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# THERMOCHEMISTRY OF CESIUM-OXYGEN SOLUTIONS AND THEIR GASEOUS ATMOSPHERES, ESTIMATED FROM A PHASE DIAGRAM

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16. Abstract

The composition of vapor above Cs-$Cs_2O$ solutions was computed from a phase diagram using an analytical method devised for binary metallic solutions. While the results should be of interest in the testing of thermionic diodes with partially oxygenated cesium reservoirs, the analytical method may also be useful in extracting thermodynamic information from other phase diagrams in which solutions and compounds are in contact.

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# CONTENTS

# THERMOCHEMISTRY OF CESIUM-OXYGEN SOLUTIONS AND THEIR GASEOUS ATMOSPHERES, ESTIMATED FROM A PHASE DIAGRAM

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## SUMMARY

A phase diagram for the cesium-oxygen system was employed, together with an analytical method for determining thermal properties of binary metallic solutions, to find chemical potentials of solutions of cesium and dicesium oxide. The composition of the vapor above such solutions was then computed for a range of temperature and solution compositions. The results should be of interest to experimenters seeking to improve the performance of thermionic diodes by using partially oxygenated cesium reservoirs.

The analytical method may be useful in obtaining thermodynamic information from other condensed phase diagrams in which solutions and solid compounds are in equilibrium.

## INTRODUCTION

The alkali metals have achieved roles of considerable importance in space power production. They have been used as working fluids in heat engines, as heat transfer media in liquid metal loops and heat pipes. An annoying problem in all of these applications has been the presence of oxygen as a contaminant in the liquid alkali metal. Among the deleterious effects attributed to this dissolved oxygen is the enhanced attack of containment structures by the liquid metal (ref. 1).

In contrast to these adverse effects of oxygen in liquid metals, a useful application has been proposed for partially oxygenated cesium in a power-producing thermonic device. A single reservoir containing a cesium-oxygen liquid solution is provided for the diode. The cesium vapor serves in its usual capacity to neutralize the space charge in the interelectrode space and to lower surface work function. Oxygen from the reservoir, arriving at the electrode surfaces, is believed to increase the binding energy of the cesium to the metal surface, resulting in lowered interelectrode gas pressure and improved diode electrical performance.

Arrival rates of gaseous cesium and oxygen at the emitter and collector must be adjusted to obtain optimum performance. Suitable concentrations of oxygen in liquid cesium must be found which will provide the desired gaseous arrival rates. The diode operator would like an estimate of these concentrations in order to prepare the mixture for evaluation in a diode. Moreover, he would like to avoid exposing the diode to corrosive concentrations of oxygen.

An experimental determination of the relation between the gas phase and liquid phase compositions in the Cs-O system at various temperatures could be a difficult undertaking. For this reason it seems desirable to estimate analytically the relation between gas phase and liquid phase compositions in the Cs-O system, the task undertaken in this report.

The method herein differs drastically from an earlier analysis of the Cs-O system (ref. 2) using the same phase diagram. Reference 2, representing a preliminary analysis of the system, employed a portion of the phase diagram not used in the present study. The data were fitted to an expression for solution chemical potential of entirely different, and less general, form than the one employed herein.

The analytical method herein was adapted from a procedure recently devised (ref. 3) for obtaining thermodynamic properties of binary metallic solutions from phase diagrams. In reference 3 only those situations were considered in which both the liquid and solid phases were solutions. On the other hand, the present report treats a system in which the solid phases are of compounds of discrete composition. Available thermodynamic data for cesium and dicesium oxide ($Cs_2O$) were used, together with a phase diagram for the Cs-$Cs_2O$ system and expressions for solution chemical potentials, to obtain the thermodynamic properties of Cs and $Cs_2O$ in solution. From this information the relation between the gas and liquid phase compositions was computed. The vapor phase compositions at given reservoir concentrations and temperatures herein are therefore expected to be more representative of the actual physical situation than those obtained in reference 2.

Although the present report deals only with the condensed Cs-$Cs_2O$ system, the general concept should have wider applicability. If suitable solid-liquid phase diagrams were available for the other liquid alkali metals used in space power applications, it should be possible in principle to determine the chemical potential of the oxygen or oxide in the liquid solution over a range of composition and temperature.

## ANALYSIS AND DISCUSSION

### Phase Diagram and Chemical Potential Expressions

Figure 1 is a phase diagram adapted from reference 4. The solution region contains only a solution of $Cs_2O$ in Cs. In region A crystalline Cs is in equilibrium with Cs-$Cs_2O$ solutions. In regions B and C, crystalline $Cs_7O$ is in equilibrium with Cs-$Cs_2O$ solutions. Crystalline $Cs_4O$ is in equilibrium with Cs-$Cs_2O$ solutions in region D, while crystalline $Cs_7O_2$ is in equilibrium with Cs-$Cs_2O$ solutions in region E. In region F, crystalline $Cs_3O$ is in equilibrium with Cs-$Cs_2O$ solutions. In the partially depicted region G, crystalline $Cs_2O$ is in equilibrium with Cs-$Cs_2O$ solutions.

The entire boundary between the single-phase solution region and the two-phase regions could be used to obtain coordinate information for use in this analysis. However, only the coordinates of the points marked a to f, listed in table I, have been used as data. These points mark the limits of appearance or disappearance of a phase or a compound, and are therefore more likely to have been determined accurately by the original investigator (ref. 5). For example, at point a, crystalline Cs and $Cs_7O$ are in equilibrium with Cs-$Cs_2O$ solution of composition $x$, where $x$ denotes mole fraction of $Cs_2O$ at point a. Departure in any direction from point a causes the disappearance of a phase.

Except for point b, the points a to f involve equilibrium between two crystalline solids and Cs-$Cs_2O$ solution. At such points, the equilibrium can be shown to be equivalent to two equilibria, each of which is between one of the two solids and the solution.

