic sodium Vapor.

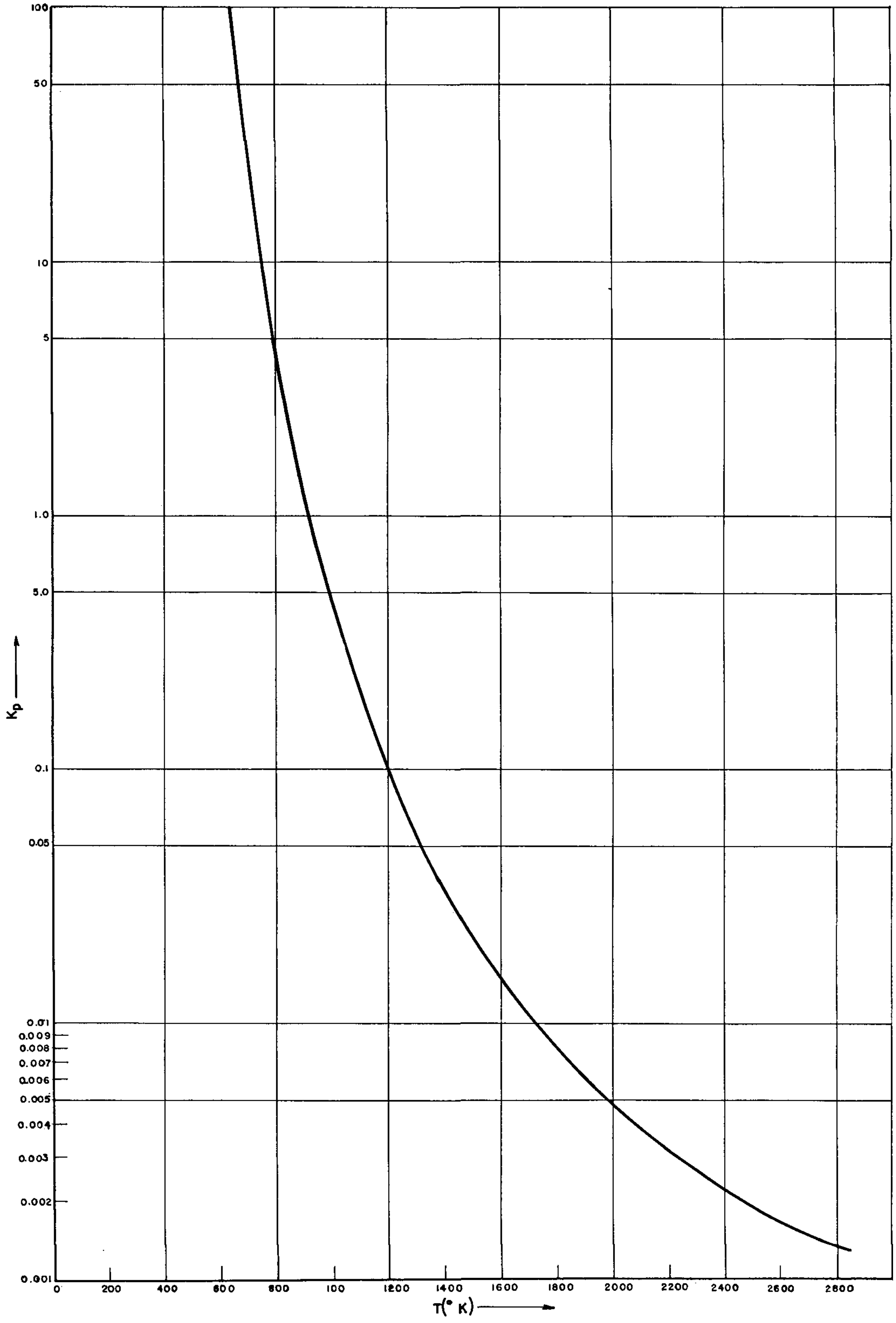

Figure 1. K_p as a Function of Temperature for the Vapor Phase Reaction: $2Na = Na_2$.

