Technical Memorandum

SCTM 256-60(14)

VAPOR PRESSURES OF THE RARE EARTHS

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VAPOR PRESSURES OF THE RARE EARTHS

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ABSTRACT

This report presents the vapor pressures versus temperature data graphically for the rare earth elements, yttrium and scandium.

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The purpose of this memorandum is to present vapor pressure versus temperature data graphically for the rare earths and certain elements with similar properties. This sort of information is of interest to those who plan to use these materials at high temperatures and/or high vacua. Vapor pressure data on the more common elements is portrayed in References 1 and 2.

Until a few years ago the thermodynamic properties of the rare earths were unknown, and therefore the vapor pressure curves for these materials could not be developed. Recently, however, with the increased availability of these elements in pure form, more information necessary to deduce vapor pressures has become available.

The vapor pressure curves (Figure 1) for europium, gadolinium, lanthanum, lutecium, niobium, scandium, samarium, ytterbium, and yttrium are plotted directly from the pressure equilibrium constant data as given in Reference 3. Some of the values of properties used in developing the equilibrium constants were estimated from the best available sources. Those elements whose curves are plotted from such data are so noted by an asterisk on Figure 1. A circled x signifies the melting point of the element.

The remainder of the rare earths' vapor pressures were calculated using data that were presented as best estimates in Reference 3. This information has no estimated errors, but considering that the known properties of the rare earths are fairly closely grouped, it would be strange if the properties of the remaining rare earths were very much different from the estimated values.

The method for calculating vapor pressures used is outlined by Joos, Reference 4. One starts by using the Clapyerm-Clausius equation

$$\frac{dp}{dT} = \frac{L_{(T)}}{T(V_v - V_c)} \qquad (1)$$

where p is pressure,
T is Absolute Temperature,
$L_{(T)}$ is the heat of transformation from the condensed phase to the vapor phase
and V_v-V_c are the molar volumes of the vapor and condensed phases respectively.

As temperatures of interest are not near the critical point $V_v - V_c \approx V_v$.

At low pressures, the vapor acts nearly like a perfect gas, and thus Equation 1 becomes

