



The Atom as the Empirical Building Block in Metallurgy

A.R. Miedema, Eindhoven

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As in many other fields of science, one can observe in metal physics a loss of contact between scientists active in fundamental research and those more interested in the technology. Partly this is because in basic research one tends to concentrate on relatively simple systems and quite sophisticated problems, whereas in applied fields, each situation may present individual, sometimes ill-defined, complications. But more important for the loss of contact, is the growing difficulty of communicating. In modern metal sciences, the trend is towards a steadily increasing number of specialisations, each branch developing its own symbols and language, which for the more basic sub-fields tend to be full of mathematical barriers. As a consequence, the exchange of ideas between historically much related fields is declining.

In this situation, there can be a renewed interest in empirical models and descrip-

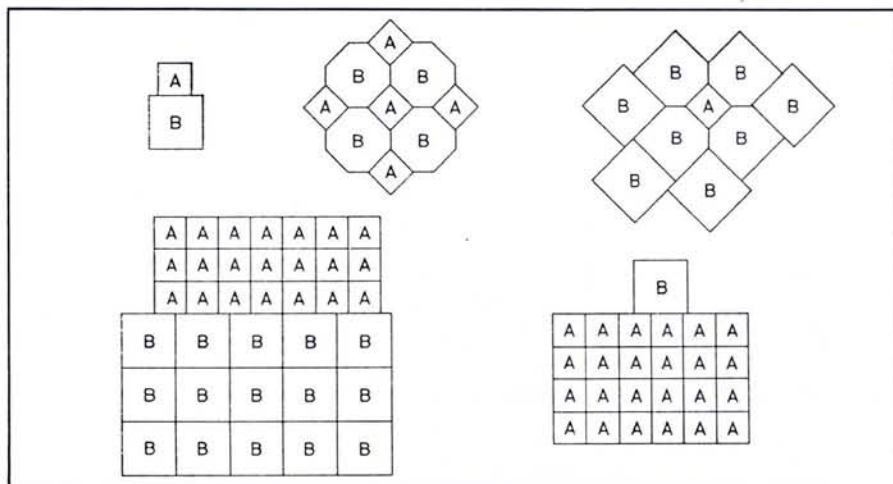
tions of a style which, on first sight, may seem to be more appropriate to the 1930s than the 1980s. Empirical models may however, offer a phenomenological picture, relevant to a number of different sub-fields of science, in this way restoring the communication. Empirical descriptions may also serve to summarize large amounts of experimental data, indicating trends and regularities that otherwise would not easily have been noticed by theoreticians, in this way improving the possibilities of confronting theoretical ideas with experiment.

In our special case¹⁾ the empirical picture is that of the atomic cell as the basic unit in considering energy effects in metals and alloys. The reference state is the energy of a metal atom in its pure bulk metal. Energy effects are then related to the change in boundary conditions when atomic cells are removed from the pure metal and placed in contact with, for instance, dissimilar metal



atom neighbours or the vacuum. The general applicability of the empirical picture in the predictions of energy effects, may become clear from Fig. 1. In this one finds a schematic drawing of a diatomic molecule, an ordered intermetallic compound, one atom of A in a liquid solution of B atoms, an interface between two crystals and an atom of B adsorbed on a substrate of metal A. First, the empirical picture suggests that there is no basic difference between the heat effect upon solution of A in B and that of forming an AB compound. In both cases²⁾ one has to deal with an energy

Fig. 1. — Energy effects in metal sciences. It is suggested that there are relations between dissociation energies of intermetallic molecules, heats of alloying for solid and liquid alloys, interfacial energies at the interface between metal crystals and heats of adsorption of metals on metallic substrates.



The article contributed by the co-winner of the 1980 Prize, O.K. Andersen, will be published in the October issue of EN.

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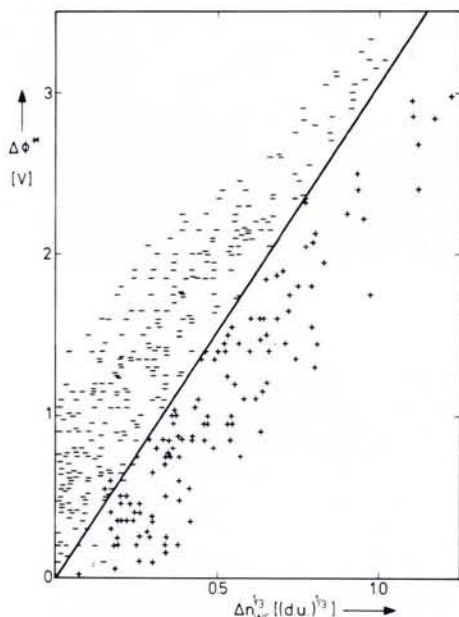


Fig. 2. — The sign of the enthalpy of formation of binary solid alloys out of a group of 38 metals. Each data point represents a binary system. Parameters are the differences in electronic work function (ϕ^* represents our table of recommended values for ϕ) and the differences in electron density at the boundary of the atomic Wigner-Seitz cells, plotted as $n_{ws}^{1/3}$.

effect generated at the cell boundaries, where A atomic cells and B atomic cells are making contact. Second, in the case of macroscopic crystals of A and B in contact³) one finds in fact the same situation; heats of alloying and interfacial energies will be interrelated.

