# About Thermodynamics of Metals in the Critical Region[1]

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# ABSTRACT

The equations of state (EOS) for 11 metals based on the "soft-sphere" thermodynamic potential have been developed for calculation thermodynamic properties in the liquid state. A technique for determination of coefficients is proposed. Phase diagrams in the region of the liquid state are calculated for some metals. The comparison with the isobarical expansion experiments is made, as well as with data on the isentropic expansion of shocked metals and sound velocity measurements. A comparison with the Birch law is made for sound velocities. The parameters of the critical point are estimated and compared with other evaluations.

# 1. INTRODUCTION

The region of liquid state on the phase diagram of matter is traditionally the most difficult for study, because the strong interparticle interaction and inhomogeneity makes it uncertain the theoretical predictions of properties of real liquids. Now there are realistic models of zero approximation, based on very simplified hard- and soft-sphere potentials. This models allow one to apply the numerical Monte-Carlo and molecular dynamics methods. The results of such calculations reproduce the basic qualitative features of specific substances and are used for the development of the semiempirical equations of state, which contain a number of parameters for the quantitative description of experimental data.

In such a way in [1] it was obtained a functional dependence of the free energy potential, i.e. EOS, of liquid phase of metals as a result of modelling of the system of particles with the soft-sphere potential $\Phi(r) = \epsilon(\zeta/r)^n$:

$$F(V,T) = RT\left\{\ln\frac{\theta_m}{T^{3/2}V} + \frac{Q}{2}(n+4)\left(\frac{V_{sph}}{V}\right)^{n/9}\left(\frac{U}{RT}\right)^{1/3}\right\} + \\ + U\left\{C_n\left(\frac{V_{sph}}{V}\right)^{n/3} - \left(\frac{V_{sph}}{V}\right)^{m}\right\} + E_{sub},$$

where $R$ — universal gas constant, $C_n$ $k$ — Madelung and Boltzman constants, $U = N\epsilon$, $V_{sph} = N\zeta^3/\sqrt{2}$, $N$ — specific concentration of matter, $E_{sub}$ — cohesive energy at $T = 0$ K, $\theta_m$ — normalization constant, which is determined from the condition $s(V_m, T_m) = 0$ ($V_m$ $T_m$ — specific weight of liquid metal and the temperature in the melting point at pressure of 1 bar), $Q$ $m$ — free parameters.

Young [1] applied the following procedure of unknown parameters determination for thermodynamic potential. In the beginning $\epsilon$ $\zeta$ were being determined by the solving of the equations $p(V_m, T_m) = 0$, $E(V_m, T_m) = H_m$ ($H_m$ — specific

enthalpy of liquid phase on the melting curve) in some fixing $n$, $m$ and $Q$. Then the results of calculations were being compared with the experimental data on isobarical expansion of metals [2], parameters $n$,$m$ and $Q$ were being changed and the procedure was repeated. On the basis of this model Young carried out the estimations of critical parameters for 16 metals (Li, Na, Al, K, Ga, Ru, Nb, Mo, Cs, Ta, Hg, Pb, U, Pt, V, and Ir). The agreement with the measurements of saturated vapor pressure for K, Ru, Cs and Hg was very good.

## 2. RESULTS

In this work we propose the different technique making the procedure of determination of EOS parameters much rigorous. Four of five unknown coefficients ($U$, $V_{sph}$, $Q$, $m$) are determined as a result of solving the system of 4 non-linear equations: $p(V_i, T_i) = p_i$, $H(V_i, T_i) = H_i$, $i = 1, 2$, where $p_i$, $V_i$, $T_i$, $H_i$ — experimental values of pressure, specific value, temperature and enthalpy. The last coefficient $n$ remains free and it is found from the value of sound velocity in molten metal. Furthermore, tabular value of cohesive energy $E_{sub}$ can be changed in the range of possible error for the agreement with the evaporation temperature of substance at normal pressure.

This model is applied at the following range of parameters: in pressure $p \lesssim 5GPa$ , in density $\rho \lesssim \rho_{melt}$ and in temperature $T_{melt} \lesssim T \lesssim$ 20000K. Calculated are phase diagrams and parameters of the critical point for eleven metals (Al, Cu, Fe, Ni, Ta, W, Ir, Mo, V, Pb, and Pt). Five of them (Cu, Fe, Ni, W, and Pt) have not been explored in [1]. On the Fig. 1 is shown the calculated phase diagram for W . Critical point parameters are collected in the table together with evaluations given by other authors [1, 3, 4, 5, 6, 7].