3749-26

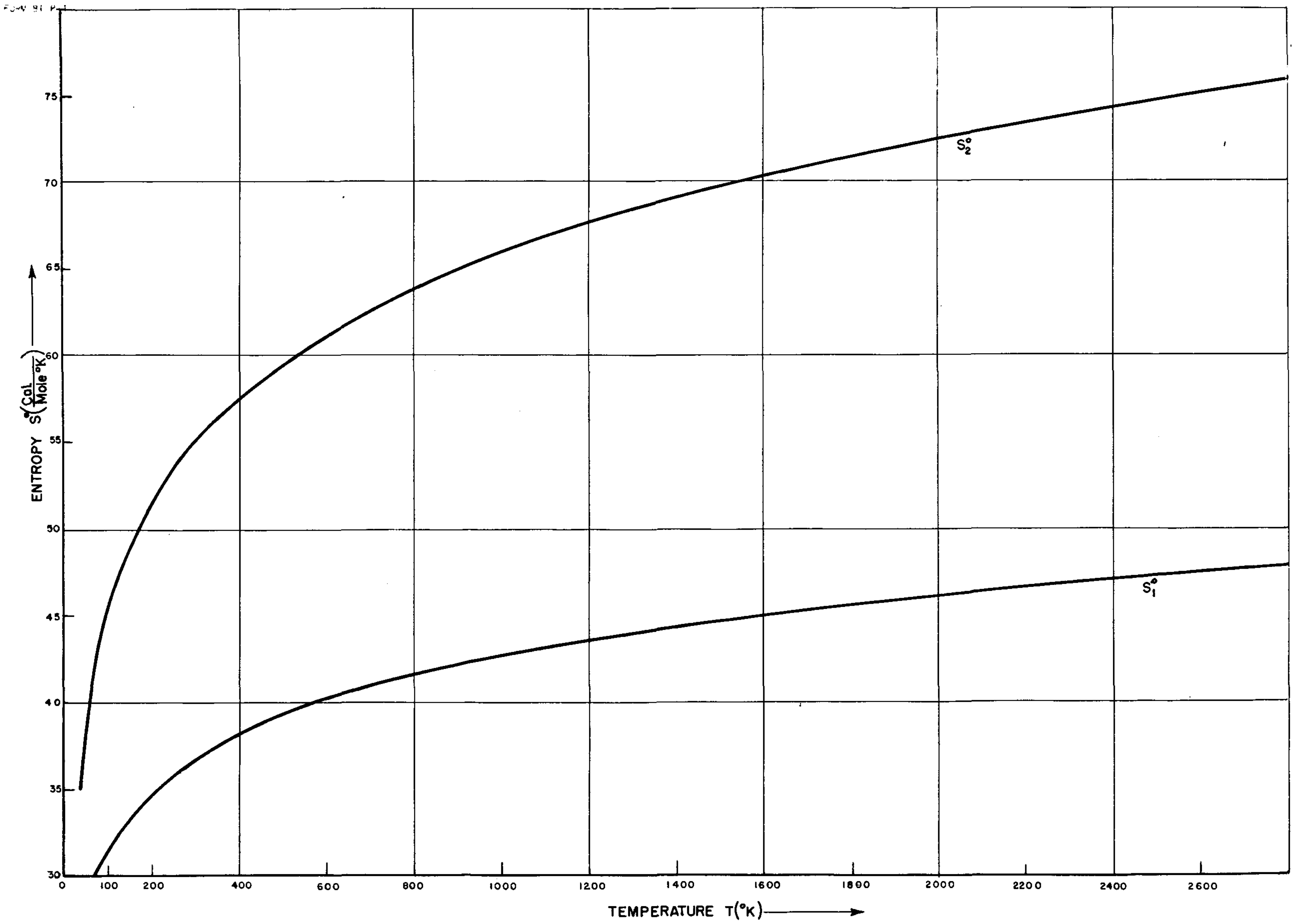

Figure 2. Entropy in $\frac{\text{cal}}{\text{Mole }^{\circ}\text{K}}$ of Monatomic and Diatomic Sodium Vapor as a Function of Temperature (Pressure = 1 Atmosphere).