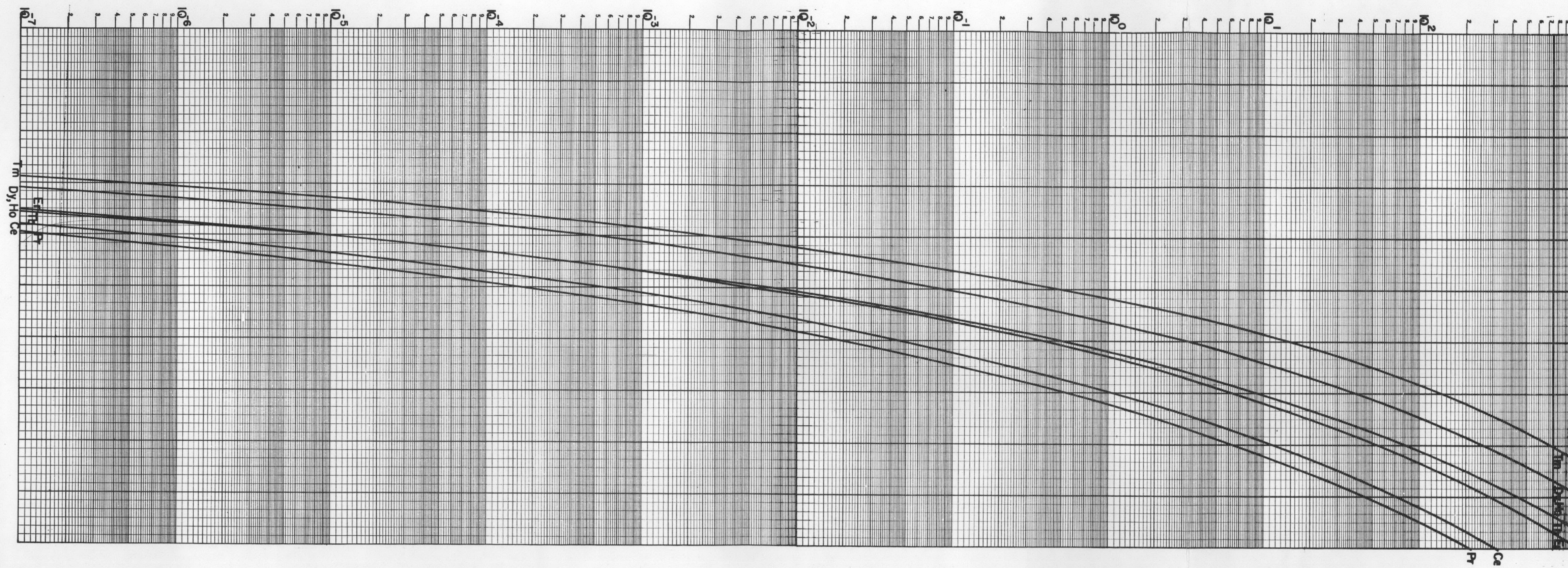

Figure 1.

$$\frac{dp}{dT} = \frac{L_{(T)}}{\frac{RT^2}{P}} \quad . \tag{2}$$

$L_{(T)}$ is a function of temperature, and thus its variation must be taken into consideration upon integrating. If we imagine first that the material of interest is to be vaporized at T and then the vapor heated to T_B, the heat required is

$$Q = C_p^V(T_B-T) + L_T \quad .$$

C_p^V is the specific heat at constant pressure for the vapor.

Another way of accomplishing this same physical change is to heat the condensed phase to T_B before allowing it to vaporize.

$$Q = C_p^S(T_m-T) + L_m + C_p^L(T_B-T_m) + L_B$$

C_p^S is the solid specific heat

L_m is the latent heat of fusion occurring at T_m the melting temperature

C_p^L is the liquid specific heat

L_B is the vaporization latent heat at the boiling point T_B.

The energy required is the same in both cases, and thus

$$L_{(T)} = C_p^S(T_m-T) + L_m + C_p^L(T_B-T_m) + L_B - C_p^V(T_{B-T}) \quad . \tag{3}$$

$$\text{Then } \ln p = \frac{1}{R}\int\left[C_p^S(T_m-T) + L_m + C_p^L(T_B-T_m) + L_B = C_p^V(T_B-T)\right]\frac{dT}{T^2} \tag{4}$$

It should be noted that phase transition latent heats as well as the functional dependence of the C_p on T must be used in calculations of this type for highest accuracies. It was felt that such a high degree of accuracy was unwarranted when using the presently available data.

When $T > T_m$ equation 4 reduces to

$$\log_{10}P_{mm} = \frac{1}{4.571}\left[-\frac{L_B+(C_p^L-C_p^V)T_B}{T} - (C_p^L-C_p^V)\log_{10}T\right] + C_1 \quad . \tag{5}$$

When $T < T_m$

$$\log_{10} P_{mm} = \frac{1}{4.571}\left[\frac{-L_B - C_p^L(T_B - T_m) - L_m - C_p^s T_m + C_p^v T_B}{T} - (C_p^s - C_p^v)\log_{10} T\right] + C_2 \quad (6)$$

The constant C_1 is found at the boiling point where p = 760 mm. C_2 is evaluated at the melting point through pressure continuity considerations.

The data used to prepare Figure 2 is presented in Table I. This method has been checked against some elements where accurate data was presented and was found to be good to about 1-10 percent. The solid specific heats in general show the largest variations, and a value which was averaged over the solid temperature range of interest was used.

