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A NEW FORMULA FOR CALCULATING
THE CHANGE IN TEMPERATURE OF
FUSION OF ALKALI AS WELL AS NOBLE METALS AT
PRESSURES UP TO 40 KB

BY

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A New Formula for Calculating the Change in
Temperature of Fusion of Alkali
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ABSTRACT

Kraut and Kennedy (1966) have proposed a new melting law at high pressures wherein the melting temperature in degree centigrade at a given pressure is a linear function of the room-temperature compression $\Delta V/V_0$ at the same pressure. The proportionality constants in their equations are determined empirically. In this present endeavor it is shown that the increase in melting temperature ΔT_m^P at a given pressure is a linear function of the product of the room-temperature compression $\Delta V/V_0$ at the same pressure and the absolute melting temperature at ordinary pressure. The proportionality constants in the present case have been calculated from simple thermodynamic considerations. The agreement between the calculated and the experimental values of these constants is quite good. The proposed law is given by

$$\Delta T_m^P = (\Delta V_f \Omega / \chi \Delta H_f) (\Delta V/V_0)_P ,$$

where ΔV_f , ΔH_f and Ω are volume change on fusion, latent heat of fusion and molar volume respectively at ordinary pressure and χ is the average room-temperature compressibility.

I. INTRODUCTION

Kraut and Kennedy (1966) have proposed an empirical melting law at high pressures. It is shown by them that ~~that~~ the melting temperature in degree centigrade at a given pressure is a linear function of the room-temperature compression $\Delta V/V_0$ at the same pressure. Their result is reproduced in fig. 1. It must be noted that although their finding is indeed very interesting and quite useful in extrapolating experimental data, the very empirical nature of the law does not permit any predictions in the absence of both high-temperature and high-pressure data. The loss of generality of their law stems from the rather unfortunate choice of centigrade rather than the absolute thermodynamic temperature scale. It is the purpose of this article to show that if Kraut and Kennedy's (1966) law is reformulated in terms of absolute temperature then a general law of melting at high pressures can be obtained which does not contain any empirical constant.

II. METHOD

If the absolute melting temperature at a given high pressure is written as T_m^P and the melting temperature at ordinary room-pressure as T_m^0 , then

$$\Delta T_m^P = (T_m^P - T_m^0) \dots\dots\dots (1)$$

where ΔT_m^P is the increase in melting temperature at a pressure P (higher than room-pressure). Let the room-temperature compression at a pressure P be $(\Delta V/V_0)_P$. By plotting ΔT_m^P versus $(\Delta V/V_0)_P$, a straight line of the form

$$\Delta T_m^P = c T_m^0 (\Delta V/V_0)_P \dots\dots\dots (2)$$

is obtained for different values of pressure P . Using Bridgman's (1948) room-temperature compression data and Newton, Jayaraman and Kennedy's (1962) melting point data for alkali metals we plot ΔT_m^P versus $T_m^P (\Delta V/V_0)_P$ as shown in fig. 2. From fig. 2 we have

$$\Delta T_m^P(\text{Li}) = 0.55 T_m^0 (\Delta V/V_0)_P \dots\dots\dots (3)$$

$$\Delta T_m^P(\text{Na}) = 1.66 T_m^0 (\Delta V/V_0)_P \dots\dots\dots (4)$$

$$\Delta T_m^P(\text{K}) = 1.60 T_m^0 (\Delta V/V_0)_P \dots\dots\dots (5)$$

$$\Delta T_m^P(\text{Rb}) = 1.75 T_m^0 (\Delta V/V_0)_P \dots\dots\dots (6)$$

Similarly for the noble metals Cu, Ag and Au, we plot ΔT_m^P from the high-temperature data of Cohen, Klement and Kennedy (1966) and $(\Delta V/V_0)_P$ from the room-temperature data of Bridgman (1949) as shown in fig. 2. And for these metals we have (from fig. 2)

$$\Delta T_m^P(\text{Cu}) = 3.96 T_m^0 (\Delta V/V_0)_P \dots\dots\dots (7)$$

$$\Delta T_m^P(\text{Ag}) = 5.26 T_m^0 (\Delta V/V_0)_P \dots\dots\dots (8)$$

$$\Delta T_m^p(\text{Au}) = 8.12 T_m^0 (\Delta V/V_0)_p \dots\dots\dots (9)$$

Now in order to calculate the constant C in eqn.(2) we proceed as follows. From eqn.(2)