From the figure one can see the good agreement with the experiment [12], the law of rectilinear diameter is true with sufficient accuracy. The dependence of

calculated sound speed on density has less slope, than the experimental one. Note, that results [12] are given in a form of approximation of Birch's law [8]. An analysis done for refractory metals shows that this and [11] calculations of sound velocity deviate from Birch's law at low values of density.

The calculated values of critical parameters lies below the estimations of hard-sphere model [3] and the corresponding state law evaluations [4]. The obtained values of the critical temperature are greater than those one from [1], which can be explained by more correct value of evaporation temperature at normal pressure. For example, for Ta the evaporation temperature at $p = 1$ bar is $T_v = 4.104$K in [1], the tabular one is $T_v = 5.626$K.

For Cu and Fe the calculations of release isentrops is held, which penetrate into the two-phase region from the liquid state. The procedure used was the follows: for the experimental value of wave velocity at sufficiently low pressure ($p < 1$ GPa) the density is selected from the condition of the best correspondence with experiment. Then the isentrope is built from this point (for the higher and lower pressures).

The result is that release isentrops can be estimated with a good accuracy even in high pressure range except for the two-phase region, in which non-equilibrium processes have a significant influence.

# 3. CONCLUSIONS

Equations of state for 11 metals have been developed on the base of the model [1] and new technique of determination of EOS parameters. The calculation of the phase diagrams of the metals has been done. A comparison with available experimental measurements on isobaric expansion and evaluations of the critical point demonstrated a good agreement. Estimations of the critical point parameters

based on the most recent experimental data are principal result of the work.

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**Table 1. The estimations of critical point parameters.**

| Substance | $T_c$ $10^3$ | $p_c$, GPa | $\rho_c$, g·cm$^{-3}$ | $Z_c$, $p_c/\rho_c RT$ | Reference |
|---|---|---|---|---|---|
| Al | 5.726 | 0.182 | 0.424 | 0.334 | [1] |
| | 7.151 | 0.546 | 0.692 | 0.359 | [3] |
| | 8.000 | 0.447 | 0.640 | 0.285 | [4] |
| | 7.222 | 0.571 | 0.806 | 0.319 | [9] |
| | 7.017 | 0.329 | 0.526 | 0.289 | This work |
| Cu | 7.625 | 0.830 | 2.370 | 0.359 | [3] |
| | 8.390 | 0.746 | 2.390 | 0.285 | [4] |
| | 7.455 | 0.461 | 1.758 | 0.271 | This work |
| Fe | 9.340 | 1.154 | 2.031 | 0.359 | [3] |
| | 9.600 | 0.825 | 2.030 | 0.285 | [4] |
| | 9.340 | 1.043 | 1.697 | 0.443 | [5] |
| | 7.371 | 0.657 | 1.625 | 0.369 | This work |
| Ni | 9.576 | 1.116 | 2.293 | 0.359 | [3] |
| | 10.330 | 0.912 | 2.190 | 0.285 | [4] |
| | 7.585 | 1.049 | 2.088 | 0.470 | [11] |
| | 7.848 | 0.873 | 1.941 | 0.407 | This work |

(Continued)

