The Mercury Photosensitized Reactions of Ethane

B. deB. Darwent and E. W. R. Steacie

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B. deB. Darwent and E. W. R. Steacie,
Division of Chemistry, National Research Council, Ottawa, Canada
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The effect of pressure on the initial stages of the mercury photosensitized reactions of ethane has been investigated at room temperature. The production of methane increases with decreasing ethane pressure and is inhibited by the presence of molybdenum oxide. It has been shown that hydrogen atoms are produced in the initial stages of the reaction. It is concluded that the initial step is a C—H split and that an active ethane molecule is not formed. The dependence of quantum yields on pressure indicates that the initial step is about 100 percent effective and that inefficiency is caused by recombination of H and C_2H_5 resulting in the formation of ethane at high pressures by deactivation, and in the formation of methyl radicals at lower pressures.

INTRODUCTION

IN a previous report on the mercury photosensitized reactions of propane[1] attention was drawn to some aspects of the mercury photosensitized reactions of the lower paraffin hydrocarbons which could not be explained on the basis of the data available. In particular the much greater $C-C$ splitting with ethane than with propane and the unaccountably low quantum yields of these reactions may be mentioned in this connection. It was also shown that the extent of $C-C$ splitting with propane increased with decreasing propane pressure, but that the extent of the splitting was very much more pronounced with ethane.

It was found that a strict comparison of the reactions of triplet mercury atoms with ethane and with propane could not be obtained from earlier work with ethane[2,3] since the reaction invariably was allowed to proceed to a point at which essentially all the radiation was absorbed by the hydrogen produced. Hence, the reaction investigated was largely that of H rather than $Hg(^3P_1)$ with ethane.

Accordingly the mercury photosensitized reactions of ethane have been re-investigated with particular attention to the purity of the ethane (very small amounts of ethylene interfere seriously) and to the initial stages of the reaction. In view of the recent work by Robb and Melville[4] molybdenum oxide has been used to determine whether H atoms are produced in the initial stages of the process.

EXPERIMENTAL

The reaction was investigated in a circulatory system essentially the same as that used in the investigation of propane.[1] A static system essentially similar to that of Robb and Melville[4] was used in the experiments in which molybdenum oxide was introduced as a detector of H atoms. In these experiments the molybdenum oxide (Eimer and Amend—"Tested Purity Reagent") was supported vertically on a sintered glass disc so that its surface was parallel with and 8 mm from the incident quartz face of the reactor. The progress of the reaction was followed by measuring the pressure of gases that were volatile at $-183°C$ in a McLeod gauge and by visual examination of the oxide layer for change in color from yellow to blue. The color change was apparent even in the very early stages of the reaction.

Analysis of the non-condensible products was accomplished by oxidation of the hydrogen on copper oxide at 220°C. In these experiments liquid nitrogen was used as the cooling agent to minimize contamination of the hydrogen-methane fraction by C_2 hydrocarbons which have a vapor pressure of the order of 10^{-2} mm at $-183°C$. The composition of the condensible

* Contribution No. 1671 from the National Research Council, Ottawa, Canada.
[1] B. deB. Darwent and E. W. R. Steacie, J. Chem. Phys. 13, 563 (1945).
[2] E. W. R. Steacie and N. W. F. Phillips, (a) J. Chem. Phys. 6, 179 (1938); (b) Can. J. Res. B16, 303 (1938).
[3] E. W. R. Steacie and R. L. Cunningham, J. Chem. Phys. 8, 800 (1940).
[4] J. C. Robb and H. W. Melville, Faraday Soc. Symposium on the Labile Molecule, Sept. 1947.

TABLE I. The mercury photosensitized reaction of ethane. Effect of time and pressure on the nature of the products.†

A. Initial Pressure of $C_2H_6 = 50$ mm

Time—Hours	1.0	1.0	2.0	3.5	4.0
H_2—cc N.T.P.	0.041	0.039	0.070	0.129	0.138
CH_4—cc N.T.P.	0.028	—	—	0.110	—