$$T_m^p - T_m^0 = C T_m^0 (V_0 - V)/V_0 \dots\dots\dots (10)$$

where $V_0 > V$. Since T_m^0 and V_0 are constants for a given element, differentiating eqn.(10) with respect to pressure P

$$dT_m/dP = (-C T_m^0 / V_0) (dV/dP) \dots\dots\dots (11)$$

We note from fig.2 that eqn.(10) holds for the entire pressure range from zero pressure up to 40 KB or higher, and the slope is continuous throughout. Thus we could choose a pressure P_1 such that $P_1 = (P^0 + \alpha)$ and $\alpha \rightarrow 0$, i.e. a pressure very close to the room-pressure P^0 . Since

$$-1/V_0 (dV/dP) = \chi \dots\dots\dots (12)$$

where χ is the compressibility of the solid, in the first approximation we could substitute the compressibility at 300°K. Thus

$$dT_m/dP = C \chi T_m^0 \dots\dots\dots (13)$$

But from the well known Clapeyron's equation

$$dT_m/dP = T_m^0 (\Delta V_f / \Delta H_f) \dots\dots\dots (14)$$

where ΔV_f and ΔH_f are the volume change and latent heat of fusion respectively at the normal melting point. The volume change on fusion is generally expressed as a fraction

$$\Delta \Omega / \Omega = (\Omega_l - \Omega_s) / \Omega_s \dots\dots\dots (15)$$

where Ω_l and Ω_s are the molar volumes of the liquid and the solid respectively at the melting point. Thus the experimental volume change of fusion must be multiplied by the molar volume of the solid at the melting point. In the first approximation Ω_s at the melting point can be replaced by the room-temperature molar volume Ω . From eqns.(13), (14) and (15)

$$C = \Delta V_f \Omega / \chi \Delta H_f \dots\dots\dots (16)$$

Thus from eqns.(2) and (16) the new melting law at high pressures could be written as

$$\Delta T_m^P = (\Delta V_f \Omega / \chi \Delta H_f) T_m^0 (\Delta V / V_0)_P \dots\dots\dots (17)$$

III. RESULTS AND DISCUSSION

In table 1 the calculated values of C from eqn.(16) are compared with the corresponding values from fig.2. In the case of Li the disagreement between the calculated and the experimental value of the slope is greatest. It must be noted that in table 1, the value of ΔV_f is written within parenthesis indicating that this value is probably less accurate. If for Li the volume change of fusion is taken

as 1.1% instead of 1.6% then an almost exact agreement between the calculated and the experimental values is obtained. Considering the approximations involved and the uncertainties in the values of ΔV_f as pointed out by Kubaschewski (1949) the agreement seems to be quite satisfactory.

IV. ACKNOWLEDGEMENT

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Table 1. Comparison of the experimental and the calculated values of the constant C. Also shown are the selected values of the relevant physical parameters used in this calculation.

Element	Ω cm ³ per gm.atom	χ cm ² /dyne x10 ⁻¹²	ΔV_f %	ΔH_f Cal. per gm.atom	Slope C	
					Experimental	Calculated
Li	13.0 ^a	8.32 ^{c,d}	(1.6) ^f	717 ^g	0.55	0.82
Na	23.7 ^a	13.63 ^{c,d}	2.5 ^f	627 ^g	1.66	1.66
K	45.5 ^a	27.63 ^{c,d}	2.55 ^f	562 ^g	1.60	1.78
Rb	56.2 ^a	36.39 ^{c,d}	2.50 ^f	540 ^g	1.75	1.74
Cu	7.601 ^b #	0.725 ^e	4.60 ^b	3118 ^g	3.96	3.70
Ag	10.969 ^b #	0.965 ^e	5.23 ^b	2730 ^f	5.26	5.11
Au	10.789 ^b #	0.573 ^e	5.56 ^b	3060 ^f	8.12	8.18

Value at the melting point.

() Indicates probably less accurate value.

a. Mott and Jones (1958).

b. Cohen, Klement and Kennedy (1966).

c. Bridgman (1948).

d. Bridgman (1958).

e. Bridgman (1949).