3749-27

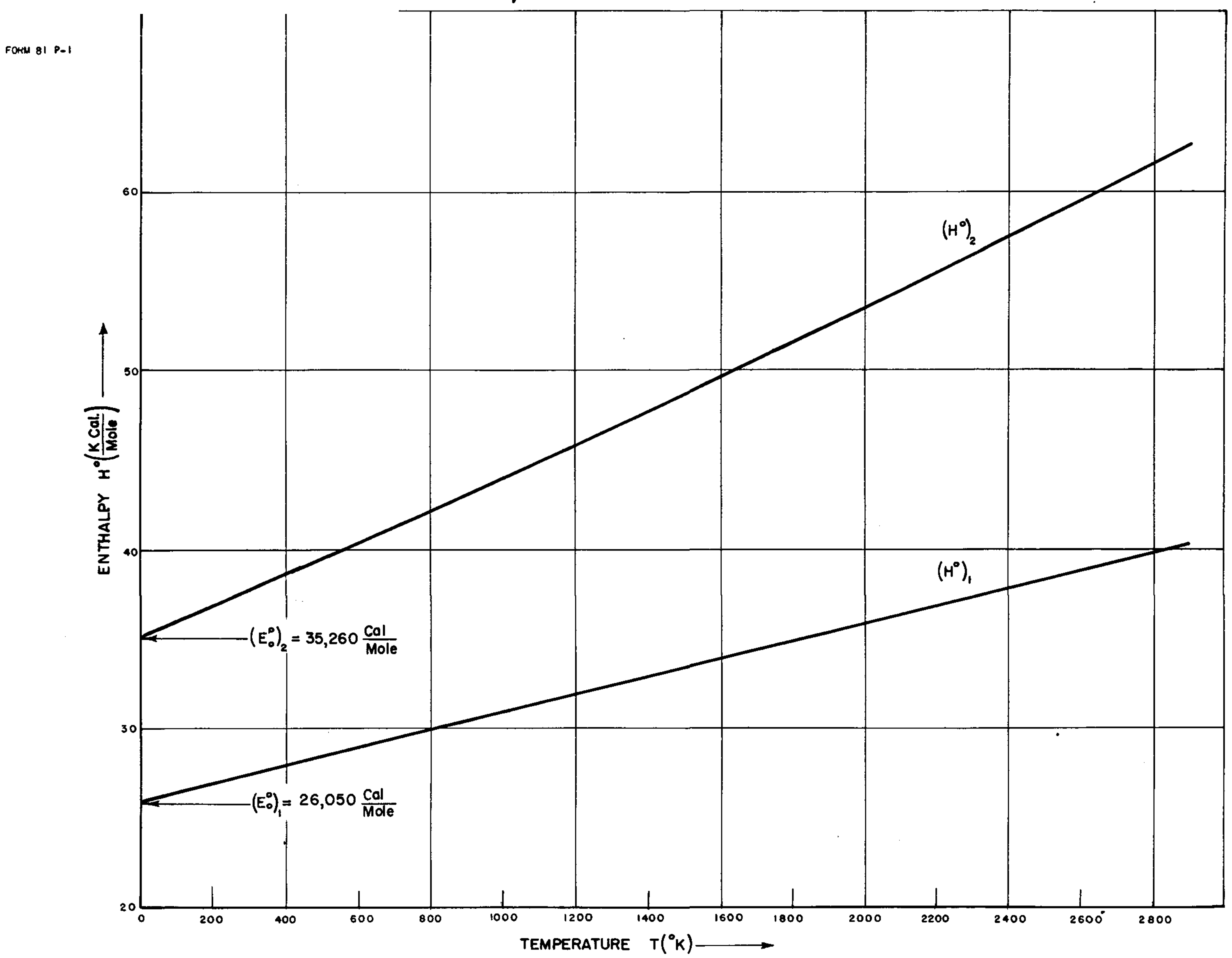

Figure 3. Enthalpy in $\frac{\text{cal}}{\text{Mole}}$ of Monatomic and Diatomic Sodium Vapor as a Function of Temperature (Pressure = 1 Atmosphere).