The following equilibria then pertain to points a to f (where s and c denote solution and crystalline states, respectively):

Point a

$$Cs(s) \rightleftharpoons Cs(c) \tag{1}$$

$$5Cs(s) + Cs_2O(s) \rightleftharpoons Cs_7O(c) \tag{2}$$

Point b

$$5Cs(s) + Cs_2O(s) \rightleftharpoons Cs_7O(c) \tag{3}$$

Point c

$$5Cs(s) + Cs_2O(s) \rightleftharpoons Cs_7O(c) \tag{4}$$

$$2Cs(s) + Cs_2O(s) \rightleftharpoons Cs_4O(c) \tag{5}$$

Point d

$$2Cs(s) + Cs_2O(s) \rightleftharpoons Cs_4O(c) \tag{6}$$

$$3Cs(s) + 2Cs_2O(s) \rightleftharpoons Cs_7O_2(c) \tag{7}$$

Point e

$$3Cs(s) + 2Cs_2O(s) \rightleftharpoons Cs_7O_2(c) \tag{8}$$

$$Cs(s) + Cs_2O(s) \rightleftharpoons Cs_3O(c) \tag{9}$$

Point f

$$Cs(s) + Cs_2O(s) \rightleftharpoons Cs_3O(c) \tag{10}$$

$$Cs_2O(s) \rightleftharpoons Cs_2O(c) \tag{11}$$

Equilibria between solid substances and the $Cs$-$Cs_2O$ solution at points a to f can be written in the general form

$$(a - 2b)Cs(s) + bCs_2O(s) \rightleftharpoons Cs_aO_b(c) \tag{12}$$

The condition for equilibrium between the solution and the crystal is then

$$(a - 2b)\mu_{Cs(s)} + b\mu_{Cs_2O(s)} = \left(F_T^o\right)_{Cs_aO_b(c)} \tag{13}$$

where $\mu_{Cs(s)}$ and $\mu_{Cs_2O(s)}$ are the chemical potentials of Cs(s) and $Cs_2O(s)$, respectively, in a solution having the temperature $T$ and composition $x$ of the diagram point in question. Also, $\left(F_T^o\right)_{Cs_aO_b(c)}$ is the standard state free energy of the solid substance $Cs_aO_b(c)$.

Expressions for the chemical potentials of the components Cs and $Cs_2O$ of the solution were taken from reference 3. The method of reference 3 consists of writing a double Taylor series in mole fraction and $T$ for the first derivative of the chemical potential of one of the solution species with respect to mole fraction. Choosing $Cs_2O$ for the Taylor series gives

$$x\left(\frac{\partial \mu_{Cs_2O}}{\partial x}\right)_{T,P} = \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \beta_{mn}(T - T_c)^m (x - x_c)^n \tag{14}$$

where $\beta_{mn}$ are constants to be determined, and $T_c$ and $x_c$ are phase diagram coordinates about which the Taylor series is expanded, where $P$ denotes pressure.

Equation (14) upon integration between the composition of pure $Cs_2O$, $x = 1$, and $x$ gives

$$\mu_{Cs_2O(s)} = \mu_{Cs_2O(l)} + \left[\sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \beta_{mn}(T - T_c)^m (-x_c)^n\right] \ln x + \sum_{n=1}^{\infty} \sum_{m=0}^{\infty} \beta_{mn}(T - T_c)^m \left[\sum_{q=0}^{n-1} \frac{(-x_c)^q}{n - q} \binom{n}{q} \left(x^{n-q} - 1\right)\right] \tag{15}$$

Here, $\mu_{Cs_2O(l)}$ is the chemical potential of pure liquid $Cs_2O$ at the temperature and pressure in question, and

$$\binom{n}{q} = \frac{n!}{(n - q)!\,q!}$$

is a binomial coefficient.

The chemical potential of the remaining solution species, in this case Cs, is then determined from that for $Cs_2O$ by combining the Gibbs-Duhem equation (ref. 6), that is,

$$y\left(\frac{\partial \mu_{Cs}}{\partial y}\right)_{T,P} = x\left(\frac{\partial \mu_{Cs_2O}}{\partial x}\right)_{T,P} \tag{16}$$

with equation (14) and integrating between $y = 1$ and $y$, the mole fraction of Cs, with the following result:

$$\mu_{Cs(s)} = \mu_{Cs(l)} + \left[\sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \beta_{mn}(T - T_c)^m y_c^n\right] \ln y$$

$$+ \sum_{n=1}^{\infty} \sum_{m=0}^{\infty} \beta_{mn}(T - T_c)^m \left[\sum_{q=0}^{n-1} \frac{(-y_c)^q}{n - q}\binom{n}{q}\left(y^{n-q} - 1\right)\right] \tag{17}$$

In reference 3 the coefficients of the $\ln x$ and $\ln y$ terms were forced to satisfy the Raoult Law conditions, requiring that

$$\mu_{Cs_2O(s)} - \mu_{Cs_2O(l)} \rightarrow RT \ln x \tag{18}$$

when $x \rightarrow 1$, and

$$\mu_{Cs(s)} - \mu_{Cs(l)} \rightarrow RT \ln y \tag{19}$$

when $y \rightarrow 1$ where R is the universal gas constant.

Recent data on the suppression of the cesium freezing point by traces of oxygen (ref. 7) show that the Raoult Law limit of equation (18) for $Cs_2O$ must be modified slightly (see appendix A). The following modification of the Raoult Law limit is adopted for $Cs$-$Cs_2O$ solution:

$$\mu_{Cs_2O(s)} - \mu_{Cs_2O(l)} \rightarrow (RT - 64)\ln x \tag{20}$$

as $x \rightarrow 1$. For the present case equation (19) is assumed to remain applicable for the cesium species.