B. Initial Pressure of $C_2H_6 = 100$ mm

Time—Hours	1.0	3.0
H_2—cc N.T.P.	0.069	0.195
CH_4—cc N.T.P.	0.018	0.071

C. Initial Pressure of $C_2H_6 = 200$ mm

Time—Hours	0.5	0.5	1.0	2.0	3.0	8.0	12.0	16.3
H_2—cc N.T.P.	0.057	0.059	0.106	0.229	0.313	0.765	1.01	1.35
CH_4—cc N.T.P.	0.003	—	0.005	—	0.037i	0.103	0.198	0.293

D. Initial Pressure of $C_2H_6 = 470$ mm

Time—Hours	0.5	1.0	3.0
H_2—cc N.T.P.	0.088	0.174	0.421
CH_4—cc N.T.P.	0.001	0.001i	0.002

E. Initial pressure of $C_2H_6 = 640$ mm

Time—Hours	0.5
H_2—cc N.T.P.	0.096
CH_4—cc N.T.P.	3×10^{-4}

† Incident Intensity of $\lambda 2537 = 1.86 \times 10^{-5}$ einstein/hour
Reaction Temp. $= 25 \pm 2°C$.
Partial Press. Hg. $= 1.2 \times 10^{-3}$ mm.
Reaction Vessel—48 mm. diam. $\times$ 60 mm. long
Reaction System—**74** cc.

products from some of the experiments was determined by mass spectrometer analysis.

The purity of the ethane was considered of great importance since ethylene, the most likely impurity, quenches $Hg(^3P_1)$ about 100 times as efficiently as ethane. The ethane used was obtained from the Phillips Petroleum Company ("Research" Grade); it was reputed to contain less than 0.1 percent ethylene, none having been detected by a mass spectrometer analysis. Independent checks on the purity of samples of this ethane were done by infra-red and mass spectrographic analyses.** No ethylene could be detected by either method. It seems certain that the ethane used contained less than 0.1 percent of ethylene.

The lamp used was of the usual mercury-neon type of low pressure arc. The quantum input was determined by measuring the rate of hydrolysis of monochloracetic acid and applying corrections[5] for the rate of the dark reaction.

RESULTS

The effect of time and pressure on the production of hydrogen and methane in the absence of molybdenum oxide is shown in Tables I and II and in Figs. 1, 2, and 3. The rate of production of hydrogen (Fig. 1) is very nearly constant in the early stages and decreases with time; at 200 mm the rate decreases from an initial value of about 0.11 cc per hour to about 0.07 cc per hour in the later stage. It seems certain that the initial rate of hydrogen production decreases markedly with decreasing pressure. The effect
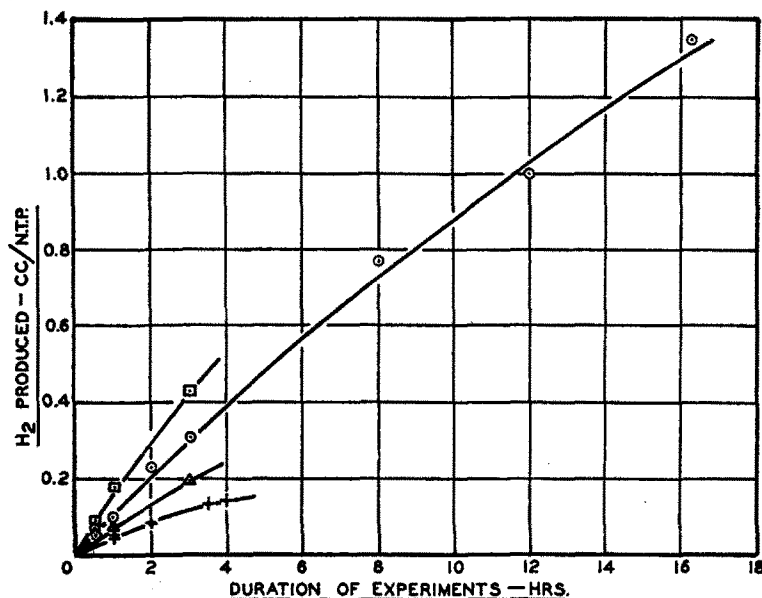