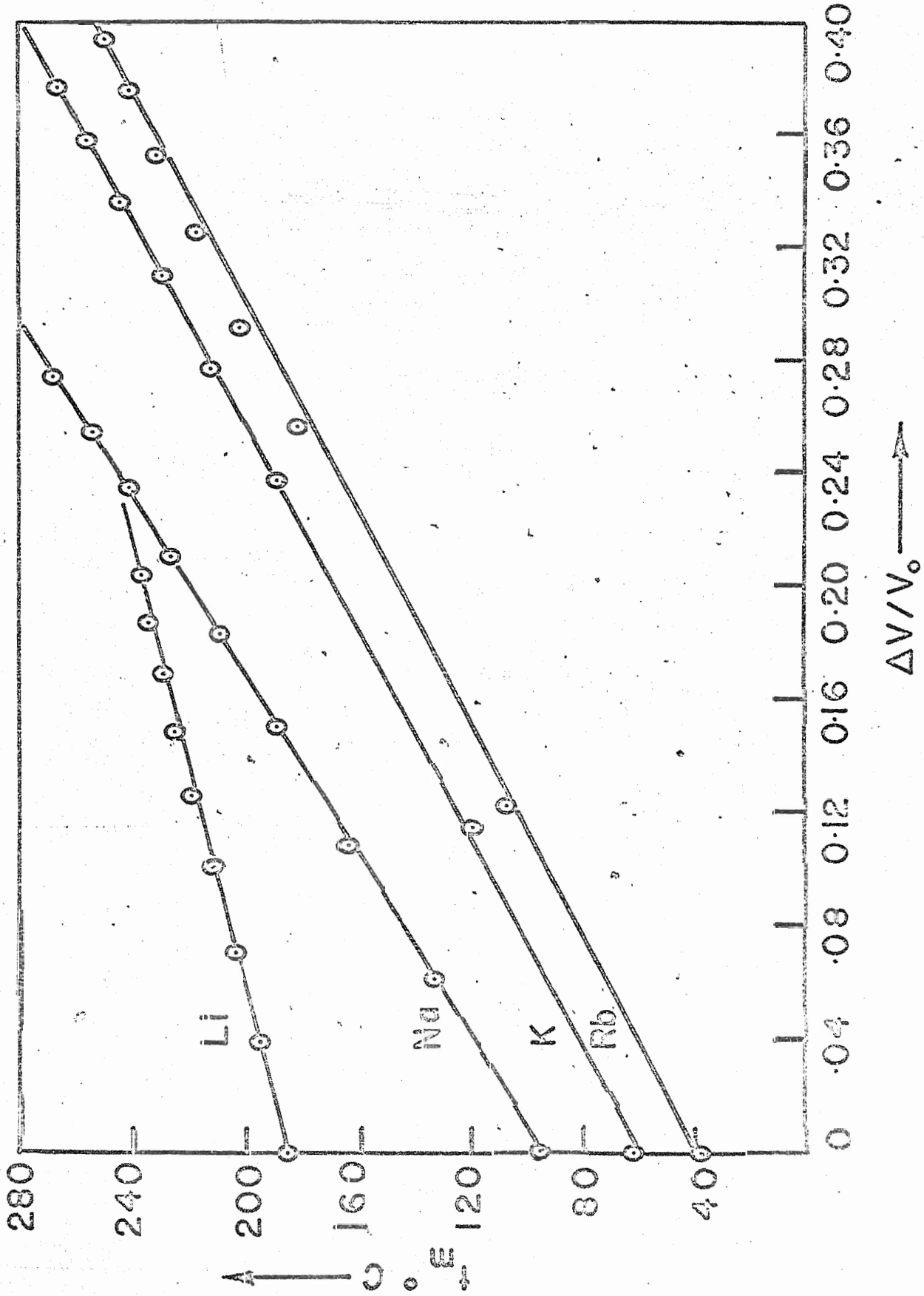
f. Smithells (1955).

g. Hultgren, Orr, Anderson and Kelley (1963).