3749-28

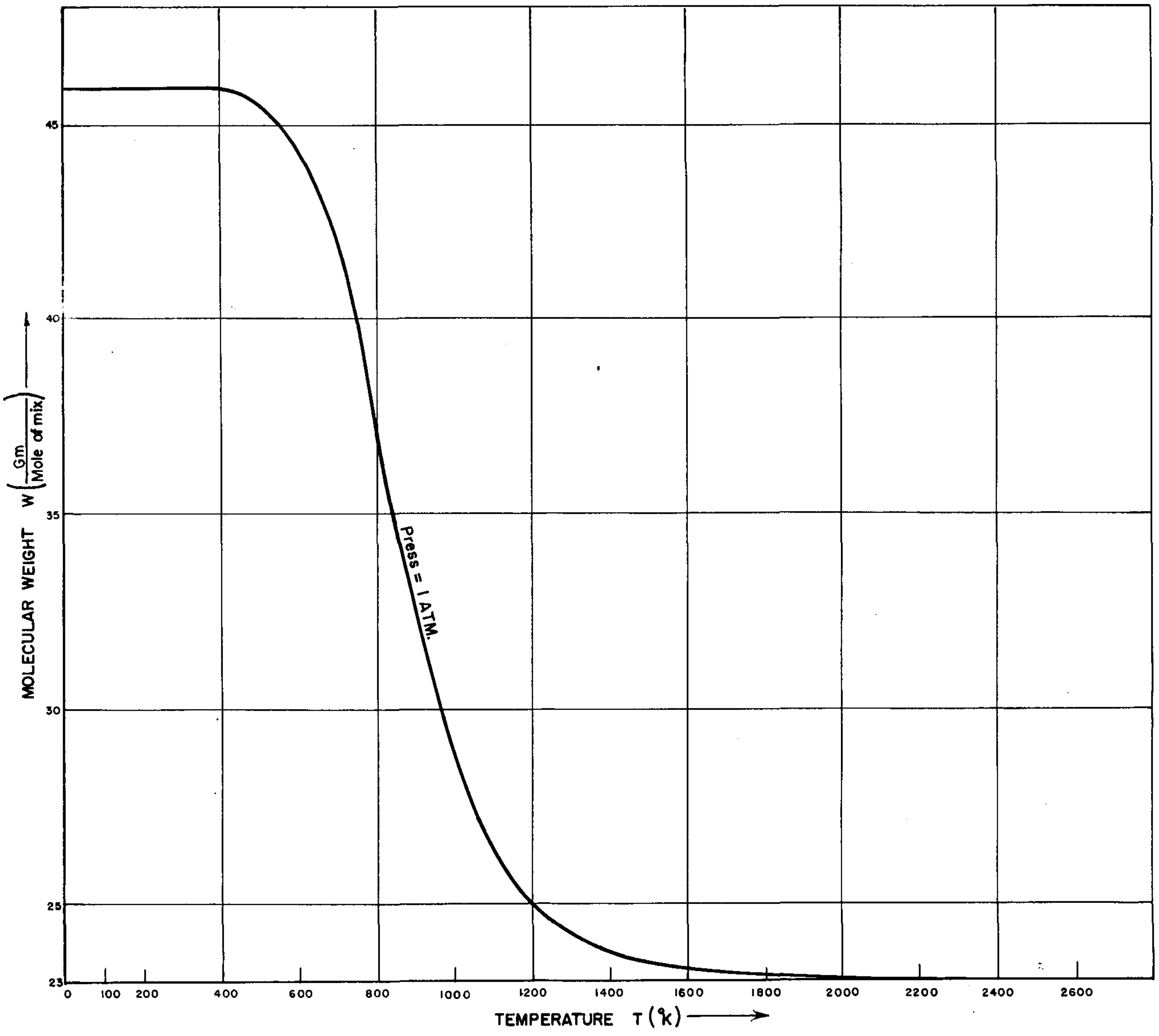

Figure 4. Molecular Weight of Equilibrium Mixtures of Monatomic and Diatomic Sodium Vapor as a Function of Temperature (pressure = 1 Atmosphere).

3749-29

APPENDIX A

THE PARTITION FUNCTION

All the required thermodynamic properties of an ideal gas may be calculated from a knowledge of its partition function Q, defined by the relation:

$$Q = g_o e^{-0/kT} + g_1 e^{-\epsilon_1/kT} + g_2 e^{-\epsilon_2/kT} + \cdots$$

$$= \sum_i g_i e^{-\epsilon_i/kT} \qquad \ldots(A\text{-}1)$$

where ϵ_i is the energy of the ith level above the ground level, and g_i is its statistical weight.

The total partition function Q may be expressed as the product of the translational (Q_k) and internal (Q_i) partition function, thusly:

$$Q = Q_k \cdot Q_i \qquad \ldots(A\text{-}2)$$

In general, the problem of computing rigorously correct values for Q_i is a complicated process, requiring that every possible vibrational, rotational and electronic energy level be considered. An approximation that is very satisfactory above about 50° K is given by the equation

$$Q_i = Q_e \cdot Q_v \cdot Q_r \cdot Q_c \qquad \ldots(A\text{-}3)$$

where Q_e is the electronic contribution, Q_v the vibrational, and Q_r the rotational contribution to the internal partition function. Finally, Q_c is a corrective term applied to account for the interaction between rotational and vibrational energy levels, which is important only at high temperatures.

