

# Simple electronegativity-based model for predicting formation of stable compounds across the periodic table

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Since Linus Pauling developed the concept of electronegativity, various heuristic models have been developed to estimate the capability of chemical elements to form stable compounds. All these models including well-known Miedema's models were believed to be applicable to particular classes of compounds and to require substantial increase of complexity to be applied more generally. Here we demonstrate that basic chemical trends in stability of all possible binary systems are well described by a simple chemical model where each element is characterized by just two numbers – electronegativity  $X$  and chemical mismatch parameter  $Y$ . These parameters were determined for the elements from a large number of theoretical enthalpies of formation, and were found to display strong periodicity and to correlate with Pauling's electronegativity and valence electron density. The proposed two-parameter chemical model explains a number of anomalies found in chemical behavior of elements. In particular, it shows why active electropositive alkali and alkaline earth metals do not react with most elements, in contrast to inert noble metals (which do form stable binary compounds with most elements).

The idea that stability of chemical compounds can be evaluated from fundamental properties of the constituent atoms is at the heart of chemistry. An early quantitative approach, proposed by Pauling in 1932, postulated that the energy of a chemical bond is enhanced when the bonded atoms possess different electronegativity, the extra bond stabilization being equal to the squared difference of electronegativities<sup>1,2</sup>. Pauling's thermochemical scale of electronegativities, determined using experimental bond energies, has become widely used, and helped to explain a vast number of facts, including dipole moments of molecules<sup>3</sup>, band gap, color and hardness of solids<sup>2–5</sup>, and geochemical behavior of the elements<sup>6</sup>.

With regard to stability of compounds, a clearly correct conclusion is that highly electronegative (e.g., Cl) and electropositive (e.g., Na) elements react exothermically, forming highly stable compounds. Figure 1 shows the heat map of the lowest enthalpies of formation in nearly all possible binary systems compared with the corresponding heat map of squared Pauling's electronegativity differences. These two maps show similarity and both display periodic trends. In general, the

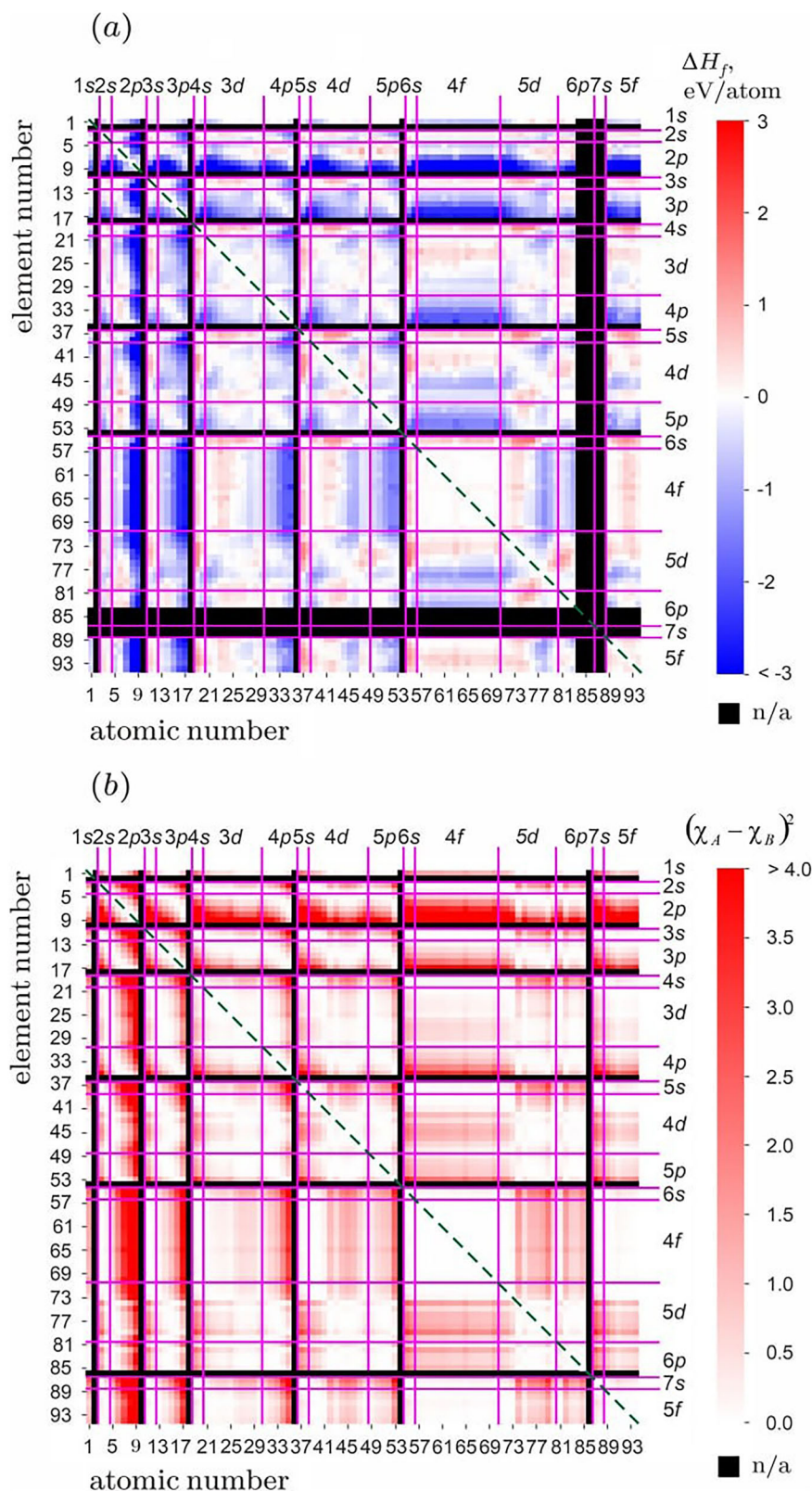
highest exothermic effect indeed occurs when the most electronegative elements react with the most electropositive ones.

Taking Pauling's idea at face value, any two elements, by virtue of having (even if slightly) different electronegativities, should form a stable compound, but this is not the case in reality. Clearly, electronegativity is not the only factor determining the formation enthalpy and stability of substances.

Miedema and coauthors<sup>7–11</sup> published a simple heuristic model for metallic alloys, casting the enthalpy of formation of a binary  $A_xB_{1-x}$  alloy in the following form:

$$\Delta H_f = f(x) \left[ -Pe(\Delta\Phi)^2 + Q(\Delta n_{ws})^2 \right] \quad (1)$$

where  $f(x)$  is a dimensionless function of composition,  $P$  and  $Q$  are fitted constants,  $e$  is the electronic charge,  $\Delta\Phi$  is the difference of work functions in pure metals A and B (work function being approximately equal to the chemical potential of the electron in the metal and close to minus Mulliken's electronegativity of the metallic solid), and  $n_{ws}$  is the



**Fig. 1 | Thermodynamics of binary compounds.** **a** Lowest enthalpies of formation  $\Delta H_f$  calculated for binary compounds using density functional theory (at  $T = 0$  K and  $P = 0$ ) and **b** squared Pauling electronegativity difference  $(\chi_A - \chi_B)^2$  between the elements. The enthalpies of formation were taken primarily from *Material Project*

database<sup>22</sup> and supplemented with hypothetical unstable and non-existent compounds ( $\Delta H_f > 0$ ) from *OQMD* repository<sup>23,24</sup>. Grid lines delineate boundaries between *s*-, *p*-, *d*-, *f*-block elements.

electron density at the boundary of the atomic Wigner–Seitz cells. The difference of chemical potentials drives charge transfer between the atoms, and the associated energy gain is to lowest order quadratic in the difference of chemical potentials. The second term is an energy penalty due to the deformation of atomic electron densities: when two different atoms are brought into contact with each other, their electron densities must become equal at the boundary between the atoms. Function  $f(x)$  in Miedema's model is a complicated semiempirical function taking into account ordered or disordered structure and atomic volumes (and their changes in the alloy), and designed to work only in alloys and intermetallics.