**Table 1 (Continued).**

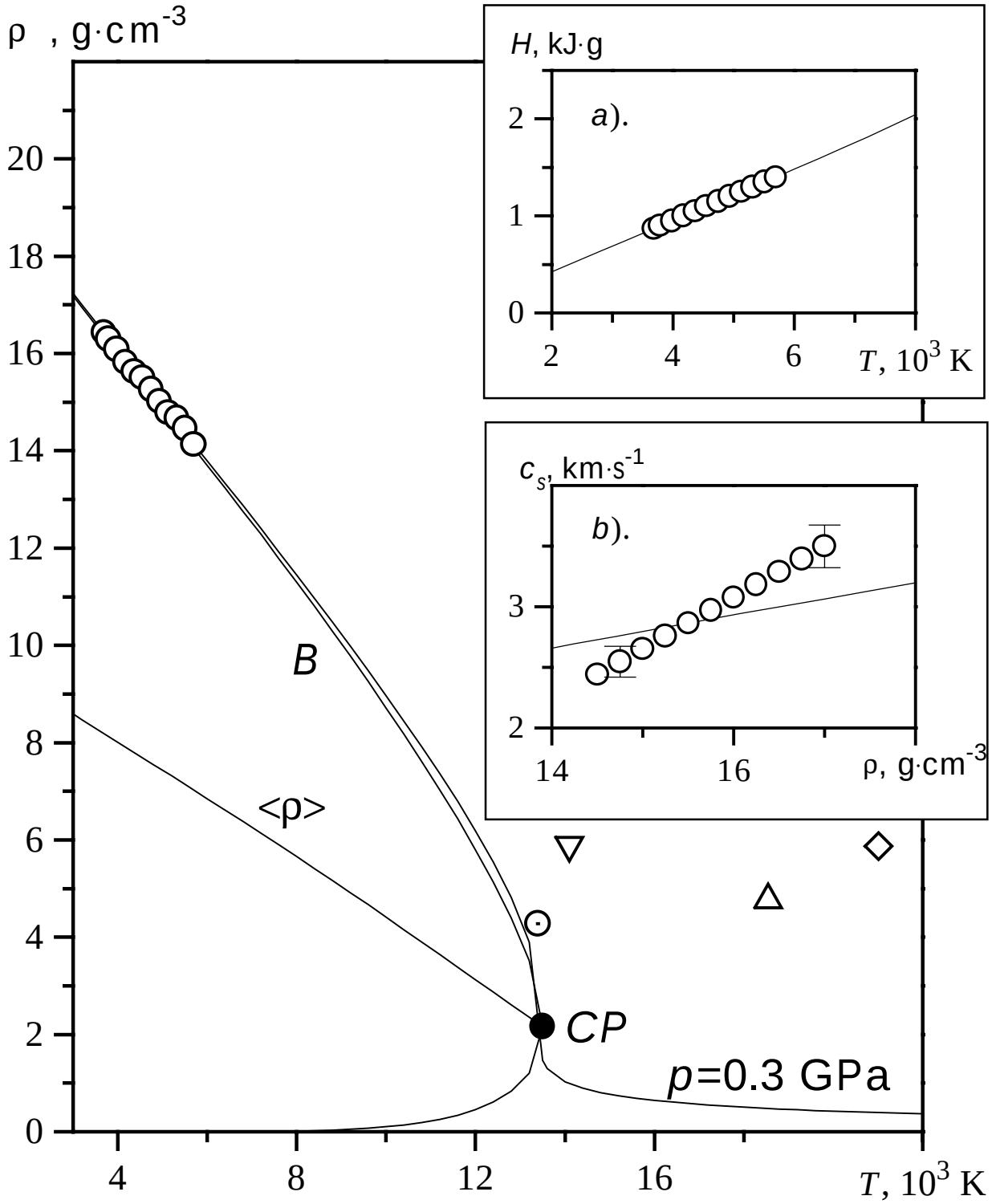
| Substance | $T_c$ $10^3$ | $p_c$, GPa | $\rho_c$, g·cm$^{-3}$ | $Z_c$, $p_c/\rho_c RT$ | Reference |
|---|---|---|---|---|---|
| Ta | 9.284 | 0.999 | 4.264 | 0.550 | [1] |
| | 17.330 | 1.222 | 4.308 | 0.359 | [3] |
| | 20.570 | 1.350 | 5.040 | 0.285 | [4] |
| | 14.470 | 0.8124 | 3.637 | 0.336 | This work |
| W | 18.540 | 1.480 | 4.762 | 0.359 | [3] |
| | 21.010 | 1.583 | 5.870 | 0.285 | [4] |
| | 14.100 | 0.509 | 5.882 | 0.140 | [6] |
| | 13.400 | 0.337 | 4.276 | 0.130 | [7] |
| | 13.500 | 0.308 | 2.167 | 0.233 | This work |
| Pb | 5.158 | 0.226 | 3.092 | 0.353 | [1] |
| | 4.668 | 0.208 | 3.097 | 0.359 | [3] |
| | 4.980 | 0.184 | 3.250 | 0.285 | [4] |
| | 5.4±0.4 | 0.250 | 3.184 | 0.362 | [10] |
| | 5.717 | 0.232 | 2.863 | 0.353 | This work |

# FIGURE CAPTIONS

Fig. 1. Phase diagram of tungsten: $p$ — isobar 0.3 GPa, $< \rho >$ — rectilinear diameter, $B$ — binodal. Experiment: $\bigcirc$ — [12] at $p = 0.3$ GPa. Evaluations of the critical point parameters: $\diamond$ — [4], $\triangle$ — [3], $\odot$ — [6], $\nabla$ — [7].

Fig. 1a. Enthalpy at $p = 0.3$ GPa. Experiment [12].

Fig. 1b. Sound velocity at $p$ =0.013 GPa. Experiment [12].


ρ , g·cm-3
20
18
16
14
12
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8
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T, 10^3 K
B
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CP
p=0.3 GPa
H, kJ·g
a).
2
1
0
2
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T, 10^3 K
c_s, km·s^-1
b).
3
2
14
16
ρ, g·cm^-3