For the case of sodium, even for the highest temperature considered here, only the ground electronic state of the molecule need be taken into account, since the excited electronic states make only negligible contributions to the partition function. Hence $Q_e = 1$.

3749.30

The vibrational partition function of an oscillator is given by:

$$Q_v = \frac{1}{1 - e^{-\theta}} \qquad \ldots\text{(A-4)}$$

where

$$\theta = \frac{h\,c\,w}{k\,T} \qquad \ldots\text{(A-5)}$$

and cw is the vibrational frequency where w is given by the expression

$$w = w_e - 2\,w_e\,x_e \qquad \ldots\text{(A-6)}$$

(w_e and $w_e\,x_e$ are spectroscopic constants).

The partition function for a rigid rotator is given by:

$$Q_r = \frac{1}{\sigma}\left(1 + \frac{\sigma}{3}\right) \qquad \ldots\text{(A-7)}$$

where

$$\sigma = \frac{h^2}{8\,\pi^2\,I\,k\,T} = \frac{B_o\,h\,c}{k\,T} \qquad \ldots\text{(A-8)}$$

and I is the moment of inertia, and B_o is a rotational constant (for the lowest vibrational state) equal to $h/(8\,\pi^2\,Ic)$. The value of B_o may be found from the equation:[10]

$$B_o = B_e - \frac{\alpha_e}{2} \qquad \ldots\text{(A-9)}$$

where B_e and α_e are spectroscopic constants.