Although both  $\Phi$  and  $n_{\text{WS}}$  could be determined from experiment, Miedema obtained them by fitting to reproduce the experimental heats of formation available at that time. For the majority of cases, the model provided correct predictions of alloying behavior, although for systems combining  $p$ - and  $d$ -metals, a negative constant had to be added to the Eq. (1). The use of asymmetric functions of concentration<sup>12</sup> or size difference factor<sup>13–15</sup> accounted for the size mismatch effects and improved the applicability of the model to systems with large difference in the atomic sizes. In addition to metallic alloys and intermetallics, Miedema's model was found to work for transition metal silicides, germanides, borides and even carbides and nitrides if a special “metallization” correction of the enthalpy for these elements was added<sup>12</sup>. Various generalizations of the model were developed to treat ternary and more complex systems<sup>16–18</sup> (see also ref. 19).

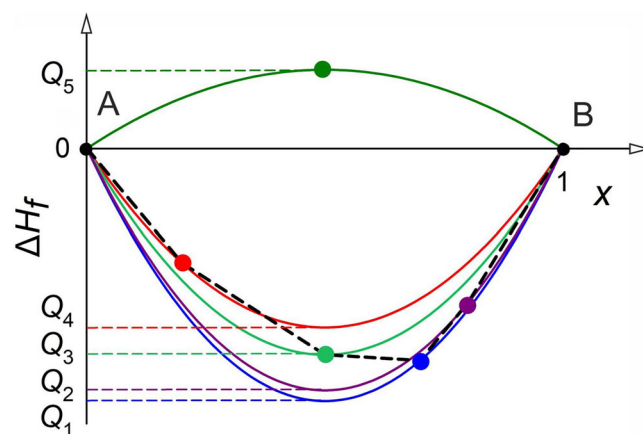
Pettifor published a hundred-page article<sup>20</sup> with a critique of Miedema's model, concluding that this model has no physical basis. Williams et al.<sup>21</sup> argued that the success of the model in correct prediction of the sign and to some extent the magnitude of the enthalpies of formation is due to the good choice of the formula that incorporates basic chemical trends regardless of which physical properties of the constituent chemical elements were taken as variables. The most common argument against Miedema's model was that in metals all long-range Coulomb interactions are completely screened. However, this criticism misses the point: stabilization by charge transfer does not require long-range interactions, but originates from the flow of the electrons from regions of high potential (less electronegative atoms) to regions of low potential (more electronegative atoms).

Here, we show that the power of Miedema's model has not been fully exploited. We propose a simplified and generalized model for predicting the existence of stable compounds which is not limited to just metallic systems, but covers all possible binary combinations from the periodic table. Instead of increasing the number of parameters and complexity of the formulae, we simplify the model and stay with the simplest physically motivated functional form, which only has two parameters per element. As will be shown below, the simplified two-parameter formula predicts the signs and magnitudes of the enthalpies of formation surprisingly well throughout the whole set of possible binary systems.

## Results

We start by recognizing that the stabilizing (negative) term in Eq. (1) can be simplified by replacing it with Pauling's squared electronegativity difference (when energies are expressed in eV, electronegativities have dimensionality  $\text{eV}^{1/2}$ ). The difference is that Pauling's scale was calibrated on energies of only single bonds in molecules and without considering destabilizing effect, whereas our electronegativities are calibrated on convex hulls of solid-state systems and including the destabilizing term. Thus, our electronegativities (which we denote as  $X$ ) will have somewhat different values and are more directly applicable to solids. Likewise, the destabilizing term in Eq. (1) can be simplified as the squared difference of another atom-specific property that can be called a chemical mismatch parameter  $Y$  (also with dimensionality  $\text{eV}^{1/2}$ ):

$$\Delta H(x) = f(x) \left[ -(X_A - X_B)^2 + (Y_A - Y_B)^2 \right] \quad (2)$$



**Fig. 2 | Convex hull construction for a binary A-B system (black dashed line) and its simplified parabolic representations.** This graph shows stable compounds  $A_xB_{1-x}$  (filled circles) in coordinates of enthalpy of formation  $\Delta H_f$  (normalized per atom) and composition  $x$ . Through each point  $\Delta H_f(x)$  indicating a stable compound we draw a parabolic curve, and then select the lowest  $Q$  value which then characterizes this binary system A-B. If elements A and B do not form stable compounds, the parabola is convex upwards and the  $Q$  parameter is positive.

When the term in brackets (which we call the interaction parameter  $Q$  and which has units of energy):

$$Q = -(X_A - X_B)^2 + (Y_A - Y_B)^2 \quad (3)$$

is negative, elements A and B exothermically form stable compounds, and otherwise when  $Q > 0$ . Both the stabilizing and destabilizing terms should be even functions of  $X$  and  $Y$ , the simplest choice (taken by Pauling and Miedema) being quadratic.

Complicated function  $f(x)$  in Miedema's model (Eq. (1)) can also be simplified. It must satisfy the condition  $f(0) = f(1) = 0$ . Here we set the simplest hypothesis that  $f(x) = 4x(1-x)$ , i. e. the function  $\Delta H_f(x)$  is a parabola with the extremum at  $x = 1/2$ , equal to  $Q$ . Such a form is used in theories of disordered solid solutions, and often describes well enthalpies of formation of ordered compounds. The full expression for the enthalpy of formation is then:

$$\Delta H_f = 4x(1-x) \left[ -(X_A - X_B)^2 + (Y_A - Y_B)^2 \right] \quad (4)$$

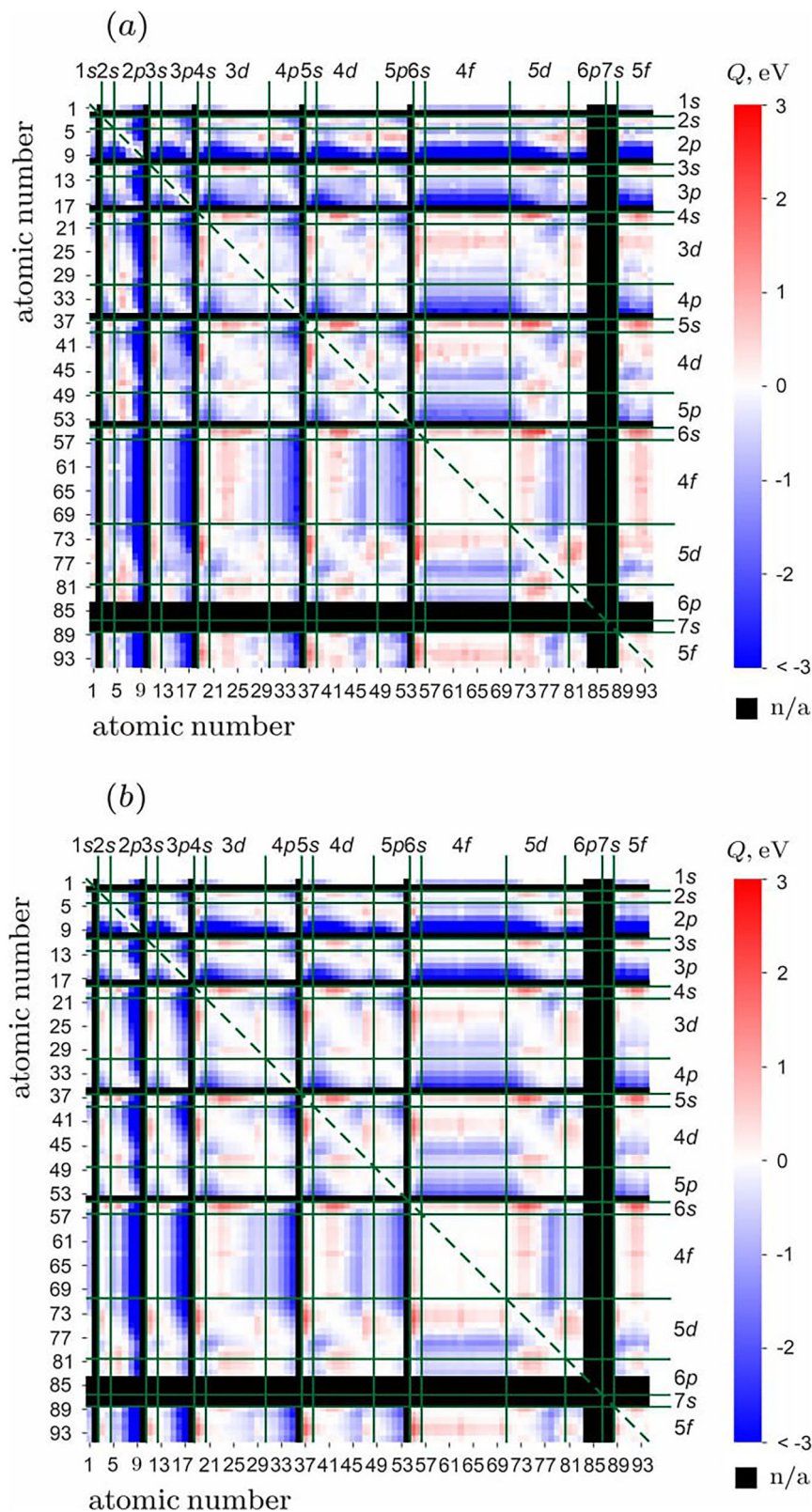
Unlike Miedema's expression (1), our formula (4) has no dimensionality conversion factors, no additive correction terms, and no complicated form of  $f(x)$ . Parameter  $X$ , instead of being the work function, is now directly related to Pauling's electronegativity, as it should be. Physical meaning of parameter  $Y$  and values of  $X$  and  $Y$  across the periodic table will be discussed below.

Thermodynamically stable compounds in a binary A-B system form a convex hull in coordinates composition–enthalpy of formation (Fig. 2). Although its shape is never strictly parabolic (but is often close to it), one can calculate  $Q$  by simply dividing  $\Delta H_f$  by  $4x(1-x)$  for each composition—in this case  $Q$  is a function of composition. The lowest (most negative) value of  $Q$  gives information about the ability of these elements to form a stable compound—if the lowest  $Q$  is negative, stable compounds must exist, and otherwise if the lowest  $Q$  is positive. Compositional variation of  $Q$  reflects such effects as structural frustrations and unavailability of chemically and sterically favorable crystal structures at certain compositions, as well as unfavorability of valence-uncompensated stoichiometries, so taking the lowest  $Q$  we minimize these effects and focus on the most essential effects behind compound formation, related to atomic properties.

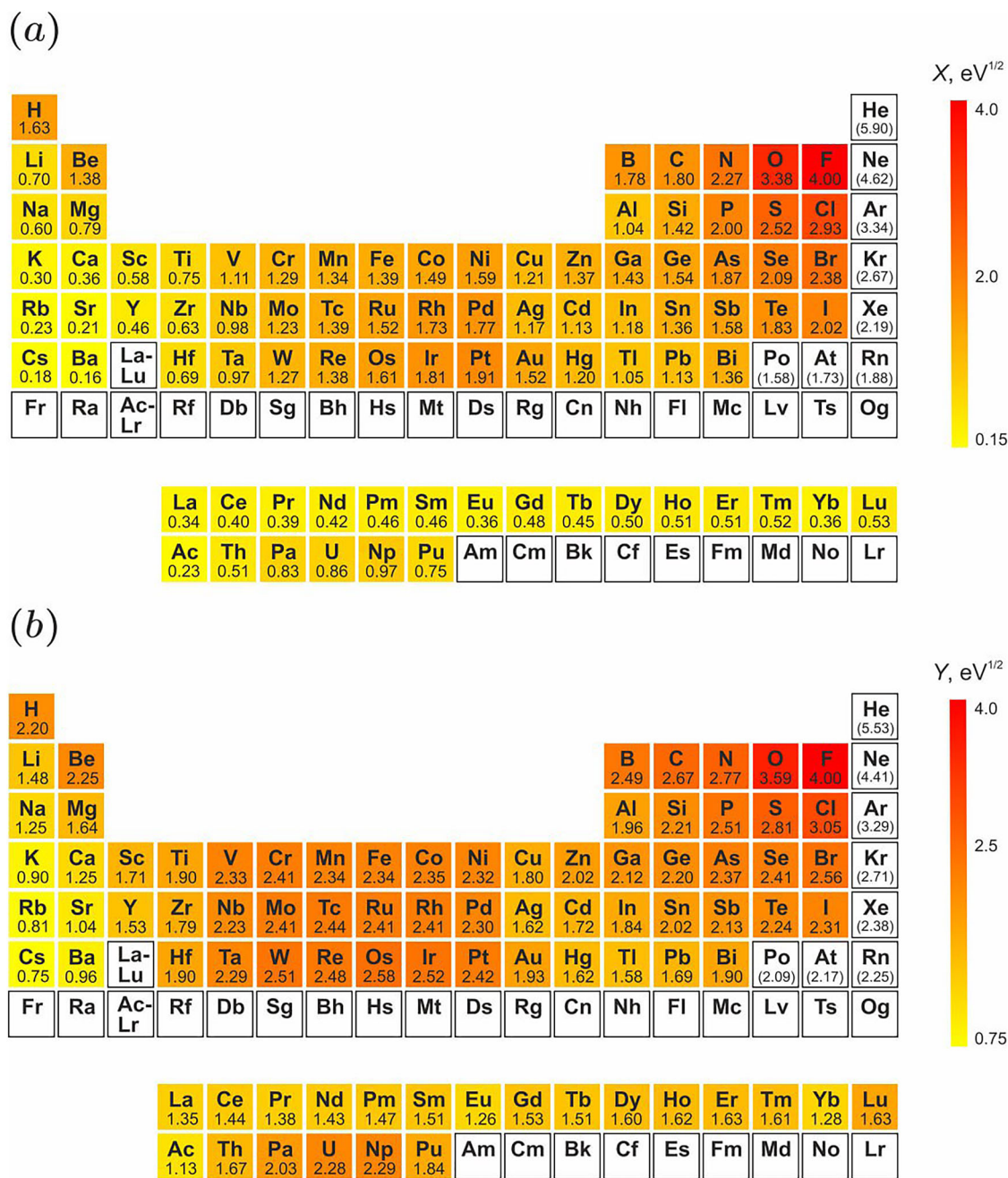
**Electronegativity ( $X$ ) and chemical mismatch parameter ( $Y$ )**