If equations (15) and (17) are to be consistent with the limiting forms of equations (19) and (20), the following equations must hold:

for Cs,

$$\sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \beta_{mn}(T - T_c)^m y_c^n = RT \tag{21}$$

and for $Cs_2O$,

$$\sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \beta_{mn}(T - T_c)^m(-x_c)^n = RT - 64 \qquad (22)$$

Expanding the left side of equations (21) and (22) by the binomial theorem and equating the coefficients of like powers of $T$ yield for $q = 0$

$$\sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \beta_{mn} y_c^n \binom{m}{0} (-T_c)^m = 0 \qquad (23)$$

$$\sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \beta_{mn} (-x_c)^n \binom{m}{0} (-T_c)^m = -64 \qquad (24)$$

for $q = 1$,

$$\sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \beta_{mn} y_c^n \binom{m}{1} (-T_c)^{m-1} = R \qquad (25)$$

$$\sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \beta_{mn} (-x_c)^n \binom{m}{1} (-T_c)^{m-1} = R \qquad (26)$$

for $q > 1$ with $q \leq m$,

$$\sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \beta_{mn} y_c^n \binom{m}{q} (-T_c)^{m-q} = 0 \qquad (27)$$

$$\sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \beta_{mn} (-x_c)^n \binom{m}{q} (-T_c)^{m-q} = 0 \qquad (28)$$

## Determination of the Unknown Coefficients

Substitution of equations (15) and (17) into equation (13) using the coordinates of phase diagram points a to f gives 11 linear equations which can be used to evaluate unknown parameters. The relations

$$\left(\Delta F_T^o\right)_{Cs_2O(c,\,l)} = \mu_{Cs_2O(l)} - \mu_{Cs_2O(c)}$$

and

$$\left(\Delta F_T^o\right)_{Cs(c,\,l)} = \mu_{Cs(l)} - \mu_{Cs(c)}$$

can be used to write these expressions in the following form:

$$\left(\Delta F_T^o\right)_{f,\,Cs_aO_b(c)} = (a - 2b)\left[\left(\Delta F_T^o\right)_{Cs(c,\,l)} + g_{Cs}(y, T)\right] + b\left[\left(\Delta F_T^o\right)_{Cs_2O(c,\,l)} + g_{Cs_2O}(x, T)\right] \qquad (29)$$

where

$$g_{Cs}(y, T) = \left[\sum_{n=0}^{N}\sum_{m=0}^{M} \beta_{mn}(T - T_c)^m y_c^n\right]\ln y + \sum_{n=1}^{N}\sum_{m=0}^{M} (-1)^n \beta_{mn}(T - T_c)^m\left[\sum_{q=0}^{n-1} \frac{(-y_c)^q}{n - q}\binom{n}{q}(y^{n-q} - 1)\right]$$

$$g_{Cs_2O} = \left[\sum_{n=0}^{N}\sum_{m=0}^{M} \beta_{mn}(T - T_c)^m(-x_c)^n\right]\ln x + \sum_{n=1}^{N}\sum_{m=0}^{M} \beta_{mn}(T - T_c)^m\left[\sum_{q=0}^{n-1} \frac{(-x_c)^q}{n - q}\binom{n}{q}(x^{n-q} - 1)\right]$$

Here $\left(\Delta F_T^o\right)_{f,\,Cs_aO_b(c)}$ is the free energy of formation of crystalline $Cs_aO_b$ at temperature T from $Cs_2O$ in its standard state (crystal below 763 K) and Cs (crystal below 301.8 K), for the reaction of equation (12). The free energies of fusion of Cs and $Cs_2O$, $\left(\Delta F_T^o\right)_{Cs(c,l)}$ and $\left(\Delta F_T^o\right)_{Cs_2O(c,l)}$, respectively, are nonzero for temperatures T representing supercooling below the melting points of the pure materials. Above the melting point the term does not appear. The method of estimating $\left(\Delta F_T^o\right)_{Cs(c,l)}$ and $\left(\Delta F_T^o\right)_{Cs_2O(c,l)}$ is discussed in appendix B.

The data points in figure 1 are used to evaluate the unknown coefficients $\beta_{mn}$. In the present case, however, the $\left(\Delta F_T^o\right)_{f,Cs_aO_b(c)}$ represent unknowns for $Cs_7O$ at three temperatures, and $Cs_4O$, $Cs_7O_2$, and $Cs_3O$ each at two temperatures. The number of $\beta_{mn}$ which can be evaluated depends upon the number D of available chemical potential expressions such as equation (1) to (11), the number P' of unknown $\left(\Delta F_T^o\right)_f$, and the value M at which the series are truncated in m, since equations (23) to (28) constitute an additional set of 2M + 2 available expressions. If M is specified, then the highest degree in n is

$$N = \frac{D + 2M + 2 - P'}{M + 1} - 1 = \frac{D - P'}{M + 1} + 1 \tag{30}$$

In general, for a fixed number of chemical potential equations, N thus computed will be noninteger. Since both n and m must be integers, such a noninteger N computed from equation (30) merely indicates that the array of $\beta_{mn}$ cannot have a full $(M + 1) \times (N + 1)$ terms. For example, $D = 11$ for the phase diagram points a to f, and $P' = 4$ since there are four unknown compounds. Let $M = 2$. By equation (30), $N = 3\frac{1}{3}$, which indicates that two terms are to be dropped. In addition to $\beta_{MN}$, either $\beta_{M,N-1}$ or $\beta_{M-1,N}$ can be eliminated. In this report the latter course was taken; terms were dropped from the M row. The consequence of dropping terms from the N column was not examined.