Applying the same type of argument to boundaries between metal atoms and the vacuum, one must expect that surface energies of metals (the surface energy is the energy required to increase the metal-vacuum interface by one unit of surface area) are related to the heat of vaporization. In the surface layer of a metal crystal, one finds atomic cells that are in contact with the vacuum for a fraction of their cell boundaries. Free atoms are in contact with the vacuum over the full cell boundary. Indeed experimentally, the heat of vaporization of metals equals to a good approximation the product of the surface area of single atoms and the surface energy as known for the macroscopic metal crystal.

In Fig. 1, the example of B atoms adsorbed on a substrate of A, illustrates that in this situation we have to do with B atoms that are partly in contact with A and partly with the vacuum. Also, upon adsorbing the B atom, some originally present interfacial area between A and the vacuum has disappeared. Along these lines one can express the enthalpy of adsorption⁴) of B on A in terms of the surface energies of A and B, the surface area of a B atom, and the heat of solution of A in B, in good agreement with experiment.

Finally, from Fig. 1 one expects also dissociation energies of diatomic mole-

cules⁵) to be predictable. For the molecule AB, one finds contacts between A and B atoms, and between both A and B and the vacuum.

By means of Fig. 1 we have made it seem plausible that the empirical picture for energy effects can indeed offer the possibility of interconnecting various specialisations in metal physics. Language problems between the empirical approach on the one hand, and either applied metallurgy or theoretical metal physics on the other, can be effectively reduced by communicating in terms of complete tables of predictions. For instance, we have published tables⁶) of the heat of solution of any metal in any metal. Such tables undoubtedly will mean something to all metal scientists. Other published predictions include the dissociation energies of arbitrary transition metal diatomic molecules, the heat of formation of equiatomic intermetallic compounds, the heat of adsorption of metals on transition metal substrates, formation enthalpies of hydrides formed from transition metal intermetallics, and tables for the interfacial energies for arbitrary metal combinations. Other results are a table of surface energies of metallic elements in the solid state (and a recipe for dealing with surface segregation in arbitrary binary alloys) and a table of formation energies of monovacancies in metals (with a recipe for dealing with vacancies at different sites in ordered alloys).

We have indicated in which way a large variety of energy effects can be predicted, once the heats of solution for arbitrary metal combinations and the surface energies of the metallic elements in the solid state are known. What remains, is to explain how heats of solution and surface energies have been found.

Heats of Alloying

Heats of alloying are derived as interfacial energies. Upon creating contacts between A and B atomic cells, there will be an energy effect related to the contact potential difference for the two metals. In an empirical approach, in which metal atoms are treated as macroscopic entities, it is relatively straightforward to assume that this negative term in the alloy formation energy is proportional to the square of the difference in electronic workfunction, ϕ , of the two metals involved.

A second term has to do with the fact that the electron density is required to be continuous across an interface between dissimilar atomic cells. In general, the original values for the electron density at the boundaries of the two metal atomic cell, n_{ws} , will be different. For pure metals, the value of n_{ws} corresponds to a minimum of energy, so that any change required in the matching of metals with different cell boundary electron density will take a

positive energy. It can be made plausible¹) that this positive contribution to the heat of alloying is proportional to the square of the difference in $(n_{ws})^{1/3}$. Hence the heat effect of alloying H is found as:

$$\Delta H \sim -P(\Delta\phi)^2 + Q(\Delta n_{ws}^{1/3})^2, \quad (1)$$

where P and Q are constants having the same value for large groups of metal combinations.

The reliability of equation (1) in predicting the sign of the heat of alloying is demonstrated in Fig. 2 for alloy systems that involve two transition metals, noble metals, alkali metals or alkaline-earth metals (i.e., metals with predominantly s-type and d-type conduction electrons). The number of elements included is 38, the corresponding number of binary systems is $38 \times 37/2 = 703$. For the majority of these systems the sign of ΔH is known. If there are stable ordered phases in a binary system, one can assume that ΔH has the negative sign. If there are no intermediate phases in a binary system while, in addition, mutual solid solubilities are small, one can safely assume that ΔH has the positive sign. In Fig. 2, each data point represents a binary system, with its sign of ΔH as derived from phase diagram information. The validity of equation (1) is illustrated by the straight line, which fairly completely separates the plus and minus signs.

The possibility of drawing such a line was expected from relation (1). It will correspond to:

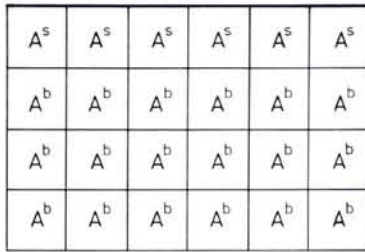
$$\Delta\phi/\Delta n_{ws}^{1/3} = (Q/P)^{1/2}. \quad (2)$$

Having demonstrated the validity of relation (1) using only qualitative experimental information, we can easily arrive at quantitative predictions, by analysing the limited available experimental information on numerical ΔH values to find the remaining constant.