In order to find the values of  $X$  and  $Y$  parameters, a large set of enthalpies of formation of various binary compounds are needed—including systems which do not form stable compounds. The data on stable compounds were primarily taken from *Materials Project*

database<sup>22</sup>, while those for unstable ones—from the *OQMD* database<sup>23,24</sup>. The enthalpies of formation in both sources were computed in the framework of density functional theory using VASP (Vienna Ab-initio Simulation Package)<sup>25–27</sup>. The data cover systems formed by almost all chemical elements from H to Pu, with the



**Fig. 3 | Heat maps of the interaction parameter  $Q$ .** **a** From the actual enthalpies of formation from the *Materials Project*<sup>22</sup> and *OQMD*<sup>23,24</sup> databases and **b** from Eq. (3) using the proposed model and  $X$  and  $Y$  values for all elements. Grid lines delineate boundaries between  $s$ -,  $p$ -,  $d$ -,  $f$ -block elements.

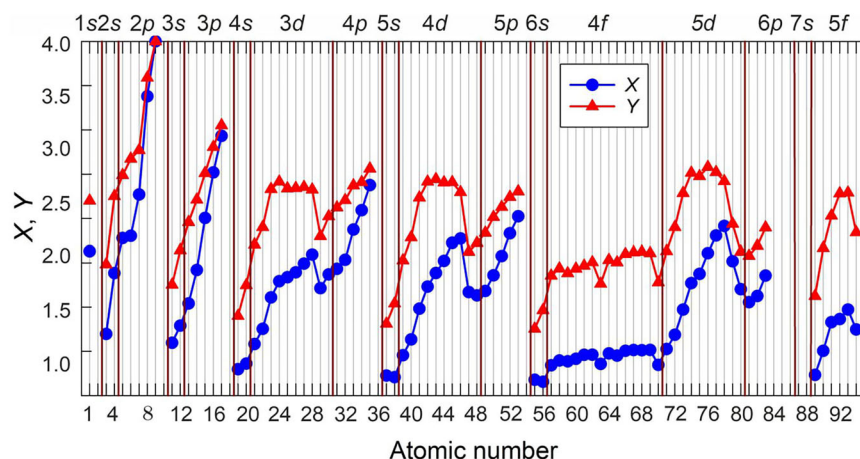


**Fig. 4 | Optimized scales of X and Y.** Optimized scales of **a** electronegativity  $X$  and **b** chemical mismatch  $Y$ . Both quantities are in the units of  $\text{eV}^{1/2}$ . The values for noble gases as well as for polonium and astatine were found by linear extrapolation and are given in parentheses.

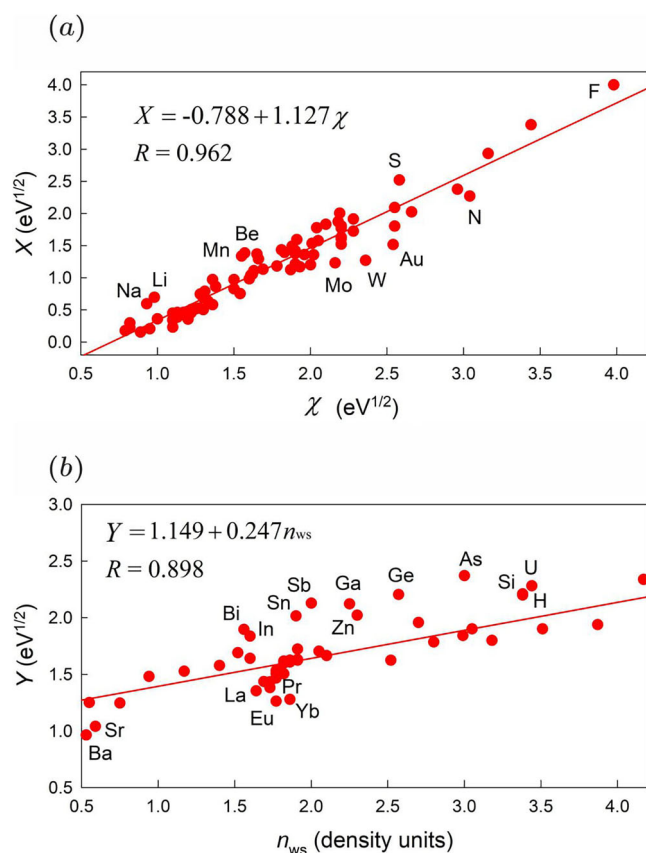
exception of noble gases and highly radioactive Ra, Po, At, and Fr. When calculating the lowest  $Q$ , we excluded compositions with low (<10%) concentration of any component, to avoid division of  $\Delta H_f$  by a very small value of  $4x(1-x)$ . Figure 3a shows the heat map of the lowest  $Q$  values determined this way, and one observes the same pattern as in the map of the lowest enthalpies of formation in Fig. 1a.

Numerical values of  $X$  and  $Y$  of the elements were found by least-squares optimization, so that the values calculated by Eq. (3) be as close as possible to the reference values obtained by density-functional calculations. Optimization started with  $X$  set at Pauling's electronegativities and varying  $Y$  values for those cases where initial  $(Y_{\text{actual}} - Y_{\text{predicted}})^2$  were positive. Then,  $X$  and  $Y$  parameters were optimized simultaneously for the whole dataset. Figure 3b shows the predicted  $Q$  values calculated using Eq. (3). One can see that our simple model gives remarkably accurate values for most binary systems.

Just like Pauling's electronegativity scale, the obtained scales of  $X$  and  $Y$  are relative, in the sense that only the differences of  $X$  (and  $Y$ ) between the two elements matter. Just as in Pauling's scale, we fixed  $X$  (and also  $Y$ ) of fluorine at the value of 4. The resulting scales are shown in Figs. 4 and 5. Both  $X$  and  $Y$  demonstrate strong periodicity (Fig. 5) and roughly similar trends across the periodic table. Within each period, the minimum values belong to alkali and alkaline earth metals, increasing with group number in the  $p$ -block. For  $d$ -elements, the dependences are nonmonotonic and have similar character for all the periods. The first two and the last two  $d$ -metals in each period have lower values of  $Y$  compared to other elements in  $d$ -series. The values of  $X$  increase almost linearly and reach maximum at the eighth element in each  $d$ -block (Ni, Pd, Pt). For  $s$ - and  $p$ -elements both  $X$  and  $Y$  factors decrease down the periodic table. For lanthanoids, they slowly increase with atomic number, with Eu and Yb being anomalous—in



**Fig. 5 | Periodicity of the electronegativity ( $X$ ) and chemical mismatch parameter  $Y$  as a function of atomic number.** Vertical bars delineate boundaries between  $s$ -,  $p$ -,  $d$ -,  $f$ -block elements.



**Fig. 6 | Correlations of model parameters with previously established quantities.** **a** Correlation of our electronegativity  $X$  with Pauling's electronegativity  $\chi_P$  and **b** correlation between our  $Y$  parameter and Miedema's parameter  $n_{ws}$ .

good agreement with chemical anomalies of these elements with half-full and full  $d$ -shell, and consistent with the recent electronegativity scale of Tantardini and Oganov<sup>28</sup>.