Since thermal properties of $Cs_7O(c)$, $Cs_4O(c)$, $Cs_7O_2(c)$, and $Cs_3O(c)$ have not been published, a total of nine unknown $\left(\Delta F_T^o\right)_f$ are represented by the 11 data points in figure 1. A reasonable number of $\beta_{mn}$ must be determined if the power series fit of the phase diagram data is to be of any value. Therefore, the number of unknown $\left(\Delta F_T^o\right)_f$ was reduced by following this sequence of computations:

(1) An initial computation was made in which $\left(\Delta F_{443}^o\right)_{f,Cs_3O(c)}$ and $\left(\Delta F_{323}^o\right)_{f,Cs_3O(c)}$ were treated as unknown. The $\left(\Delta F_T^o\right)_f$ for $Cs_7O(c)$, $Cs_4O(c)$, and $Cs_7O_2(c)$ were ex-

panded as functions of T about the point 298 K by the relation

$$\left(\Delta F^{\circ}_{T}\right)_{f} = \Delta F^{\circ}_{298\ f} - \int_{298}^{T} \left(\Delta S^{\circ}_{T}\right)_{f} (dT) \tag{31}$$

where $\left(\Delta S^{\circ}_{T}\right)_{f} = -\left[\partial\left(\Delta F^{\circ}_{T}\right)_{f}\Big/\partial T\right]_{P}$. The entropy of formation $\left(\Delta S^{\circ}_{T}\right)_{f}$ was estimated roughly for the initial computation. In this manner the number of unknown $\left(\Delta F^{\circ}_{T}\right)_{f}$'s was reduced to five. The potentially large error in extrapolating $\left(\Delta F^{\circ}_{T}\right)_{f, Cs_3O(c)}$ by equation (31) over nearly 150° C was avoided by solving for $\left(\Delta F^{\circ}_{T}\right)_{f, Cs_3O(c)}$ at two temperatures. Computation (1) yielded a number of $\beta_{mn}$, together with $\left(\Delta F^{\circ}_{443}\right)_{f, Cs_3O(c)}$, $\left(\Delta F^{\circ}_{323}\right)_{f, Cs_3O(c)}$, $\left(\Delta F^{\circ}_{298}\right)_{f, Cs_7O(c)}$, $\left(\Delta F^{\circ}_{298}\right)_{f, Cs_4O(c)}$, and $\left(\Delta F^{\circ}_{298}\right)_{f, Cs_7O_2(c)}$ listed in table II as ratios $\Delta F^{\circ}_{T}/R$.

(2) The $\left(\Delta F^{\circ}_{443}\right)_{f, Cs_3O}$ and $\left(\Delta F^{\circ}_{323}\right)_{f, Cs_3O}$ found in computation (1) were treated as knowns. A number of unknown $\beta_{mn}$ were determined, together with $\left(\Delta F^{\circ}_{323}\right)_{f, Cs_7O_2}$, $\left(\Delta F^{\circ}_{283}\right)_{f, Cs_7O_2}$, $\left(\Delta F^{\circ}_{298}\right)_{f, Cs_4O}$, and $\left(\Delta F^{\circ}_{298}\right)_{f, Cs_7O}$, listed in table II as $\Delta F^{\circ}_{T}/R$.

(3) The $\left(\Delta F^{\circ}_{443}\right)_{f, Cs_3O(c)}$, $\left(\Delta F^{\circ}_{323}\right)_{f, Cs_3O(c)}$, $\left(\Delta F^{\circ}_{323}\right)_{f, Cs_7O_2(c)}$, and $\left(\Delta F^{\circ}_{283}\right)_{f, Cs_7O_2(c)}$ from computations (1) and (2) were treated as known. Then several $\beta_{mn}$, along with the $\left(\Delta F^{\circ}_{283}\right)_{f, Cs_4O(c)}$, $\left(\Delta F^{\circ}_{265}\right)_{f, Cs_4O(c)}$, $\left(\Delta F^{\circ}_{265}\right)_{f, Cs_7O(c)}$, $\left(\Delta F^{\circ}_{271}\right)_{f, Cs_7O(c)}$ and $\left(\Delta F^{\circ}_{276}\right)_{f, Cs_7O(c)}$ were computed (table II).

(4) The latter $\left(\Delta F^{\circ}_{f}\right)$ for $Cs_4O(c)$ and $Cs_7O(c)$ were regarded as known. Then $\left(\Delta F^{\circ}_{443}\right)_{f, Cs_3O(c)}$, $\left(\Delta F^{\circ}_{323}\right)_{f, Cs_3O(c)}$, $\left(\Delta F^{\circ}_{323}\right)_{f, Cs_7O_2(c)}$, and $\left(\Delta F^{\circ}_{283}\right)_{f, Cs_7O_2(c)}$ were redetermined (table II), essentially verifying the values found in computations (1) and (2).

In computations (1) to (4), M was set to 1, 2, and 3 with N adjusted accordingly. The case M = 0 (no temperature dependence of chemical potentials in solution) is shown in appendix C to be incapable of satisfying thermodynamic requirements.

While appreciable change occurred in $\left(\Delta F^{\circ}_{T}\right)_{f}$ between M = 1 and M = 2, negligible change often occurred between M = 2 and M = 3. At each computation, values of $\left(\Delta F^{\circ}_{T}\right)_{f}$

determined for $M = 2$ were accepted for use in the next computation, however. The double precision computer solution for the coefficients $\left(\Delta F_T^o\right)_f$ and $\beta_{mn}$ gave warning of possible loss of significance for $M = 3$. For this reason, results for only $M = 2$ were used in the succession of computations (1) to (4).

In the sequence of computations (1) to (4), $x_c$ was set to zero and $y_c$ to 1. The choice $x_c = 0.5$, $y_c = 0.5$ gave no difference in results. The effect of varying $T_c$ was not studied; in all cases, the choice $T_c = 0$ was made.

In addition to the $\left(\Delta F_T^o\right)_f$ determined in computations (1) to (4), table II lists the number, if any, of $\beta_{mn}$ required to be dropped from the $(M + 1) \times (N + 1)$ array.