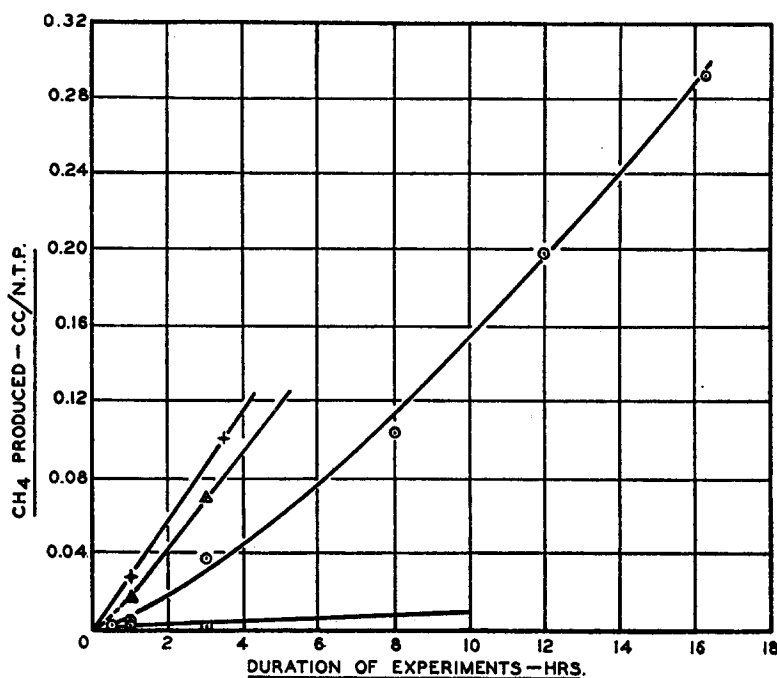FIG. 1. Effect of time and pressure on the production of H_2.
+ Ethane pressure 50 mm
⊙ Ethane pressure 200 mm
△ Ethane pressure 100 mm
⊡ Ethane pressure 470 mm

⁵ R. N. Smith, P. A. Leighton and W. G. Leighton, J. Am. Chem. Soc. 61, 2299 (1939).

FIG. 2. Effect of time and pressure on the production of methane.
+ Ethane pressure 50 mm
⊙ Ethane pressure 200 mm
△ Ethane pressure 100 mm
□ Ethane pressure 470 mm

of time and pressure on the production of methane (Fig. 2) is opposite to their effect on hydrogen. The experiments at 200 mm show what appears to be an induction period in the production of methane, since the rate increases from about 0.009 cc/hr. to a constant value of about 0.024 cc/hr. This "induction period" becomes shorter with decreasing ethane pressure and appears to vanish at 50 mm; even at 100 mm the induction period is so short that an estimate of the initial rate is very uncertain. An attempt has been made (Table II and Fig. 3) to express

TABLE II. Effect of pressure on initial quantum yields of methane and hydrogen production.††

C₂H₆ pressure—mm	50	100	200	470	640
ϕ_{H_2} (Uncorrected)	0.121	0.188	0.255	0.423	0.475
(Corrected)	0.145	0.199	0.255	0.423	0.475
ϕ_{CH_4} (Uncorrected)	0.068	0.043	0.014	0.005	0.002
(Corrected)	0.082	0.045	0.014	0.005	0.002

†† Conditions as in Table I.

the initial rates of formation of methane and hydrogen as a function of the pressure of ethane. The initial rates, estimated from Figs. 1 and 2 have been corrected for quenching by applying the results of Steacie and Phillips[2] for the extinction of λ2537 by ethane; this method was

adopted in preference to the use of collision cross sections obtained from quenching experiments as their conditions were more nearly those pertaining in the present investigation. In any case the difference between the two methods is not great. The plot of reciprocal pressure against $1/\phi_{H_2}$ and against ϕ_{CH_4} was adopted in Fig. 3, in order to obtain information about the reaction at very high pressures. An interesting result obtained here is the continued increase of ϕ_{H_2} with pressure, even above 200 mm, at which pressure quenching is complete and methane production negligible. Extrapolation, shown as a broken line in Fig. 3, to infinite pressure indicates the possibility that ϕ_{H_2} approaches unity as $p\rightarrow\infty$ and hence the efficiency approaches 100 percent at high pressures. This increase of rate with increasing pressure, even after correcting for quenching, is in agreement with the results obtained with propane.