The optimized  $X$  values display excellent correlation with Pauling's electronegativity (Fig. 6a)—moderate outliers are Li, Be, S (for which our electronegativity is above the correlation line) and N, Mo, W, Au (for which our electronegativity is below the correlation line). Our  $X$ -scale somewhat mitigates the obvious drawbacks of Pauling's electronegativity scale since it gives better periodicity and smoothness in changing the properties of elements throughout

the periodic table. In particular, the  $X$  values for Mo, W and Au now match the general trend for  $d$ -metals well, whereas their Pauling's electronegativities are greatly overestimated<sup>28</sup>. Correlations of  $X$  parameter with other electronegativity scales are slightly worse than with Pauling's one (Pauling:  $R = 0.96$ , Allen:  $R = 0.94$ , Mulliken:  $R = 0.92$ , Tantardini–Oganov:  $R = 0.87$ ).

It is desirable for an electronegativity scale to correctly predict the polarity of chemical bonds. We compared predictions of our  $X$ -scale, Pauling's<sup>29</sup> and Mulliken's<sup>30</sup> electronegativity scales with atomic charges calculated using Bader analysis<sup>31–35</sup>. The latter was cautiously used as the “ground truth”. Predictions based on our  $X$ -scale are perfect for cases with large electronegativity differences, and are overall very good for  $d$ -metals. In particular, it predicts that molybdenum and tungsten should donate electron density to boron, arsenic and osmium—whereas Pauling's scale incorrectly predicts the opposite (Supplementary Table S1). At the same time, lanthanoids and actinoids have lower  $X$ -parameters than light alkali metals, which results in the incorrect direction of charge transfer in the Li–Eu pair (Mulliken's scale gives the same result). Mulliken's electronegativities correctly predict that hydrogen pulls electron density from all metals and also from boron, phosphorus and arsenic (for our scale, the same is the case except for Rh, Pd, Os, Ir, Pt, B, P, As).

Chemical mismatch parameter  $Y$  correlates well with the original Miedema's mean valence electron densities  $n_{sw}$  ( $R = 0.90$ ), see Fig. 6b. Semimetallic elements (Bi, Sb, Ge, As, Si) have  $Y$ -values above the correlation line, lanthanoids, Sr and Ba have  $Y$ -values below the correlation line. There is also substantial correlation with Slater's atomic radii ( $R = 0.85$ ) and Pauling's electronegativities ( $R = 0.88$ ) and some relationship with the chemical hardness<sup>36,37</sup> although the corresponding correlation is moderate ( $R = 0.64$ ), see Supplementary Fig. S1.

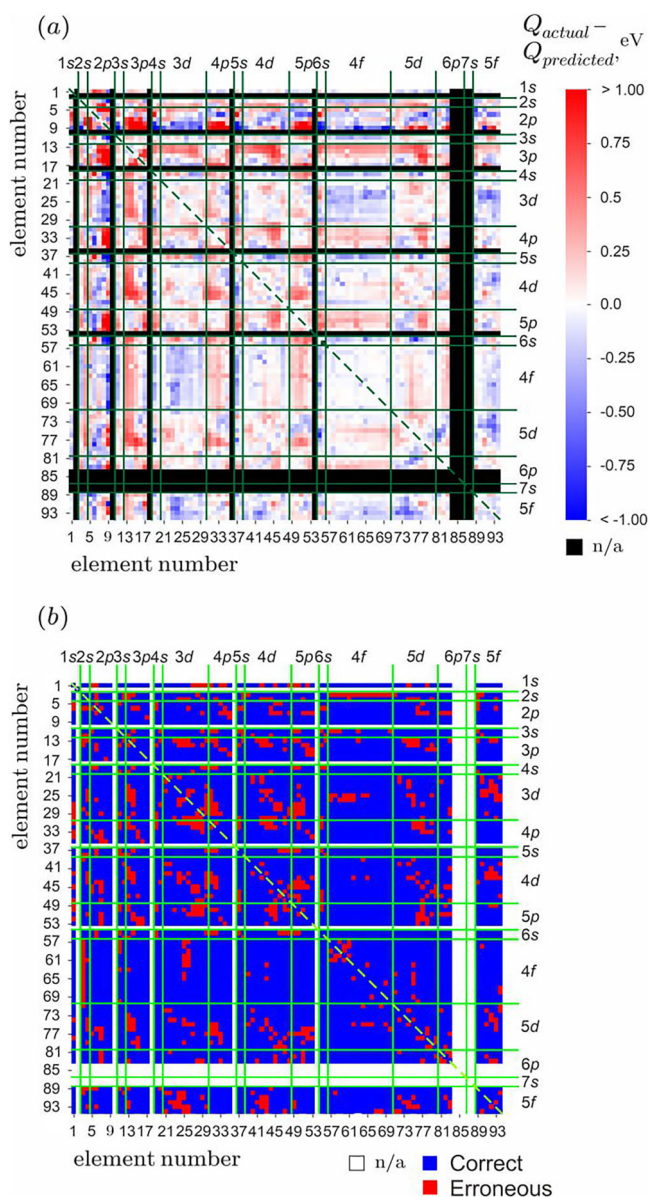
### Performance of the model

Our simplest model characterizing each element by just two parameters gives surprisingly accurate estimates of the enthalpies of formation. The mean squared prediction error for  $Q$  is 0.087 eV<sup>2</sup> and the sign of the enthalpy of formation is correctly predicted in 87.2% cases—the errors being mostly for weakly positive or weakly negative  $Q$  values, see Table 1.

Of course, such a simple model cannot perfectly encompass all chemistry; Fig. 7a shows the differences  $Q_{\text{actual}} - Q_{\text{pred}}$  for all binary systems. One can notice that the model overall underestimates the magnitude of negative  $Q$  (i.e., underestimates the magnitude of the exothermic effect), but this has little impact on the signs of  $Q$ . In particular, for alloys of  $p$ - and  $d$ -metals Miedema included an additional term in Eq. (1) in order to account for extra stabilization caused

**Table 1 | Percentages of correct and incorrect predictions of compound formation**

| $Q_{pred}$ interval, eV | Percentage of binary systems in this interval | True negative, % | False negative, % | True positive, % | False positive, % | Percentage of correct predictions |
|-------------------------|-----------------------------------------------|------------------|-------------------|------------------|-------------------|-----------------------------------|
| $\leq -0.625$           | 23.75                                         | 23.75            | –                 | –                | –                 | 100                               |
| $-0.625 < Q \leq -0.15$ | 23.38                                         | 22.58            | 0.80              | –                | –                 | 96.65                             |
| $-0.15 < Q \leq 0$      | 14.25                                         | 9.44             | 4.82              | –                | –                 | 66.20                             |
| $0 < Q \leq 0.15$       | 19.68                                         | –                | –                 | 13.68            | 6.00              | 69.53                             |
| $0.15 < Q < 0.625$      | 14.83                                         | –                | –                 | 13.77            | 1.06              | 92.84                             |
| $\geq 0.625$            | 4.10                                          | –                | –                 | 4.02             | –                 | 97.9                              |

**Fig. 7 | Accuracy of the model.** **a** Differences between actual and predicted interaction parameters  $Q$  calculated for all the available binary systems and **b** map of correct and incorrect predictions of stability. Red grid lines delineate boundaries between  $s$ -,  $p$ -,  $d$ -,  $f$ -block elements.