## Composition of Vapor Above Cs-Cs$_2$O Solution

The $\beta_{mn}$ found in computation (4) were entered in equations (15) and (17), and the chemical potentials of $Cs_2O(s)$ and $Cs(s)$ were determined for a range of temperatures and pressures of interest in thermionic diode experimentation. The partial pressures, $p_{Cs}$, of Cs and $p_{Cs_2O}$, of $Cs_2O$, in the atmosphere above the solution were then computed, assuming ideal behavior in the gas phase, from the following relations:

$$RT \ln p_{Cs_2O} = \mu_{Cs_2O(s)} - \mu_{Cs_2O(g)} \tag{32}$$

$$RT \ln p_{Cs} = \mu_{Cs(s)} - \mu_{Cs(g)} \tag{33}$$

The ratio, r, of cesium to oxygen atom concentration in the gas phase given by

$$r = \frac{p_{Cs} + 2p_{Cs_2O}}{p_{Cs_2O}} \tag{36}$$

was then computed.

Figure 2 presents plots of $\log_{10} r$ and $\log_{10} p_{Cs}$ for a range of temperatures and reservoir compositions where $p_{Cs}$ is in torr. The thermochemical data for $Cs_2O(g)$ and $Cs(g)$ were from references 8 and 9, respectively. The sources of the other thermochemical data required are discussed in appendix B.

As an example, an iteration using figure 2 for a condition of 1 torr cesium pressure and a cesium-oxygen ratio, r, of $10^6$ yields $T \approx 565$ K and $x_{Cs_2O} \approx 0.30$. If the

$x_{Cs_2O}$ is converted back to equivalent atomic oxygen by the expression $x_0 = x_{Cs_2O}/(1 + x_{Cs_2O})$, $x_0 \approx 0.19$. The flatness of the curves of $\log_{10}p_{Cs}$ up to quite high reservoir oxygen concentration assures that for ordinary diode operation the cesium reservoir temperature required for a given cesium pressure will not be changed greatly over cesium-only operation. In the foregoing computations the presence in the gas phase of CsO, $Cs_2O_2$, and $Cs_2$ was not considered. These molecules have been observed in mass spectrographic studies (ref. 10). However, sample calculations suggest that they are relatively unimportant in the temperature and composition range of this study.

### Effect of Uncertainties in Thermochemical Data on Computed Vapor Composition

The results in figure 2 can be expected to be quite sensitive to thermal data used for the computations. Probably the least well defined set of data are the thermodynamic properties of $Cs_2O(g)$. Recent determinations of the heat of atomization of $Cs_2O(g)$ by the same team of investigators using two methods yielded values of 117±9 kilocalories per mole (ref. 11) and 131±3 kilocalories per mole (ref. 10). The published tabulations used to compute the data in figure 2 were based upon the former value, 117 kilocalories per mole.

In the preparation of reference 2, thermochemical data, based upon the 131-kilocalorie-per-mole value, were computed for $Cs_2O(g)$. When these data are used to calculate vapor composition, the results of figure 3 are obtained. Comparison of figures 2 and 3 shows the dependency of the r on the two sets of assumed thermochemical data. For example, at 400 K, r from figure 3 is nearly five orders of magnitude smaller than that from figure 2, while at 700 K the difference is only about a decade. For a cesium-oxygen ratio of $10^6$ at 1-torr cesium pressure, figure 3 gives $T \approx 550$ K and $x \approx 0.02$.

## CONCLUDING REMARKS

This report presents the results of computations of vapor phase compositions above reservoirs containing solutions of cesium and dicesium oxide. Cesium vapor pressure and the ratio of cesium to oxygen atom concentration in the vapor phase were computed over a range of temperatures and solution compositions. The results are intended to serve as a guide in the performance testing of thermionic diodes connected to reservoirs containing partially oxygenated cesium.

Some unavoidable uncertainties exist in the numerical values computed herein. First, the thermal properties reported for $Cs_2O(c)$, $Cs_2O(l)$, and particularly $Cs_2O(g)$ are not yet well substantiated. Also, the computations necessitated a lengthy extrapolation of the free energy of $Cs_2O(l)$ into the supercooled region. Moreover, the rapidity of convergence of the Taylor series fitted to the phase diagram is not known.

The computations herein, limited to the cesium-oxygen system, serve to illustrate a method of extracting thermodynamic information from phase diagrams involving contact of liquid solutions with one or more solid compounds of definite composition. The method is an adaptation of a procedure for obtaining solution thermodynamic properties from binary phase diagrams in which both liquid and solid phases are solutions. The present procedure or some variation of it may prove useful for investigating the thermodynamic properties of other systems in which compounds of fixed composition are present as a solid phase.

Lewis Research Center,
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# APPENDIX A

## MODIFICATION OF THE RAOULT LAW LIMIT FOR $Cs$-$Cs_2O$ SOLUTION FROM $Cs$ FREEZING POINT SUPPRESSION

The Raoult Law limit which equation (15) would normally be expected to satisfy, namely,

$$\mu_{Cs_2O(s)} - \mu_{Cs_2O(l)} \rightarrow RT \ln x \tag{18}$$

must be modified because of recent experimental data. In reference 7 determinations of the suppression of the freezing points of cesium and rubidium by oxygen were reported. The freezing point for Cs decreased linearly with increasing oxygen to concentrations exceeding 500 ppm oxygen by weight. The slope of the line of freezing point against concentration, converted to the present basis of mole fraction $Cs_2O$ in $Cs$-$Cs_2O$ solution, was

$$\left(\frac{\partial T}{\partial x}\right)_P = -311\ K$$

Along the boundary between the solution region and region A in figure 1, the chemical potentials of Cs(s) and Cs(c) must be equal. Thus, equations (1) and (13) yield

$$\left(F_T^o\right)_{Cs(c)} = \mu_{Cs(s)} \tag{A1}$$

The total derivative of equation (A1) along this boundary at fixed P is

$$\left[\frac{\left(\partial F_T^o\right)_{Cs(c)}}{\partial x}\right]_P = \left[\frac{\partial \mu_{Cs(s)}}{\partial T}\right]_{x,P} \left(\frac{\partial T}{\partial x}\right)_P + \left[\frac{\partial \mu_{Cs(s)}}{\partial x}\right]_{T,P} \tag{A2}$$