Table I

Element	T_m °K	L_m cal/gm mol	T_B °K	L_B cal/gm mol	C_p^s *	C_p^L * cal/gm mol	C_p^v *
Ce	1077	2200*	3200	75,000	--	8.00	6.00
Dy	1773	4100*	2600	60,000	8.25	8.00	6.00
Er	1800	4100*	2900*	70,000*	8.25	8.00*	7.00
Ho	estimated*	to be*	nearly the*	same as*	dysprosium*	*	*
Pr	1208	2400*	3290	79,500	--	8.00	6.00
Tb	1700*	3900*	2800*	70,000	8.5	8.00	6.00
Tm	1400*	4400*	2400*	51,000*	8.00	8.00	5.20

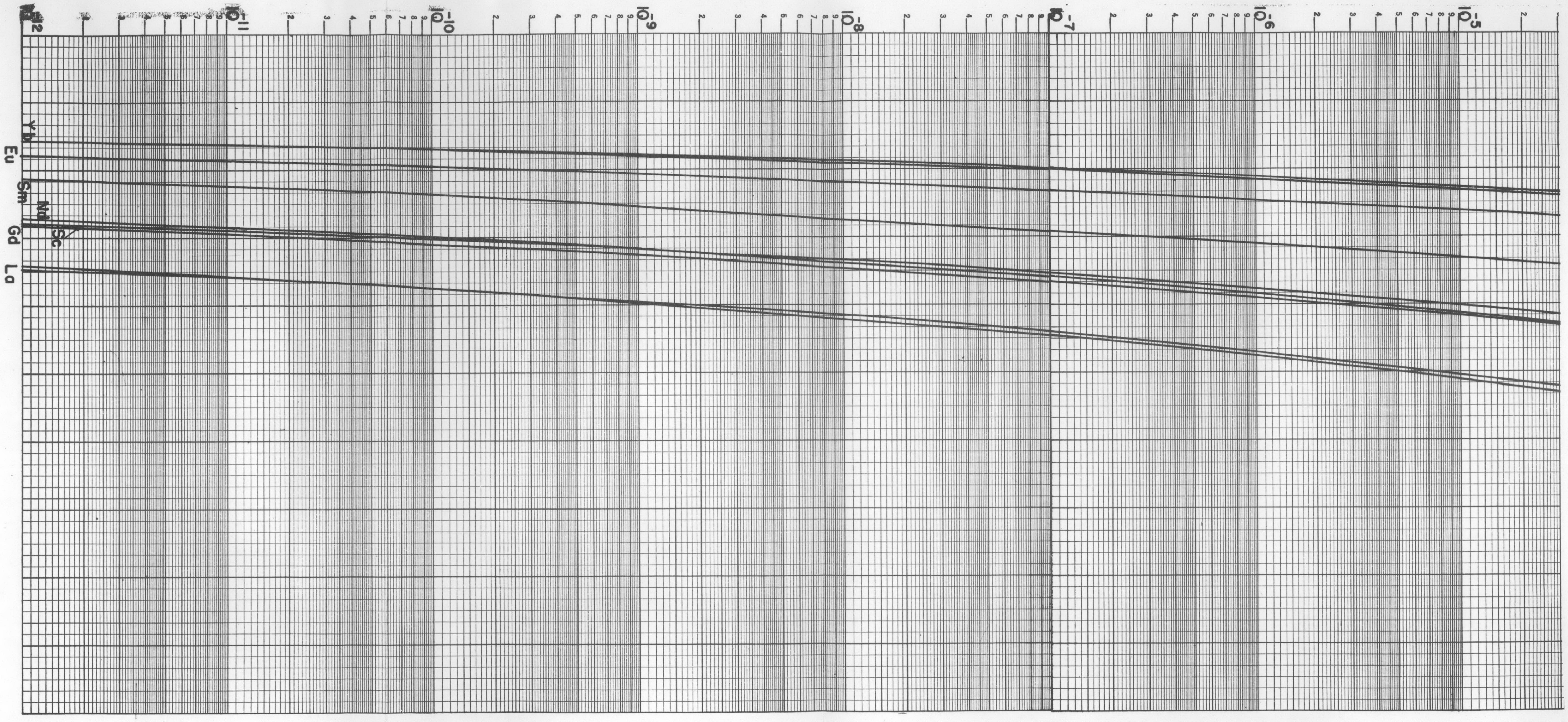

Figure 2.