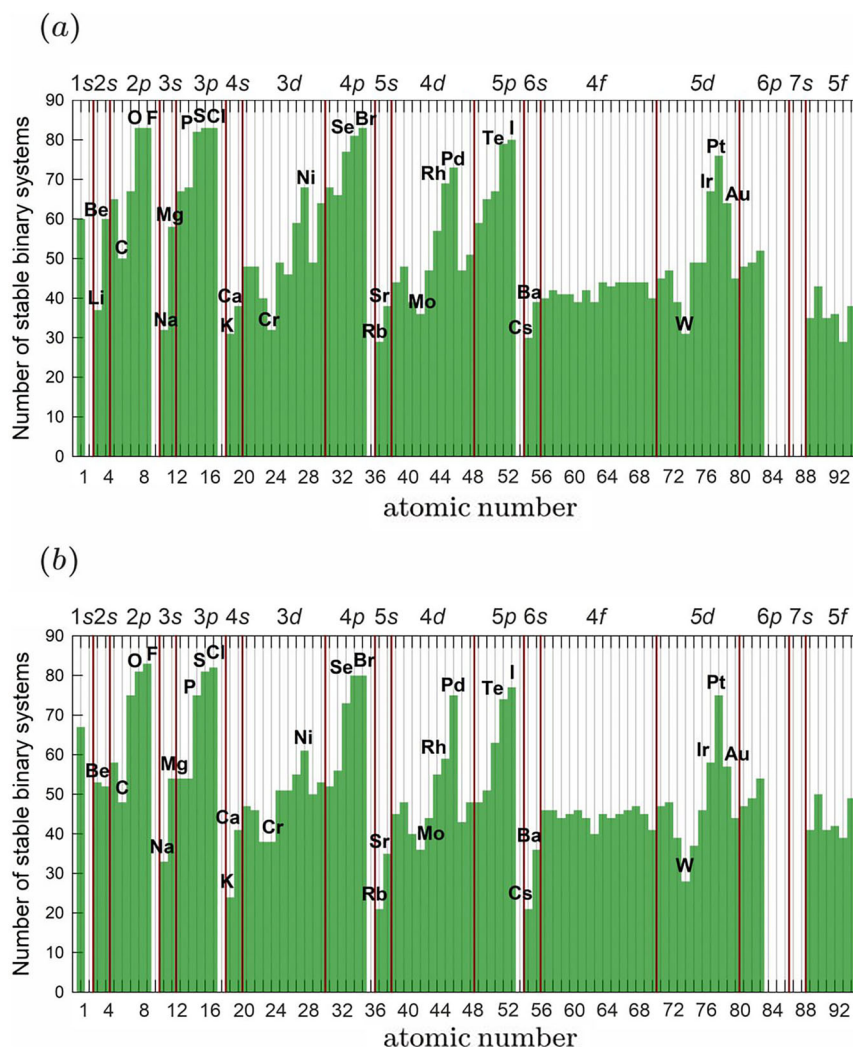
by  $p$ - $d$  hybridization<sup>8,11</sup>; neglect of this correction leads to a periodic pattern in the error map of Fig. 7a. We view these shortcomings as minor, given the combination of simplicity and the ability to correctly capture the characteristic periodic trends in the stability map of binary compounds (cf. Fig. 3a, b) and stability and instability of compounds in most systems without time-consuming procedures of crystal structure prediction and quantum-chemical calculations.

### Chemical trends

Using the databases and our model, one can easily find the number of elements that a given element will form stable compounds with. The resulting highly non-trivial statistics of compound formation across the periodic table (Fig. 8a) are nearly perfectly reproduced by our model (Fig. 8b); we shall discuss these below. One can also explore in more detail the chemistry of any element of interest by creating stability maps of its compounds. Figures 9 and 10 display stability maps of compounds of three elements—oxygen, sodium and carbon. Such stability maps are a new type of graph, enabling a very compact representation of the reactivity of any element. Supplementary Figs. S2–9 give such maps also for compounds of fluorine, nitrogen, sulfur, iodine, lead, boron.

Let us now discuss some interesting chemical trends:

1. The most electronegative elements (F, O, Cl, S) form stable compounds with almost all elements, with the exception of noble gases (fluorine, however, forms stable compounds with Kr, Xe and Rn), see Figs. 8 and 9. Large stabilizing term in Eq. (4) (due to electronegativity difference) between these elements and most of the rest of the periodic table outweighs the chemical mismatch factor in Eq. (4). Figure 9 shows the stability map of binary compounds of oxygen.
2. For the less electronegative halogen, iodine (see Supplementary Fig. S6), we see that it is able to form compounds with almost all elements (except C, Ru, Os, and the noble gases), but the magnitude of  $Q$  is greatly reduced, especially for elements of groups IV–XVI. This is the reason why such compounds as  $I_2O_5$  and many metal iodides decompose at high temperatures into the elements: high entropy of  $I_2$  gas outweighs weak enthalpy of formation of the compounds. This method is widely used for producing high-purity metals, e.g., Ti and Zr. We also see that Pb–I bonding is stronger than Sn–I, hence Sn-based hybrid perovskites will be less stable to decomposition than Pb-based ones.
3. The intuitive expectation that the most electropositive highly active elements (alkali and heavy alkaline earth metals) should react with most elements is clearly broken: these elements do not form stable compounds with most elements. The reason is that these elements have very distinct ultralow  $Y$ -parameters and the destabilizing term  $(Y_A \cdot Y_B)^2$  in Eq. (4) in many binary systems is

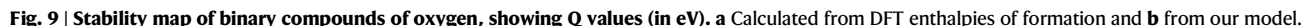


**Fig. 8 | Number of stable binary systems involving each chemical element. a** from DFT enthalpies of formation, **b** from our model.

