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Thermodynamic Properties of Alkali-Metal Vapors

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Thermodynamic Properties of Alkali-Metal Vapors

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The thermodynamic properties of metal vapors are of considerable interest to advanced technology. Since these substances are used or are being considered as working fluids in nuclear reactors, magnetohydrodynamic power generators, thermionic devices, ion propulsion systems, and current rectifiers, there is additional practical, as well as theoretical, interest in their relatively high vapor pressure and ease of ionization.

The equation of state and the derived quantities enthalpy, internal energy and heat capacity, as well as transport properties of metal vapors, can be determined once the potential energies of the interactions of atoms and molecules in the vapor are known. As the alkali-metal vapors contain only one valence electron, two atoms in their ground state will interact along one of two possible potential curves, depending whether their electron spins are parallel or anti-parallel. These curves correspond to the lowest $^3\Sigma$ and $^1\Sigma$ states of the diatomic molecule. The potential energy curves of lithium are shown in Fig. 1. It can be seen that the $^3\Sigma$ curve is purely repulsive except, perhaps, at very large distances where the dispersion forces predominate.

In the present state of knowledge of such interactions, calculations which do not take into account the existence of two or more interactions are physically meaningless. Estimations of Lennard-Jones potential parameters from boiling points and densities for calculation of the

properties of the vapor at elevated temperatures, although widely used,^{1,2} have no real physical bases and lead to incorrect results.

Because band spectral data exist and have been analyzed for the alkali metal molecules, the "true" potential energy curves for the $^1\Sigma_g^+$ molecular state can be determined over limited ranges of internuclear separation by means of the Rydberg-Klein-Rees technique.³ The shapes of the curves were obtained by plotting the potentials in reduced coordinates:

$$V^*(r^*) = V(r)/\epsilon, \text{ the reduced potential energy, and}$$

$$r^* = r/r_e, \text{ the reduced internuclear separation}$$

where

V = potential energy

r = internuclear separation

ϵ = depth of potential well

r_e = equilibrium internuclear separation

Comparing these curves to the shapes of empirical potential showed that Lennard-Jones (12-6) potential was inapplicable. The Rydberg potential, in reduced form:

$$V_R^*(r^*) = -[1+b(r^*-1)] \exp \{-b(r^*-1)\}$$

¹ L. B. Robinson, "Thermodynamic and Transport Properties of a Cesium Plasma", Adv. Energy Conv. 3, 19 (1963).

² M. Gottlieb and R. Zollweg, "Thermal Conductivity of Cesium Vapor", Adv. Energy Conv. 3, 37 (1963).

³ J. T. Vanderslice, E. A. Mason, and W. G. Maish, "Ground State of Hydrogen by the Rydberg-Klein-Rees Method", J. Mol. Spectr. 3, 17 (1959); [Erratum: 5, 83 (1963)].

gave the best fit. This was also shown by Varshni⁴ from other considerations. The values of b were calculated from the band spectral constants and no attempt was made to adjust them for a better fit. Comparison of potential shapes in reduced form for sodium is shown in Fig. 2.

Calculations of the second virial coefficient, $B(T)$, in the virial equation of state

$$\frac{P\tilde{V}}{RT} = 1 + B(T)/\tilde{V} + C(T)/\tilde{V}^2 + \dots$$

were made by direct numerical integration from the relationship⁵

$$B(T) = 2\pi N_A \int_0^{\infty} \left\{ 1 - \exp \left[-\frac{V(r)}{kT} \right] \right\} r^2 dr$$

where

N_A = Avagadro's number

T = temperature

k = Boltzmann's constant

by defining the following reduced integrals

$$B^*(b, T^*) = B(T)/2\pi N_A r_e^3 = \int_0^{\infty} \left\{ 1 - \exp \left[-\frac{V^*}{T^*}(r^*) \right] \right\} r^{*2} dr^*$$

where

$$T^* = kT/\epsilon$$

⁴ Y. P. Varshni, "Comparative Study of Potential Energy Functions for Diatomic Molecules", Rev. Mod. Phys. 29, 664 (1957).

⁵ O. Sinanoğlu and K. S. Pitzer, "Equations of State and Thermodynamic Properties of Gases at High Temperatures; 1. Diatomic Molecules", J. Chem. Phys., 31, 960 (1959).

The equilibrium internuclear separation, r_e , was used to give the reduced integral rather than the usual collision diameter since it is experimentally determined and should not be subject to adjustment for best fit.