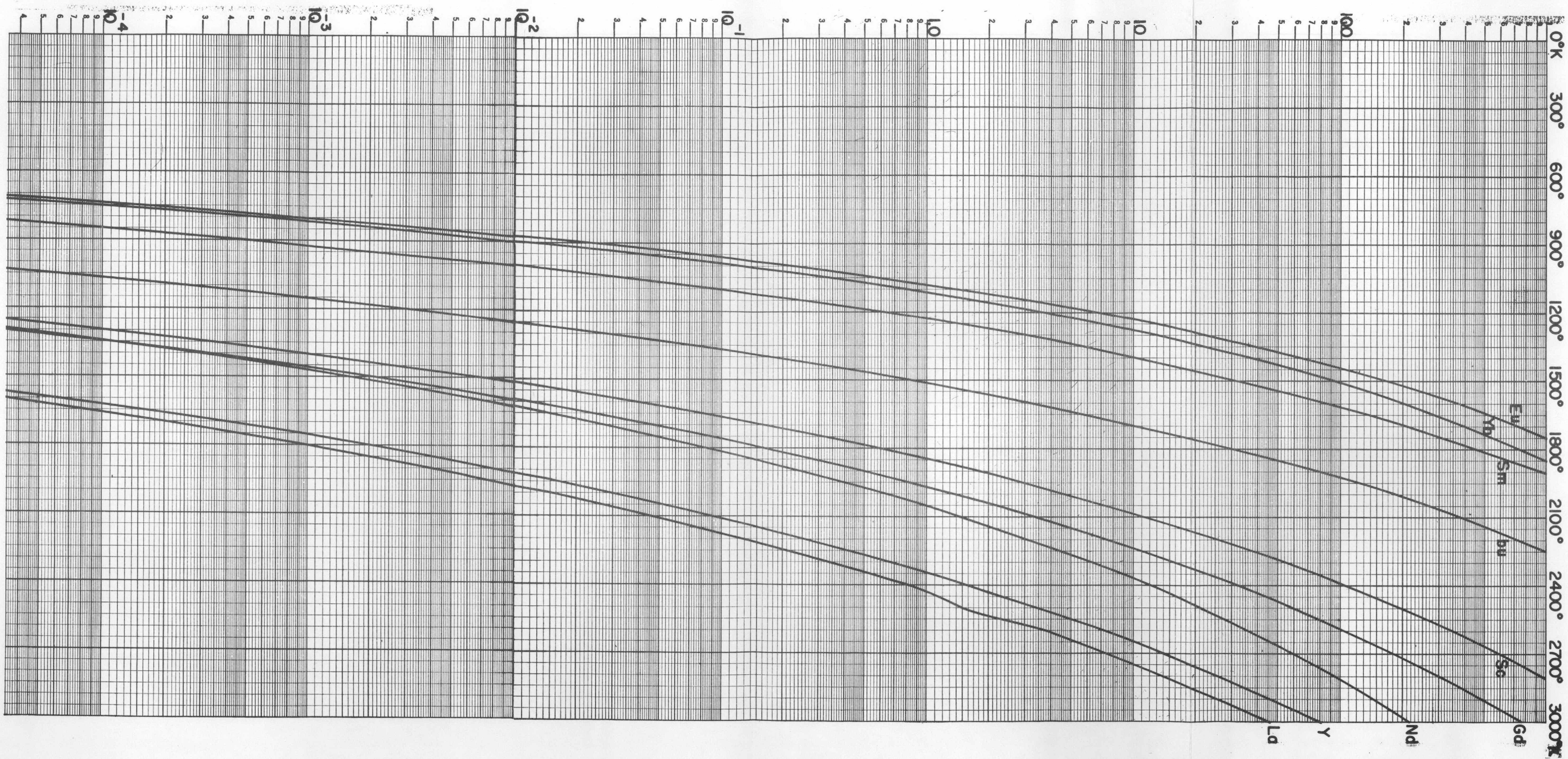

Figure 2 (Cont.).

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2. Vapor Pressure Curves for the More Common Elements, Sheet A and Sheet B, prepared by Richard E. Honig. Published by Radio Corporation of America.

3. Thermodynamic Properties of the Elements, D. R. Stull and G. C. Sinke, American Chemical Society.

4. Theoretical Physics, Georg Joos, Hafner Publishing Company.

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