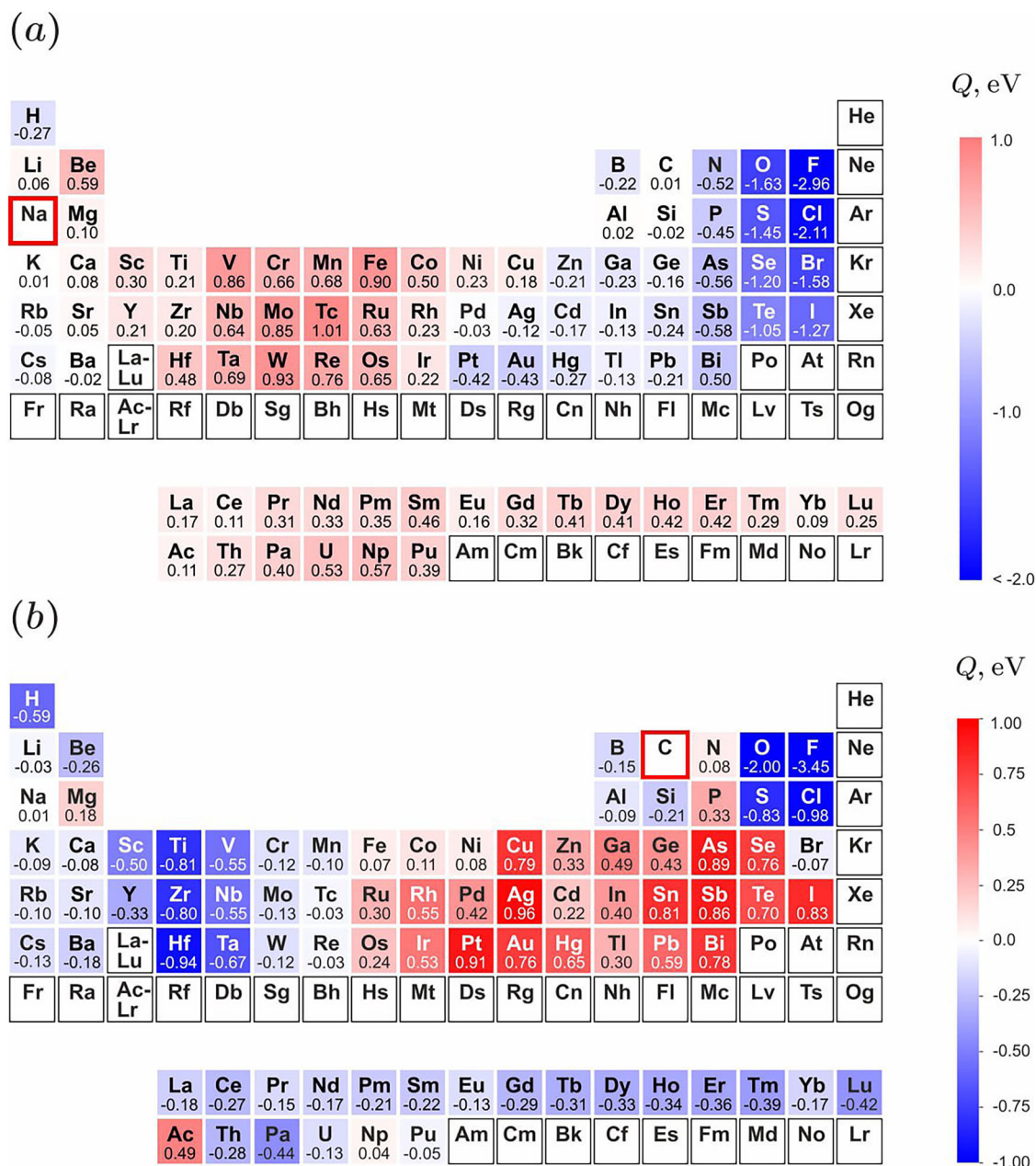
- large enough to outweigh the stabilizing term. Figure 10a gives the stability map for compounds of sodium as an important example. Some nuclear power plants use liquid sodium as the primary coolant, and it is important that liquid sodium does not corrode steel pipes at high temperatures. According to Fig. 10a, the best materials of such pipes are alloys of iron, vanadium, molybdenum and tungsten: their chemical affinity to sodium is the lowest ( $Q$  is largest positive).
4. Likewise, the intuitive expectation that inert metals (Au, Pt and platinoids) should not form stable compounds with most elements is surprisingly broken too: these elements form stable compounds with most elements (see Fig. 8), including  $d$ -,  $f$ - and most  $s$ -metals.
  5. Unlike their heavier analogs, light alkaline earth metals Be and Mg do form compounds with most elements. This can be explained by their more compact sizes, leading to larger  $Y$ -values, more similar to other elements.
  6. For binary systems of  $f$ -elements with each other  $Q$ -values are close to zero, which indicates the tendency to form disordered alloys (in contrast to stoichiometric and ordered intermetallic compounds). The same is also true for systems of  $f$ - and  $d$ -metals, though in this case stable compounds are more common. On the other hand, most pairs of  $d$ -metals have stable compounds, because of the large nearly linear increase of

electronegativity  $X$  in each  $d$ -block from III to X groups, while  $Y$ -parameter of these elements varies non-monotonically and in a narrower range.

7.  $d$ -metals with closed  $d$ -shells (groups XI and XII), i.e., Cu, Ag, Au and to a lesser extent Zn, Cd, Hg, are more inert than other  $d$ -metals due to a pronounced drop in their  $Y$ -factors: e.g., the enthalpy of formation of CuS is  $-0.28$  eV/atom, while that of FeS is  $-0.76$  eV/atom, and that of MnS is  $-1.14$  eV/atom. The  $Q$ -value calculated for the Ag-O system is  $-0.45$  eV, compared with  $-1.86$  eV for Ru-O.
8. Interesting trends are seen in carbides (Fig. 10b): early transition metals (groups III–VII) form stable carbides, whereas late ones (groups IX–XII) do not. The boundary (between groups VII–VIII) is very important as it contains carbides of iron (steel and cast iron) and technetium (spent nuclear fuel—see ref. 38).
9. Group VI metals (Cr, Mo and W) also exhibit unexpected behavior in that they form stable compounds with surprisingly few elements (Fig. 8), and this unexpected behavior is reproduced perfectly by our model. The reason is that in each  $d$ -series, group VI elements (Cr, Mo, W) have the maximum values of the  $Y$ -parameter, very different from most metals (Fig. 5). The intermediate values of electronegativities along with the high values of chemical mismatch parameters  $Y$  make Cr, Mo and W form far fewer stable binary systems than other  $d$ -metals.



Introduction of the interaction parameter  $Q$  allows us to quantify chemical affinity of the elements to each other and build its maps across the periodic table (stability maps). These maps represent



**Fig. 10 | Stability map showing  $Q$  values (in eV) of binary systems, calculated from DFT enthalpies of formation. **a** For sodium and **b** for carbon.**

chemistry of each element in a very compact and insightful form and have been shown above to lead to technologically important conclusions.

Statistics of the reactivity of the elements are very unexpected: “active” alkali and alkaline earth metals react with the fewest elements (second only to noble gases), whereas “inert” noble metals (gold, platinum and platinumoids) form stable compounds with an unexpectedly large number of elements. Our simple model reproduces and explains this behavior.

The extension of this model to ternary and more complex systems is straightforward and explains, among other things, acid-base interactions. For example, for the  $\text{Na}_2\text{O}-\text{CO}_2$  system we can estimate  $X$  and  $Y$  values of  $\text{Na}_2\text{O}$  and  $\text{CO}_2$  as arithmetic means of the atomic parameters. Substituting them into Eq. (3), we obtain  $Q(\text{Na}_2\text{O}-\text{CO}_2) = -0.18$  eV. The variety of such, ternary and more complex, compounds of the alkali and alkaline earth elements is large (in contrast to binary ones),

because  $Y$ -parameters of bases such as  $\text{Na}_2\text{O}$  is much less outstanding than that of elemental Na, leading to much smaller destabilizing term  $(\Delta Y)^2$  in Eq. (3); the stabilizing term  $-(\Delta X)^2$  is also reduced, but the balance favors stability of compounds in a wide range of systems.

Our model can also be extended to high pressure, but some expectations about high-pressure reactivity can be drawn a priori. It has been shown<sup>37</sup> that the spread of electronegativities increases with pressure, so the stabilizing term  $-(\Delta X)^2$  should overall increase with pressure. At the same time, we expect a decrease in the destabilizing term  $(\Delta Y)^2$ : elements with anomalously low  $Y$ -values (e.g., alkali metals) are characterized by large size and high compressibility. Under pressure their  $Y$ -parameters will rise the most, approaching  $Y$ -values of other elements. As a result of increasing stabilizing and decreasing destabilizing effects, we expect more elements to react with each other under pressure. For example, K-Fe system has no stable binary compounds at ambient conditions, but such compounds have been

predicted to appear under high pressure<sup>40,41</sup>. However, this expectation is based on the interpretation of  $\chi$ -parameter as a measure of mean valence electron density of an atom, and needs to be checked.