The presence of molybdenum oxide alters the nature of the reaction in that the formation of methane is almost completely inhibited. Thus the non-condensible gas produced in 5 hours from 45 mm of ethane with a layer of MoO₃ 8 mm from the incident face contained only 8 percent CH₄ whereas, in the absence of MoO₃ and with 50 mm of ethane, CH₄ amounted to about 40
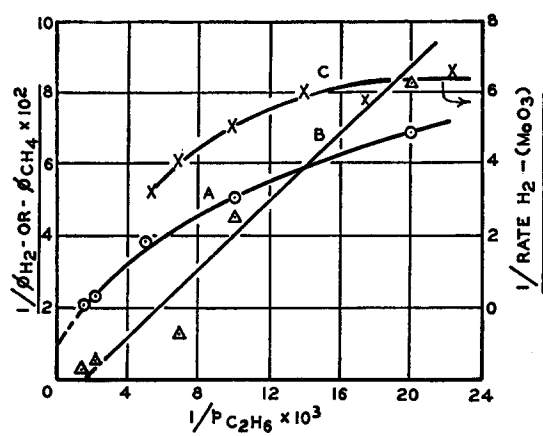
FIG. 3. Effect of pressure on initial rates of production of hydrogen and methane. (All rates corrected for quenching.)

Curve A: $1/\phi H_2$ vs. $1/p \times 10^3$
Curve B: $\phi CH_4 \times 10^2$ vs. $1/p \times 10^3$
Curve C: Reciprocal rate of production of hydrogen (mm min.$^{-1}$) vs. $1/p \times 10^3$ in presence of MoO_3

percent of the non-condensible fraction. Formation of the characteristic blue color on the surface of the oxide indicated the presence of hydrogen atoms. The effect of pressure on the rate of production of hydrogen in the presence of molybdenum oxide is shown in Table III.

TABLE III. Effect of pressure on the rate of production of hydrogen in the presence of molybdenum oxide.‡

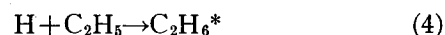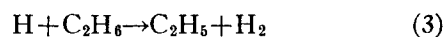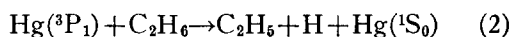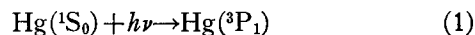| C_2H_6 pressure—mm	45.0	56.5	71	101	143.5	205
Rate of production of H_2—mm/min. $\times 10^4$	1.2	1.43	1.47	1.8	2.4	2.9

‡ Distance of oxide layer from incident face = 8 mm.

These experiments were of 30 min. duration and, in that time, the amount of hydrogen produced was so small that one can be reasonably sure that its contribution to the total quenching was negligible; in the least favorable case, at the end of 30 minutes, only about 1.5 percent of the radiation was absorbed by the hydrogen. It was demonstrated that the rate of production of non-condensible gas in the presence of molybdenum oxide is independent of time up to 2 hours and that this rate decreases with decreasing ethane pressure (Fig. 3). In one experiment acetone was decomposed by photosensitization in the presence of molybdenum oxide and little or no change in color of the oxide occurred. The mercury photosensitized decomposition of ace-

tone has recently been shown[6] to yield methyl radicals so that it is unlikely that the blueing obtained with ethane was caused by alkyl radicals.
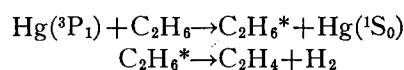
DISCUSSION

The results obtained in the investigation of the mercury photosensitized decomposition of ethane are compatible with a mechanism which is essentially of the same type as that suggested by Steacie and Phillips.[2b] This mechanism involves a C—H split as the initial act, methane originates from "atomic cracking" and the ultimate products from atom and radical recombination. However, evidence has been obtained which leads to the belief that "atomic cracking" actually proceeds via the formation of an active molecule and it is considered that the over-all process is best represented by the following series of reactions:

$$Hg(^1S_0) + h\nu \rightarrow Hg(^3P_1) \tag{1}$$

$$Hg(^3P_1) + C_2H_6 \rightarrow C_2H_5 + H + Hg(^1S_0) \tag{2}$$

$$H + C_2H_6 \rightarrow C_2H_5 + H_2 \tag{3}$$

$$H + C_2H_5 \rightarrow C_2H_6^* \tag{4}$$

$$C_2H_6^* \rightarrow 2CH_3 \tag{5}$$

$$C_2H_6^* + M \rightarrow C_2H_6 + M \tag{6}$$
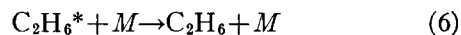
followed by the usual radical recombination reactions.