Since $\left(F_T^o\right)_{Cs(c)}$ is a function of T only, the left side of equation (A2) yields

$$\left[\frac{\left(\partial F_T^o\right)_{Cs(c)}}{\partial x}\right]_P = \left[\frac{\left(\partial F_T^o\right)_{Cs(c)}}{\partial T}\right]_P \left(\frac{\partial T}{\partial x}\right)_P = -\left(S_T^o\right)_{Cs(c)}\left(\frac{\partial T}{\partial x}\right)_P \tag{A3}$$

By equations (14) and (16) for $x \rightarrow 0$, $y \rightarrow 1$

$$\left[\frac{\partial \mu_{Cs(s)}}{\partial x}\right]_{T,P} = -\sum_{n=0}^{\infty}\sum_{m=0}^{\infty} \beta_{mn}(T - T_c)^m(-x_c)^n \tag{A4}$$

By equation (17), for $x \rightarrow 0$

$$\left[\frac{\partial \mu_{Cs(s)}}{\partial T}\right]_{x,P} = \left[\frac{\partial \mu_{Cs(l)}}{\partial T}\right]_{T,P} = -\left(S_T^o\right)_{Cs(l)}\left(\frac{\partial T}{\partial x}\right)_P \tag{A5}$$

Combining equations (A2) to (A5) for the condition along the boundary between the solution region and region A, where $T \rightarrow 301.8$ K, the melting point of pure cesium, and $x \rightarrow 0$, $y \rightarrow 1$, gives

$$\sum_{n=0}^{\infty}\sum_{m=0}^{\infty} \beta_{mn}(T - T_c)^m(-x_c)^n = -\left(\frac{\partial T}{\partial x}\right)_P \left[\left(S_T^o\right)_{Cs(l)} - \left(S_T^o\right)_{Cs(c)}\right]_{\substack{x \rightarrow 0 \\ T \rightarrow 301.8\ K}} \tag{A6}$$

Assume a linear temperature dependence such that, for $x \rightarrow 0$ and $T \geq 301.8$ K,

$$\sum_{n=0}^{\infty}\sum_{m=0}^{\infty} \beta_{mn}(T - T_c)^m(-x_c)^n = C + RT \tag{A7}$$

where $C$ is a constant to be determined. Thus, equation (18) for $Cs_2O$ should be modified by the addition of constant $C$.

By combining equations (A6) and (A7) for $T = 301.8$ K with $(\partial T/\partial x)_P = -311$ K, and the entropy of melting for Cs from reference 9, the value for $C$ turns out to be -64.

# APPENDIX B

## SOURCES OF THERMAL DATA

The thermodynamic properties of $Cs_2O(c)$ were taken from reference 12. The properties of $Cs(c)$ and of $Cs(l)$ above the melting point were from reference 9.

The free energy of $Cs_2O(l)$ below the melting point was estimated as follows: Reference 12 gives an algebraic expression for the free energy of formation of $Cs_2O(l)$ above the melting point. The constant pressure specific heat difference

$$\Delta C_p = \left(C_p\right)_{Cs_2O(l)} - 2\left(C_p\right)_{Cs(l)} - \frac{1}{2}\left(C_p\right)_{O_2(g)} \tag{B1}$$

deduced from reference 12 was 4.00 calories per mole. Using this value, a specific heat for $Cs(l)$ of 7.4550 calories per (mole)(K) from reference 9 and for $O_2(g)$ of 7.9974 calories per (mole)(K) from reference 13, the specific heat of $Cs_2O(l)$ at the melting point was estimated as 22.9 calories per (mole)(K). Using data from references 9, 12, and 13, the free energy and entropy of $Cs_2O(l)$ at the melting point were determined. The common assumption was made that the constant pressure specific heat of liquids are constant with temperature (ref. 14). Use of the specific heat estimated for the melting point enabled the free energy of $Cs_2O(l)$ to be extrapolated below the melting point.

In similar fashion the free energy of $Cs(l)$ below its normal melting point was estimated.

# APPENDIX C

## THE REQUIREMENT FOR $M > 0$

Equation (29) for the present purposes can be written in the form

$$\left(\Delta F_T^o\right)_{Cs_aO_b(c)} - (a - 2b)\left(\Delta F_T^o\right)_{Cs(c, l)} - b\left(\Delta F_T^o\right)_{Cs_2O(c, l)} - (a - 2b)(C_{Cs} + RT)\ln y$$

$$- b\left(C_{Cs_2O} + RT\right)\ln x = (a - 2b)f_{Cs}(y, T) + bf_{Cs_2O}(x, T) \qquad \text{(C1)}$$

where

$$f_{Cs}(y, T) = \sum_{n=1}^{N} \sum_{m=0}^{M} (-1)^n \beta_{mn}(T - T_c)^m \left[\sum_{q=0}^{n-1} \frac{(-y_c)^q}{n - q} \binom{n}{q}(y^{n-q} - 1)\right]$$

$$f_{Cs_2O}(x, T) = \sum_{n=1}^{N} \sum_{m=0}^{M} \beta_{mn}(T - T_c)^m \left[\sum_{q=0}^{n-1} \frac{(-x_c)^q}{n - q} \binom{n}{q}(x^{n-q} - 1)\right]$$

Here $C_{Cs}$ and $C_{Cs_2O}$ are constants by means of which the customary Raoult Law limits can be modified if required, as demonstrated for $Cs_2O$ in appendix A. In the present case $C_{Cs_2O}$ has been chosen zero. Equation (C1) applies along phase diagram lines separating the solution region of figure 1 and some other region A to F where the solution contacts $Cs_aO_b(c)$.