## Data availability

Data are available on request to A.R.O. Source data are provided with this paper.

## References

- Pauling, L. The nature of the chemical bond. IV. The energy of single bonds and relative electronegativity of atoms. *J. Am. Chem. Soc.* **54**, 3570–3582 (1932).
- Pauling, L. *The Nature of the Chemical Bond and the Structure of Molecules and Crystals: An Introduction to Modern Structural Chemistry*. Chapter 3 (Cornell University Press, Ithaca, New York, 1960).
- Newnham, R. E. *Physical properties of materials: Anisotropy, Symmetry, Structure*. (Oxford University Press Inc., Oxford and New York, 2005).
- Li, K., Wang, X., Zhang, F. & Xue, D. Electronegativity identification of Novel Superhard materials. *Phys. Rev. Lett.* **100**, 235504 (2008).
- Lyakhov, A. O. & Oganov, A. R. Evolutionary search for superhard materials: methodology and applications to forms of carbon and TiO<sub>2</sub>. *Phys. Rev. B* **84**, 092103 (2011).
- Urusov, V. S. “Energetic Crystal Chemistry” (in Russian). (Nauka, 1975).
- Miedema, A. R. A simple model for alloys. Part I. Rules for the alloying behavior of transition metals. *Philips Techn. Rev.* **33**, 149–160 (1973).
- Miedema, A. R. A simple model for alloys. Part II. The influence of ionicity on the stability and other physical properties of alloys. *Philips Techn. Rev.* **33**, 196–202 (1973).
- Miedema, A. R. The electronegativity parameter for transition metals: heat of formation and charge transfer in alloys. *J. Less Comm. Met.* **32**, 117–136 (1973).
- Miedema, A. R., Boom, R. & De Boer, F. R. On the heat of formation of solid alloys. *J. Less Comm. Met.* **41**, 283–298 (1975).
- Miedema, A. R. On the heat of formation of solid alloys. II. *J. Less Comm. Met.* **46**, 67–83 (1976).
- De Boer, F. R., Boom, R., Matten, W. C. M., Miedema, A. R. & Niessen, A. K. *Cohesion in Metals: Transition Metal Alloys*. Chapter IV (North-Holland, 1989).
- Zhang, R. F., Sheng, S. H. & Liu, B. X. Predicting the formation enthalpies of binary intermetallic compounds. *Chem. Phys. Lett.* **442**, 511–514 (2007).
- Zhang, R. F. & Rajan, K. Statistically based assessment of formation enthalpy for intermetallic compounds. *Chem. Phys. Lett.* **612**, 177–181 (2014).
- Gallego, L. G., Somoza, J. A. & Alonso, J. A. Glass formation in ternary transition metal alloys. *J. Phys.: Condens. Matter* **2**, 6245–6250 (1990).
- Zhang, R. F. & Liu, B. X. Proposed model for calculating the standard formation enthalpy of binary transition-metal systems. *Appl. Phys. Lett.* **81**, 1219–1221 (2002).
- Gonçalves, A. P. & Almeida, M. Extended Miedema model: predicting the formation enthalpies of intermetallic phases with more than two elements. *Phys. B* **228**, 289–294 (1996).
- Das, N. et al. Miedema model based methodology to predict amorphous-forming-composition range in binary and ternary systems. *J. Alloy. Compd.* **550**, 483–495 (2013).
- Zhang, R. F., Zhang, S. H., He, Z. J., Jing, J. & Sheng, S. H. Miedema calculator: a thermodynamic platform for predicting formation enthalpies of alloys within framework of Miedema’s theory. *Comput. Phys. Commun.* **209**, 58–69 (2016).
- Pettifor, D. G. A quantum-mechanical critique of the Miedema rules for alloy formation. *Solid State Phys.* **40**, 43–92 (1987).
- Williams, A. R., Gelatt, C. D. Jr. & Moruzzi, V. L. Microscopic basis of Miedema’s empirical theory of transition-metal compound formation. *Phys. Rev. Lett.* **44**, 429–433 (1980).
- Jain, A. et al. Commentary: the materials project: a materials genome approach to accelerating materials innovation. *APL Mater.* **1**, 011002 (2013).
- Saal, J. E., Kirklin, S., Aykol, M., Meredig, B. & Wolverton, C. Materials design and discovery with high-throughput density functional theory: the open quantum materials database (OQMD). *JOM* **65**, 1501–1509 (2013).
- Kirklin, S. et al. The open quantum materials database (OQMD): assessing the accuracy of DFT formation energies. *npj Comput. Mater.* **1**, 15010 (2015).
- Kresse, G. & Furthmüller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput. Mater. Sci.* **6**, 15–50 (1996).
- Kresse, G. & Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **54**, 11169–11186 (1996).
- Kresse, G. & Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B* **59**, 1758–1775 (1999).
- Tantardini, C. & Oganov, A. R. Thermochemical electronegativities of elements. *Nat. Commun.* **12**, 2087 (2021).
- Allred, A. L. Electronegativity values from thermochemical data. *J. Inorg. Nucl. Chem.* **17**, 215–221 (1961).
- Mulliken, R. S. A new electroaffinity scale; together with data on valence states and on valence ionization potentials and electron affinities. *J. Chem. Phys.* **2**, 782–793 (1934).
- Bader, R. F. W. “Atoms in Molecules: A Quantum Theory” (Clarendon Press, 1994).
- Tang, W., Sanville, E. & Henkelman, G. A grid-based Bader analysis algorithm without lattice bias. *J. Phys. Condens. Matter* **21**, 084204 (2009).
- Sanville, E., Kenny, S. D., Smith, R. & Henkelman, G. An improved grid-based algorithm for Bader charge allocation. *J. Comp. Chem.* **28**, 899–908 (2007).
- Henkelman, G., Arnaldsson, A. & Jónsson, H. A fast and robust algorithm for Bader decomposition of charge density. *Comput. Mater. Sci.* **36**, 354–360 (2006).
- Yu, M. & Trinkle, D. R. Accurate and efficient algorithm for Bader charge integration. *J. Chem. Phys.* **134**, 064111 (2011).
- Pearson, R. G. Absolute electronegativity and hardness: application to inorganic chemistry. *Inorg. Chem.* **27**, 734–740 (1988).
- Dong, X., Oganov, A. R., Cui, H., Zhou, X.-F. & Wang, H.-T. Electronegativity and chemical hardness of elements under pressure. *PNAS* **119**, e2117416119 (2022).
- Wang, Q. G. et al. Explaining stability of transition metal carbides – and why TcC does not exist. *RSC Adv.* **6**, 16197–16202 (2016).
- Yue, C. et al. Formation of copper boride on Cu(111). *Fund. Res.* **1**, 482–487 (2021).
- Parker, L. J., Atou, T. & Badding, J. V. Transition element-like chemistry for potassium under pressure. *Science* **273**, 95–97 (1996).
- Adeleke, A. A. & Yao, Y. Formation of stable compounds of potassium and iron under pressure. *J. Phys. Chem. A* **124**, 4752–4763 (2020).

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## Author contributions

A.R.O: conceptualization, development of the model and manuscript writing. M.G.K. research, results, manuscript writing.

## Competing interests

The authors declare no competing interests.

## Additional information

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