The results reported above give no indication of the formation of an active molecule, capable of being deactivated, in the initial act since the rate of production of hydrogen increases continually with pressure. Hence, if an active ethane molecule is formed initially it is never deactivated and always decomposes, even at high pressures; the process is therefore indistinguishable from reaction (2). Also, mass spectrometer analysis showed no detectable amounts of ethylene in the products, an indication that reactions of the types:

$$Hg(^3P_1) + C_2H_6 \rightarrow C_2H_6^* + Hg(^1S_0)$$
$$C_2H_6^* \rightarrow C_2H_4 + H_2$$

do not occur in the reactions under discussion. On the other hand, strong evidence in favor of

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[6] E. W. R. Steacie and B. deB. Darwent, J. Chem. Phys. (in press).

reaction (2) has been obtained: The immediate discoloration of molybdenum oxide under conditions such that quenching by hydrogen was negligible and the fact that hydrogen and butane (identified by mass spectrometer analysis and reported previously[2, 3]) are the sole products at high pressures indicate strongly that the initial products are a hydrogen atom and an ethyl radical.

Information has also been obtained about the mechanism by which methane is produced in these reactions. The marked reduction in the rate of formation of methane by the presence of molybdenum oxide, which removes and therefore lowers the stationary concentration of hydrogen atoms, is strong proof that methane arises from some reaction involving H atoms. The large decrease in the initial rate of production of methane with increasing ethane concentration is strong evidence against reactions of the type:

$$H + C_2H_6 \rightarrow CH_4 + CH_3 \qquad (7)$$
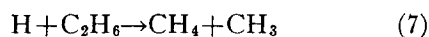
as being an important process for methane production, since, if H_2 is produced mainly by reaction (3) the ratio of the rates of production of methane to hydrogen would be

$$\frac{\text{Rate } _{CH_4}}{\text{Rate } _{H_2}} = \frac{k_7[H][C_2H_6]}{k_3[H][C_2H_6]} = \text{const.}$$

whereas the above ratio increases strongly with decreasing ethane pressure. Hence it is concluded that methane arises from reactions involving H and C_2H_5 and, because of the effect of pressure on ϕ_{H_2} as discussed below, reactions (4) and (5) have been postulated instead of the one stage process

$$H + C_2H_5 \rightarrow 2CH_3$$
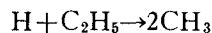
which is the equivalent of reactions (4) and (5) if the active ethane molecule formed in reaction (4) is never deactivated as in reaction (6).

The effect of pressure on the quantum yield of hydrogen formation is good evidence for reactions (4), (5) and (6). The continued increase in ϕ_{H_2} with ethane pressure above 200 mm, at which point the production of methane is negligible, indicates that the inefficiency is due to some process which removes H and C_2H_5 without the formation of methyl radicals. If all H atoms

recombined

$$2H + M \rightarrow H_2 + M \qquad (8)$$
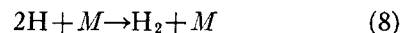
ϕ_{H_2} would have a maximum value of 0.5 and we could thus account for its low value. However, the results of Farkas and Sachsse[7] on the mercury photosensitized ortho-para-hydrogen conversion, and recent work of Trost and Steacie[8] on the reactions of H with the lower paraffin hydrocarbons, indicate that reaction (3) is 300–400 times as fast as (8) under the conditions pertaining in our experiments. Hence it is unlikely that reaction (8) is a major source of inefficiency. Reactions (4), (5) and (6) account excellently for the inefficiency found at high pressures. If the reaction

$$2C_2H_5 \rightarrow C_4H_{10} \qquad (9)$$

is included, the usual steady state calculations applied to reactions (1)–(6) and (9) give

$$1/\phi_{H_2} = 1 + \frac{k_2[C_2H_5]}{k_1[C_2H_6]}.$$

At high pressures $[C_2H_5]$ will be approximately constant and $1/\phi_{H_2}$ will be nearly linear with $1/p$ and will extrapolate to unity at $1/p = 0$ as shown in Fig. 3; at lower pressures $[C_2H_5]$ becomes a complicated function of p and decreases with decreasing pressure. This leads to the departure from linearity at large values of $1/p$ as shown in Fig. 3. At low pressures, where $C_2H_6^*$ formed in reaction (4) decomposes by the first order process (5), other reactions, of the type