We note here for Eq. (A-7) that:

$$\ln Q_r \cong -\ln \sigma + \frac{\sigma}{3} \qquad \ldots\text{(A-10)}$$

For the anharmonicity correction term, Mayer and Mayer[11] gives the following expression:

$$\ln Q_c = A/\theta - B + C\theta - D\,\theta^2 - E\,\theta^3 \qquad \ldots\text{(A-11)}$$

where

$$\theta = \frac{h\,c\,w}{k\,T} \qquad \text{...(A-5)}$$

The constants A, B, C, D, and E of Eq. (A-11) are given by the expressions:

$$\left.\begin{aligned} A &= 8\gamma + \delta + 2x \\ B &= \frac{\delta}{2} + 2x \\ C &= \frac{\delta}{12} + \frac{5x}{6} \\ D &= \frac{x}{6} \\ E &= \frac{\delta}{720} - \frac{x}{120} \end{aligned}\right\} \qquad \text{...(A12)}$$

The constants γ, δ, and x are dimensionless and independent of temperature; they are calculated from the spectroscopic constants α, B_e, w_e, and $w_e x_e$ according to the equations:

$$\left.\begin{aligned} \gamma &= \frac{B_e}{w_e} \\ \delta &= {}^{\alpha_e}/_{B_e} \\ x &= \frac{w_e x_e}{w_e} \end{aligned}\right\} \qquad \text{...(A-13)}$$

The translational partition function is given by the expression:

$$Q_k = \frac{(2\pi m k T)^{3/2}}{h^3} \frac{V}{N_o} \qquad \text{...(A-14)}$$

or the equivalent form

$$\begin{aligned} Q_k &= \frac{(2\pi m k T)^{3/2}}{h^3} \frac{R\,T}{N_o\,P} \\ &= \left(\frac{2\pi M k T}{h^2 N_o}\right)^{3/2} \frac{R\,T}{P\,N_o} \end{aligned} \qquad \text{...(A-15)}$$

3749.32

where M is the molecular weight, N_o the Avogadro's Number, P the pressure, T the absolute temperature, and R the gas constant.

3249-33

APPENDIX B

THE ENERGY OF DISSOCIATION (ΔE_o^o) OF DIATOMIC SODIUM VAPOR

Gordon, in an earlier work[12], assumed for the energy of dissociation of the diatomic sodium vapor, the value of ΔE_o^o = 0.76 electron volts = 17,515 $\frac{\text{cal}}{\text{mol}}$, based on the original data of Loomis and co-workers.[13,14]

We use here the recently recalculated value of ΔE_o^o = 0.73 electron volts = 16,836 cal/mol as presented in Herzberg's new book[3] on the "Spectra of Diatomic Molecules".

$$Na_2^{23} = Na + Na, \qquad \Delta E_o^o = +\,16{,}836\ \frac{\text{cal}}{\text{mol}}$$

This value of ΔE_o^o is based on thermochemical measurements,* and refers to dissociation from the ground state to normal products (unexcited sodium atoms). All the dissociation energies listed in Herzberg[3] (Herzberg uses the symbol D_o^o for ΔE_o^o), have been recalculated from the original data to conform with the new physical constants and conversion factors recommended by Dumond and Cohen.[4]

---

*For Na_2 molecules, there is the possibility of an "activation lip",[15] i.e., there are vibrational levels beyond the dissociation limit as determined from the chemical estimate of the dissociation energy.[16] Thus the Birge-Sponer extrapolation, plotting the spectroscopic data of Loomis and co-workers[13,14] predicts a dissociation energy of 0.76 ± 0.02 ev. This is in contrast to the chemical evidence of Lewis,[16] which gives for the ground state the dissociation energy of 5900 ± 100 cm^{-1} = 0.73 ev ± 0.012 ev.

3749-34

APPENDIX C

THE EQUILIBRIUM COMPOSITION OF SODIUM VAPOR

Consider the vapor phase reaction:

$$Na + Na = Na_2$$

The equilibrium constant for this reaction is

$$K_p = \frac{p_2}{p_1^{\,2}} = \frac{p_t\, x_2}{(p_t\, x_1)^2} = \frac{x_2}{(x_1)^2\, p_t} \qquad \ldots(C\text{-}1)$$

where p_1 and p_2 are partial pressures, and x_1 and x_2 are mol fractions of Na and Na_2 respectively. p_t is the total pressure.