If a derivative of equation (C1) is taken along such a bounding line, recalling that the $F_T^o$ are functions of temperature only, the result is

$$
-\left[\left(\Delta S_T^o\right)_{\mathrm{Cs}_a\mathrm{O}_b(c)} - (a - 2b)\left(\Delta S_T^o\right)_{\mathrm{Cs}(c,l)} - b\left(\Delta S_T^o\right)_{\mathrm{Cs}_2\mathrm{O}(c,l)}\right]\left(\frac{\partial T}{\partial x}\right)_P
$$

$$
-(a - 2b)\left[R\left(\frac{\partial T}{\partial x}\right)_P \ln y - \left(C_{\mathrm{Cs}} + RT\right)\frac{1}{y}\right] - b\left[R\left(\frac{\partial T}{\partial x}\right)_P \ln x + \left(C_{\mathrm{Cs}_2\mathrm{O}} + RT\right)\frac{1}{x}\right]
$$

$$
= (a - 2b)\left[-\left(\frac{\partial f_{\mathrm{Cs}}}{\partial y}\right)_T + \left(\frac{\partial f_{\mathrm{Cs}}}{\partial T}\right)_y \left(\frac{\partial T}{\partial x}\right)_P + b\left(\frac{\partial f_{\mathrm{Cs}_2\mathrm{O}}}{\partial x}\right)_T + \left(\frac{\partial f_{\mathrm{Cs}_2\mathrm{O}}}{\partial T}\right)_x \left(\frac{\partial T}{\partial x}\right)_P\right] \qquad \text{(C2)}
$$

If $M = 0$, the entire right side of equation (C2), containing terms in $f_{\mathrm{Cs}}$ and $f_{\mathrm{Cs}_2\mathrm{O}}$, is temperature independent. The $\Delta S_T^o$ on the left side of (C2) are temperature dependent, while $(\partial T/\partial x)_P$ is determined by the local geometry of the phase diagram. When $M = 0$, equation (C2) can be satisfied only at isolated points along the phase diagram lines, if at all.

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## TABLE I. - COORDINATES OF POINTS a TO f IN FIGURE 1

| Point | Temperature, T | | Mole fraction $Cs_2O$ in solution, $x_{Cs_2O}$ |
|---|---|---|---|
| | $^oC$ | K | |
| a | -2 | 271.15 | 0.11275 |
| b | 3 | 276.15 | .16667 |
| c | -8 | 265.15 | .24405 |
| d | 10 | 283.15 | .27160 |
| e | 50 | 323.15 | .31699 |
| f | 170 | 443.15 | .50000 |

## TABLE II. - FORMATION FREE-ENERGY RATIOS, $\Delta F^o_T/R$, FOR $Cs_3O$, $Cs_7O_2$, $Cs_4O$, AND $Cs_7O$ FROM PHASE DIAGRAM COORDINATES OF FIGURE 1

| Species | Temperature, K | Computation | | | |
|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 |
| | | Formation free energy ratio, $\Delta F^o_T/R$, K | | | |
| $Cs_3O$ | 443 | -541 | ----- | ---- | -564 |
| | 323 | -526 | ----- | ---- | -526 |
| $Cs_7O_2$ | 323 | ----- | -1213 | ---- | -1214 |
| | 283 | ----- | -1259 | ---- | -1259 |
| | 298 | -1307 | ----- | ---- | ----- |
| $Cs_4O$ | 283 | ----- | ----- | -677 | ----- |
| | 265 | ----- | ----- | -660 | ----- |
| | 298 | -700 | -699 | ---- | ----- |
| $Cs_7O$ | 265 | ----- | ----- | -819 | ----- |
| | 271 | ----- | ----- | -825 | ----- |
| | 276 | ----- | ----- | -830 | ----- |
| | 298 | -847 | -846 | ---- | ----- |
| Number of $\beta_{mn}$ dropped | | 0 | 2 | 0 | 2 |

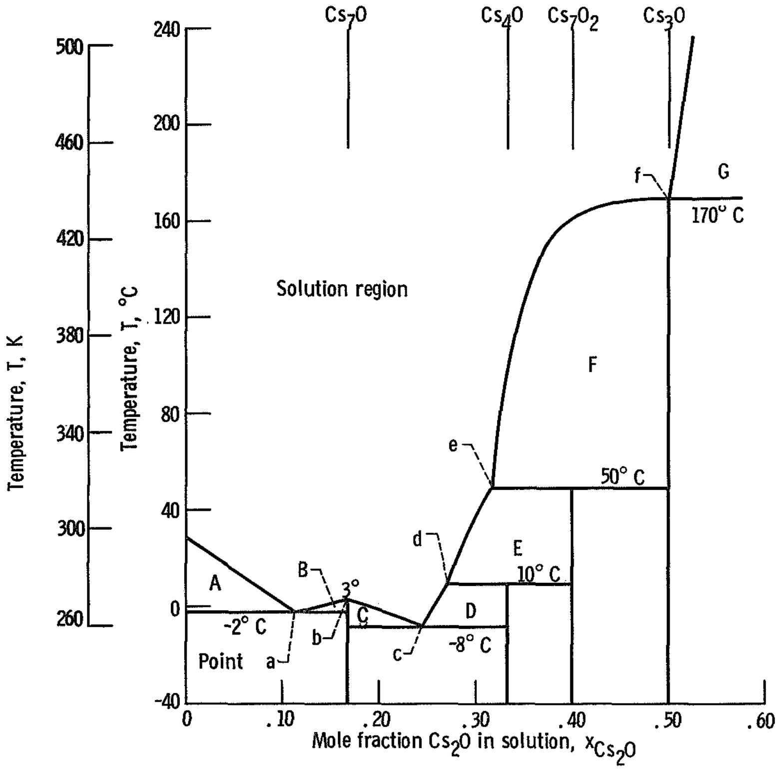

Figure 1. - Phase diagram adapted from reference 4.