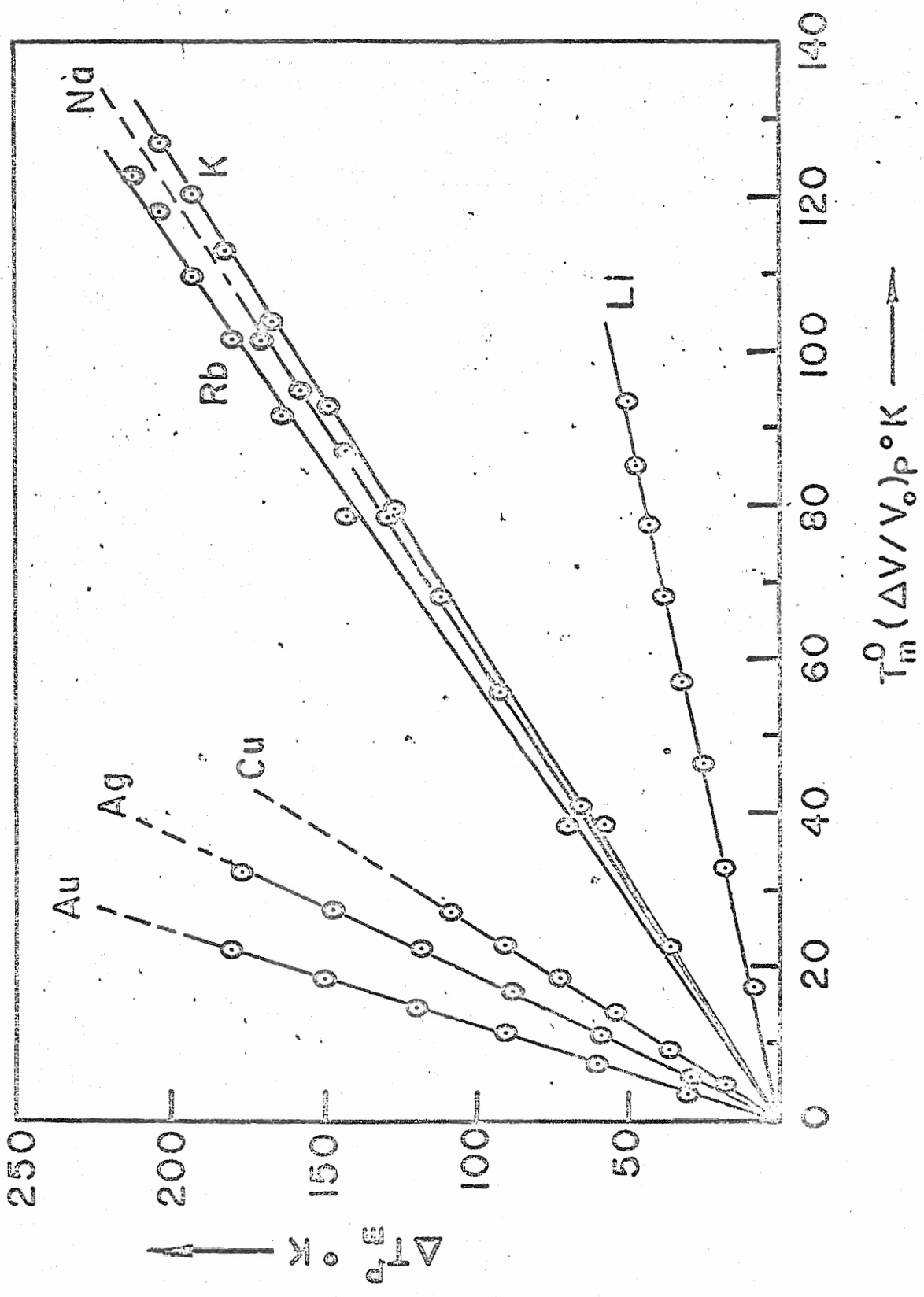
FIGURE CAPTIONS

Fig. 1. Melting temperature in degree centigrade versus isothermal compression at room-temperature in alkali metals. The points on the graph are at 5 KB pressure intervals starting from zero pressure (After Kraut and Kennedy, 1966).

Fig. 2. Change in melting temperature at a pressure P versus the product of the absolute melting temperature at ordinary pressure and the isothermal room-temperature compression at the pressure P . For the alkali metals the pressure range is 0 to 40 KB and for the noble metals 0 to 30 KB. The points on the graph are at 5 KB intervals.



K Mukherjee - fig. 1



v. N. Kiselev, fig. 2