Now for every mole of monatomic sodium vapor originally present, let

y = moles of Na vapor that associated
n_1 = moles of Na vapor at equilibrium
n_2 = moles of Na_2 vapor at equilibrium
n_t = total moles at equilibrium.

Then we have at equilibrium

$$n_1 = 1 - y$$
$$n_2 = {}^{y}/_{2}$$
$$n_t = n_1 + n_2 = 1 - {}^{y}/_{2}$$

Hence

$$n_t = \frac{1 + n_1}{2} \qquad \ldots(C\text{-}2)$$

$$x_1 = \frac{n_1}{n_t} = \frac{2\, n_1}{1 + n_1} \qquad \ldots(C\text{-}3)$$

$$x_2 = \frac{n_2}{n_t} = \frac{1 - n_1}{1 + n_1} \qquad \ldots(C\text{-}4)$$

3749.35

Thus Eq. (C-1) can be rewritten as

$$K_p = \frac{1 - (n_1)^2}{4\,(n_1)^2\,p_t} \qquad \text{...(C-5)}$$

From a knowledge of the value of K_p at any temperature as calculated from Eq. (31), we may determine the equilibrium composition of sodium vapor at any temperature T and pressure p_t by solving simultaneously Eqs. (C-5), (C-3), and (C-4).

The molecular weight W of a mixture of monatomic and diatomic sodium vapor, in which the mole fractions are x_1 and x_2 respectively, may be obtained from the relationship:

$$W = M_1\,x_1 + M_2\,x_2 \qquad \text{...(C-6)}$$

where M_1 and M_2 are the molecular weights of the monatomic and of the diatomic molecule respectively.

3749-36

REFERENCES

1. Inatomi, T. H., and W. C. Parrish, "Thermodynamic Diagrams for Sodium", NAA-SR-62, July 13, 1950.
2. Mayer, J. E., and M. G. Mayer, Statistical Mechanics, John Wiley and Sons, Inc., New York, 1948, pp 164-166.
3. Herzberg, Gerhard, Molecular Spectra and Molecular Structure I. Spectra of Diatomic Molecules, 2nd Ed., D. Van Nostrand Co., Inc., New York, 1950. Table 39 pp 501, 554, 555.
4. Dumond, J. W. M., and E. R. Cohen, A Least-Squares Adjustment of the Atomic Constants as of December, 1950 - A Report to the National Research Council Committee on Constants and Conversion Factors of Physics.
5. Mayer, J. E., and M. G. Mayer, Op. Cit., p. 449
6. Krieger, F. J., A Table of Vibrational Contributions of a Harmonic Oscillator to Thermodynamic Functions, Project Rand Ra-15088, Douglas Aircraft Co., July 1, 1948.
7. Herzberg, G., Op. Cit., p. 480
8. Selected Values of Chemical Thermodynamic Properties, National Bureau of Standards, Series I, Vol. I, Table 92-1, June 30, 1949.
9. Moore, C. E., Atomic Energy Levels, U. S. Department of Commerce, National Bureau of Standards, Vol. I., Circular 467, June 15, 1949, p. 89.
10. Herzberg, G., Op. Cit., p. 106.
11. Mayer, J. E., and M. G. Mayer, Op. Cit., p. 165.
12. Gordon, A. R., "The Free Energies and Vapor Pressure of the Alkali Metals", J. Chem. Physics, 4, 100 - 102 February 1936.
13. Loomis, F. W., Phys. Rev., 38, 2153 (1931).
14. Loomis, F. W., and R. E. Nusbaum, "Magnetic Rotation Spectrum and Heat of Dissociation of the Sodium Molecule", Phys. Rev., 40, 380 (1932).
15. King, G. W., and J. H. VanVleck, "Dipole-Dipole Resonance Forces", Phys. Rev., 55, 1169, June 15, 1939.
16. Lewis, C., Zeits F. Physik, 69, 786 (1931).

3749-37