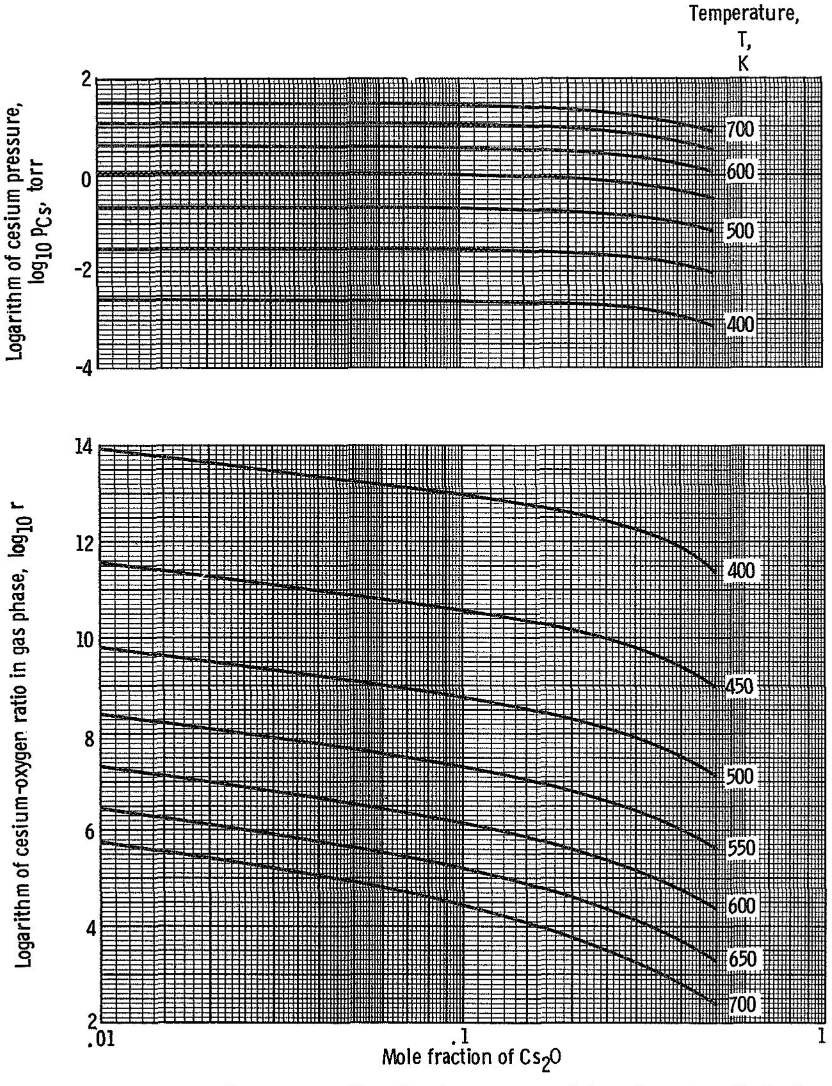

Figure 2. - Cesium-oxygen ratio and cesium pressure of atmosphere above Cs-$Cs_2O$ solution over a range of composition and temperature. Computations based on 117-kilocalorie-per-mole atomization energy for $Cs_2O(g)$ from reference 11.

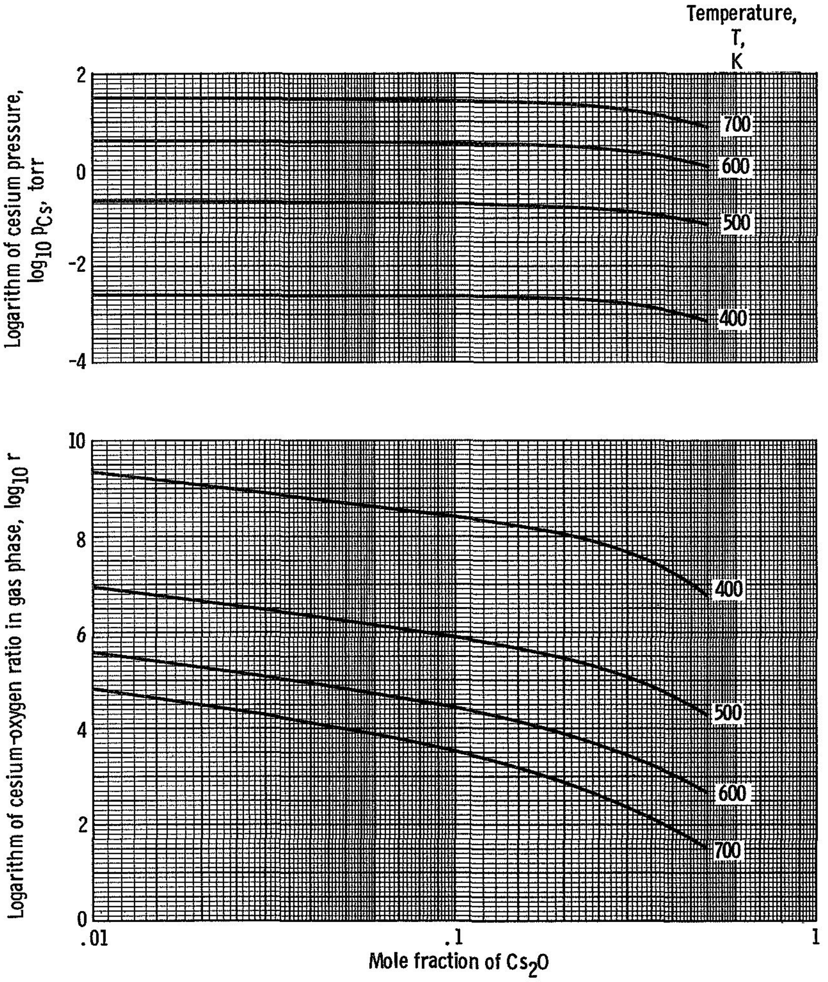

Figure 3. - Cesium-oxygen ratio and cesium pressure of atmosphere above $Cs$-$Cs_2O$ solution over a range of composition and temperature. Computations based upon 131 kilocalorie-per-mole atomization energy for $Cs_2O(g)$ from reference 10.

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