$$CH_3 + H \rightarrow CH_4 \qquad (10)$$

$$2CH_3 \rightarrow C_2H_6 \qquad (11)$$
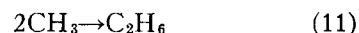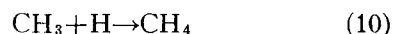
may occur and would further contribute to the inefficiency.

The increase in the rate of formation of methane and the decrease in the rate of formation of hydrogen with duration of the experiment is undoubtedly due to increased quenching by hydrogen in the later stages. Complete quenching by hydrogen will double the rate of production of H atoms and if these atoms disappear mainly by reactions (3) and (4), the stationary H-atom

[7] L. Farkas and H. Sachsse, Zeits. f. physik. Chemie B27, 111 (1935).
[8] W. R. Trost and E. W. R. Steacie, J. Chem. Phys. (in press).

concentration will be approximately doubled. This will lead to double the rate of production of CH_3 and a corresponding loss of H by reactions (4) and (10), causing a decrease in the rate of formation of H_2, as found in the experiments at 200 mm.

The relation between ϕ_{H_2} and pressure is similar to that found with propane.[1] It now appears likely that the initial step in the triplet mercury sensitized reactions of ethane and propane is about 100 percent efficient and that any inefficiency is due to secondary processes of the type discussed above. The case of methane and neopentane will be discussed in a later communication.

The present results show that the initial rate of production of methane is much smaller than formerly reported. However, it has been found that the C−C split is about 20 to 50 times as prevalent with ethane as with propane under similar conditions. A re-investigation of the rates of the reactions of H with ethane and propane[8] has shown that the propane reaction is approximately four times as fast as that of ethane. If the reaction of H with ethyl to form methyl is five to ten times as fast as the corresponding reaction with propyl, a mechanism of the type suggested above will be consistent with the difference in the extents of C−C split with ethane and propane in these reactions.

The Temperature Coefficient of the Surface Tension of Liquid Metals

ADAM S. SKAPSKI

Institute for the Study of Metals, University of Chicago, Chicago, Illinois

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The author's approach is based on the conception of "structure" of liquids. From rather simple assumptions about the symmetry of configuration of the nearest neighbors the entropy change connected with bringing up N-Avogadro's atoms from the bulk of the liquid into its free surface is estimated and the temperature coefficient of the surface tension is calculated therefrom.

Two entropy terms are taken into consideration. The first term ΔS_{osc} is due to the difference in the frequency of oscillation of the atom inside and on the surface, and is calculated from the respective number of neighbors. This term allows the calculation of the lower limit of the temperature coefficient of the surface tension (because the "unsharpness" of the free surface is not accounted for). The second term allows us to estimate—again from the number of the nearest neighbors in the bulk and on the surface—the maximal value ΔS_{conf}, to account for the "unsharpness" of the surface.

The experimental data lie well within the calculated limits and almost coincide with the values calculated from $(\Delta S_{osc} + \frac{1}{2}\Delta S_{conf})/A$ where A is the surface occupied by N-Avogadro's atoms. The influence of the thermal expansion is expressed by the change of A with temperature.

THEORETICAL attempts to calculate the temperature coefficients of the surface tension of liquid metals—known to be lower than those of so-called "normal liquids" (with Eötvös constant $K_E = 2$)—have not been hitherto very successful. The first general theory, proposed by Frenkel[1] and based on Debye's wave picture of thermal movements of molecules in solids and on Thomson's theory of capillary waves, gave much too high results for liquid metals. Recently Frenkel and Gubanov[2] built up another theory,

based this time on the assumption that in a surface of an amorphous body the stresses are equal to zero, not the displacements as was originally postulated by Debye. They succeeded (with some additional assumptions about the dependence of the potential energy on temperature) in expressing the temperature coefficient of the surface tension as a function of the thermal expansion and of the entropy change, the latter being mainly responsible for the behavior of liquid metals; the agreement between theory and