For the $^1\Sigma$ curves the Rydberg potential was used and the results agreed well with the results of Sinanoglu⁵ with minor differences for lithium. For the $^3\Sigma$ curves a purely repulsive potential was constructed from the Morse potential

$$V_M^*(r^*) = \{\exp[-2c(r^*-1)] - 2 \exp[-c(r^*-1)]\}$$

according to the suggestion of Keyes.⁶ This led to the "antibonding" Morse potential

$$V_{MA}^*(r^*) = \{\exp[-2c(r^*-1)] + 2 \exp[-c(r^*-1)]\}$$

where the constant c was chosen to give the same exponential slope as the Rydberg potential

$$c = b - \log_e 2 \quad .$$

The results of the integrations are represented by B^1 and B^3 for the singlet and triplet respectively. These must be combined according to Sinanoglu⁵ to give

$$B(T) = \frac{1}{4} B^1 + \frac{3}{4} B^3 \quad .$$

Over the range of temperature of interest, B^1 was large, negative and decreasing with increasing temperature and B^3 smaller, positive and decreasing only slowly with temperature. At low temperatures the singlet potential contribution is dominant and

⁶ R. W. Keyes, "Morse Potentials for Excited States of Diatomic Molecules", J. Chem. Phys. 29, 523 (1953).

$$B(T) \approx \frac{1}{4} B^1$$

This shows that even if the Lennard-Jones potential had the correct shape, it would have to be weighted by 1/4 to give the correct results. At some high temperature the contribution from the triplet potential becomes dominant and $B(T)$ changes sign and becomes positive. In the approximation where the second virial coefficient is adequate to give the equation of state, $B(T_B) = 0$ defines the Boyle temperature, T_B . Were it not for the positive contribution of the triplet, the Boyle temperature would be predicted to be extremely high.

The results of these calculations are compared graphically to limited experimental data available. Fig. 3 shows the second virial coefficient plotted against reciprocal temperature for potassium. The contribution from the singlet potential, the total corrected for the contribution of the triplet, and equations fit by Battelle⁷ and the Naval Research Laboratory⁸ to their experimental data are shown.

It can be seen that the agreement is extremely good, considering that no adjustable constants have been used. The NRL equation, based on a wider range of experimental data, shows incorrect curvature at high temperatures which would not yield the Boyle temperature while the Battelle equation predicts the correct curvature and agrees well with theory over an extremely wide temperature range in slope and magnitude.

⁷ A. W. Lemmon, H. W. Deem, E. A. Eldridge, E. H. Hall, J. Matolich, and J. F. Walling, "Engineering Properties of Potassium", NASA-CR-54017 (BATT-4673-Final) (December 31, 1963).

⁸ C. T. Ewing, J. P. Stone, J. R. Spann, E. W. Steinkuller, D. D. Williams, and R. R. Miller, "High Temperature Properties of Sodium and Potassium, 12th Progress Report, July 1-September 30, 1963", NRL Report 6094 (June 9, 1964).

In Figure 4 the theoretical results for sodium are compared with an equation based on NRL data.⁹ The agreement is excellent but again the curvature of the NRL equation is incorrect at high temperatures. A comparison was also made with recent results for cesium from NRL¹⁰ and shown in Fig. 5 and the agreement is satisfactory. Since no corrections were made in these calculations for diatomic and higher polymeric species or ions, it is believed that these might reduce some of the discrepancies.

As the true potential is known over a limited range of internuclear separations near the minimum of the potential curve, and since this portion of the curve makes the greatest contribution to the integrals used in the virial coefficient, these calculations are being repeated to determine the effect of the empirical potential fit to the results. Calculations are in progress for the third virial coefficient and the thermodynamic properties will be calculated and tabulated for the alkali-metal vapors when these are completed.

To determine the effect of diatomic species in the vapor the potential energy curves for the $M-M_2$ and M_2-M_2 interactions, where M is the metal atom, will be synthesized using the technique of Amdur.¹¹ Since the fraction of dimers in the vapor, which can be estimated from the second virial coefficient, is small, the errors produced in these estimations will be diminished.

⁹ J. P. Stone, C. T. Ewing, J. R. Spann, E. W. Steinkuller, D. D. Williams, and R. R. Miller, "High Temperature Properties of Sodium, Potassium, and Cesium, 14th Progress Report, January 1-March 31, 1964", NRL Report 6128 (June 4, 1964).

¹⁰ C. T. Ewing, Naval Research Laboratory (private communication).

¹¹ I. Amdur, E. A. Mason and J. E. Jordan, "Scattering of High Velocity Neutral Particles. X. He- N_2 ; A- N_2 . the N_2-N_2 Interaction", J. Chem. Phys. 27, 527 (1957).

FIGURE CAPTIONS

- Figure 1 Potential Energy Curve for Lithium
- Figure 2 Reduced Potential Energy Curve for Sodium
- Figure 3 Second Virial Coefficient of Potassium vs Reciprocal Temperature
- Figure 4 Second Virial Coefficient of Sodium vs Reciprocal Temperature
- Figure 5 Second Virial Coefficient of Cesium vs Reciprocal Temperature

POTENTIAL ENERGY CURVES FOR Li_2

FIG. 1

FIG. 2

FIG. 3

FIG. 4

FIG. 5