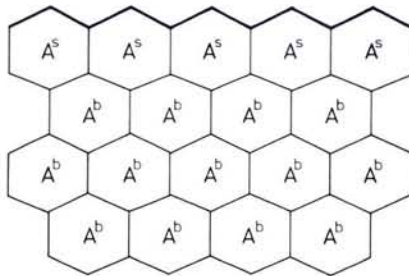
We note that diagrams, similar to Fig. 2, and with a similar straight line, also exist for liquid metals. It turns out that in combinations of transition metals with metals having p-type conduction electrons, there is an additional negative term to ΔH , which we only mention here.

Solid Metal Surface Energies

The experimental information on surface energies of solid metallic elements is limited, whereas the data are fairly complete for liquid metals. In the empirical approach one expects only a small difference between solids and liquids, as we illustrate by means of Fig. 3. In principle, it is an oversimplification to present the surface of a crystal as a flat interface, Fig. 3a. In a crystalline lattice, the atomic cells will lead to a metal-vacuum interface that on a microscopic scale will have a certain roughness. This roughness leads to a higher surface energy; variations in the roughness factor will be responsible for



(a)



(b)

Fig. 3. — The surface of a crystal, which is flat in the case of cubic Wigner-Seitz atomic cells, but which has a certain roughness for a more realistically shaped cell.

some variation in the surface energy for different crystal planes of a single crystal (± 5 percent).

One can expect a liquid metal-vacuum surface to be somewhat more flat than a crystalline one, or at least the surface of the liquid to have an energy similar to that of an energetically favourable crystal plane. Comparing the values of the surface energies, obtained after extrapolation of the data to zero temperature, of those metals for which reliable information is available covering both the liquid and solid phase, one finds the difference between solid and liquid to be an approximate factor of 1.13. This constant factor opens the possibility of producing a table of surface energies of "the average crystal plane" for all solid metals, starting from experimental data on liquids.

Interfacial Energies

As a demonstration of additional problems to be dealt with, in order to arrive at quantitative treatments, we can mention interfacial energies. According to Fig. 1, the interfacial energy between two macroscopic pieces of metal, is proportional to the heat of solution of A in B per unit surface area of A atoms. Assuming an average shape of atomic cells we derive:

$$\gamma_{AB} = 2.5 \times 10^{-9} \Delta H(\text{sol})_{A \text{ in } B} / (V_A)^{2/3} \quad (3)$$

where V_A stands for the molar volume of metal A. It is easy to see that this cannot contain the whole problem. Even in the case of a crystal in contact with its own melt, or when two grains are in contact in a polycrystalline solid, there is an interfacial energy. A simple description of the first can be based on experiments on supercooling;

the contribution in the second has been found in metallurgy to be related to the surface energy. In quantitative predictions of interfacial energies, such contributions have to be included, for instance by adding in the case of solid-solid interfaces, the average value of a large angle grain boundary⁷⁾.

In this degree of detail, all examples of Fig. 1 need some additional discussion. In heats of alloying, one must have some idea of the extent to which atomic cell dimensions may change upon alloying. In calculations of heats of adsorption, one must pay attention to the volume of the adsorbate cell as well as the fraction of its surface area in contact with the substrate and the variation of this fraction with degree of coverage. For molecules, magnetic properties and special free atom configurations need special attention.

In treating these details, a number of additional assumptions have been made which sometimes tend to spoil the attractive simplicity of the starting point, Fig. 1. However, what remains is a description without much mathematics, which can be formulated in terms of picture and common language, thus offering the advantage of easy accessibility, also to non-experts.

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REFERENCES

1. For a detailed introduction to our work see Miedema A.R., de Chatel P.F. and de Boer F.R., *Physica B1* **00** (1980) 1 and Miedema A.R., *Philips Technical Review* **36** (1976) 217; **38** (1979) 257.
2. A series of papers on heats of alloying has been published (in cooperation with R. Boom, F.R. de Boer and P. Bouten) in *J. Less-Common Metals* **32**, **45**, **46**, **65**, **71**.
3. A series of papers on surface energies, surface segregation, interfacial energies and vacancy formation enthalpies has been published (with R. Boom and F.J. den Broeder) in *Z. Metallkunde* **69** and **70**.
4. Dissociation energies of diatomic intermetallic molecules (with K.A. Gingerich) can be found in *J. Phys. B* **12**.
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6. Miedema A.R. et al. *Calphad* **1** (1977) 341.
7. The treatment of solid-solid interfacial energies was suggested by Turnbull about 30 years ago. What is new is the fact that now heats of solution and surface energies are available, so that quantitative predictions can be made for arbitrary systems.

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