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Pauling's Second Rule and Its Applications: From Inorganic Compounds to Understanding the Function of ATP

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Abstract

Pauling's five rules for ionic crystals emerged as a generalization of the first experimentally determined crystal structures of inorganic compounds (primarily minerals). It was later discovered that the second rule (the rule of bond valence balance) is particularly powerful and universal. This essay explains how this rule can be used to explain very easily the differences in the chemistry of entire classes of chemical compounds (e.g., silicates and phosphates), as well as to elucidate the function of ATP as the universal energy currency for all life forms.

Keywords: mineralogy, biochemistry, chemical bonding

In Pauling's own words [1, 2] his second rule is stated as follows:

"Let ze be the electric charge of a cation and v its coordination number; we then define the strength of the electrostatic bond to each coordinated anion as

$$s = z/v \tag{1}$$

and make the postulate that in a stable ionic structure the valence of each anion, with changed sign, is exactly or nearly equal to the sum of the strengths of the electrostatic bonds to it from the adjacent cations, that is, that

$$\xi = \sum_i s_i = \sum_i z_i/v_i \ , \tag{2}$$

in which - ξe is the electric charge of the anion and the summation is taken over the cations at the centers of all the polyhedra of which the anion forms a corner".

Now it is well known that this rule is applicable not only to ionic crystals, but is universal. However, instead of electric charge in Eq. (1-2) one should use valence (i.e., the number of electrons donated or taken towards the formation of chemical bonds). The atomic charge is a vague concept with multiple possible definitions (see [3] for a very recently proposed new definition), whereas valence is well defined (at least in non-metallic substances). Also, s is now called bond valence – and it can be imagined that the valence of the cation is equally partitioned between all bonds formed by it, so each bond having the same valence s.

Let us illustrate how this rule works by considering silicates, all of which at normal pressure contain silicon in the tetrahedral coordination (Fig. 1a), surrounded by four oxygens (hence, silicon's coordination number v = 4). The valence of silicon is also equal 4, hence according to Eq. (1) the Si-O bond valence $s = 4/4 = 1$. Analogous calculation for the C-O bond in the CO_3-group (Fig. 1b) gives $s = 4/3$.

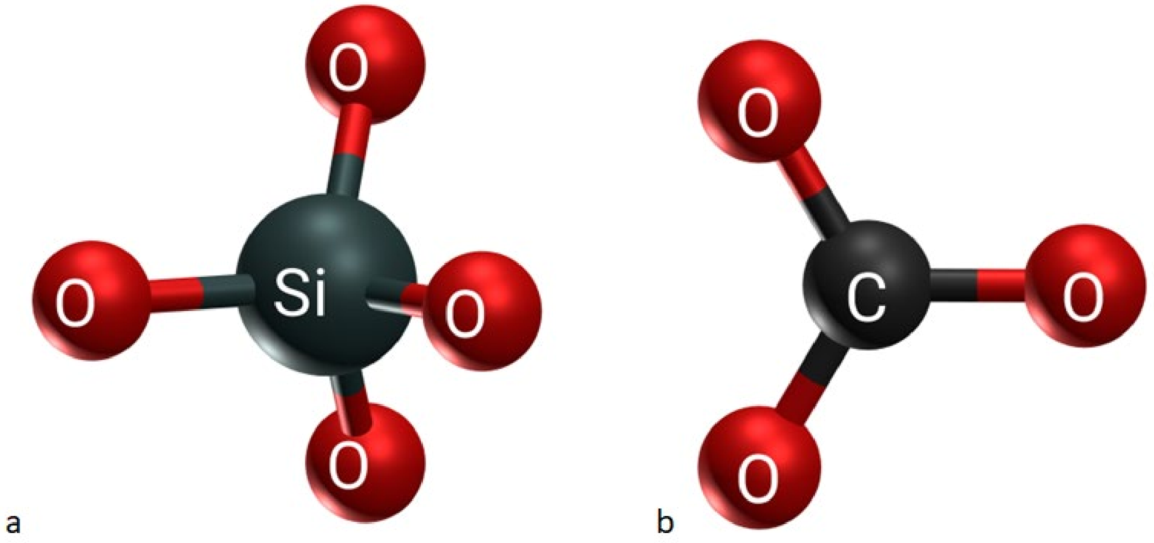

Figure 1. SiO_4-tetrahedron and CO_3 triangle found in all silicates and carbonates, respectively, at ambient pressure. The geometries shown here were taken from the crystal structure of minerals zircon ($ZrSiO_4$) and calcite ($CaCO_3$), but very similar geometries will be found in all other cases.

To satisfy Pauling's second rule, Eq. (2), the sum of bond valences on a given oxygen should equal oxygen's valence (equal to 2). How can this be satisfied? For silicates there are two ways – (1) an oxygen is shared by two SiO_4-tetrahedra, receiving one valence unit from each of the two neighboring silicon atoms (see Fig. 2a, where this is shown for SiO_2 quartz and $MgSiO_3$ enstatite), (2) an oxygen is shared by one SiO_4-tetrahedron (taking one valence unit from its silicon) and other cation polyhedra, the number of which is such that Eq. (2) is satisfied as precisely as possible. From these polyhedra the remaining one valence unit must come. Fig. 2c shows the structure of zircon $ZrSiO_4$, which can be assembled from SiO_4-tetrahedra and ZrO_8-units. The bond valence of each Zr-O bond is equal to the valence of Zr (it is equal to 4) divided by its coordination number (it is 8 in this structure), that is s(Zr-O)= ½. In the structure of zircon, each oxygen should therefore be bonded to one silicon and two zirconium atoms. Indeed, this is the case.

Note that it is forbidden for three SiO_4-tetrahedra to share the same oxygen atom – in this case the sum of Si-O bond valences on that oxygen would be equal to 3, which is very different from the valence of oxygen (two). Indeed, all the huge number of known silicate structures as well as all SiO_2 modifications (including glass) built from SiO_4-tetrahedra satisfy this rule. SiO_4-tetrahedra are allowed to polymerize sharing common oxygens, but no more than two tetrahedra can share the same oxygen.

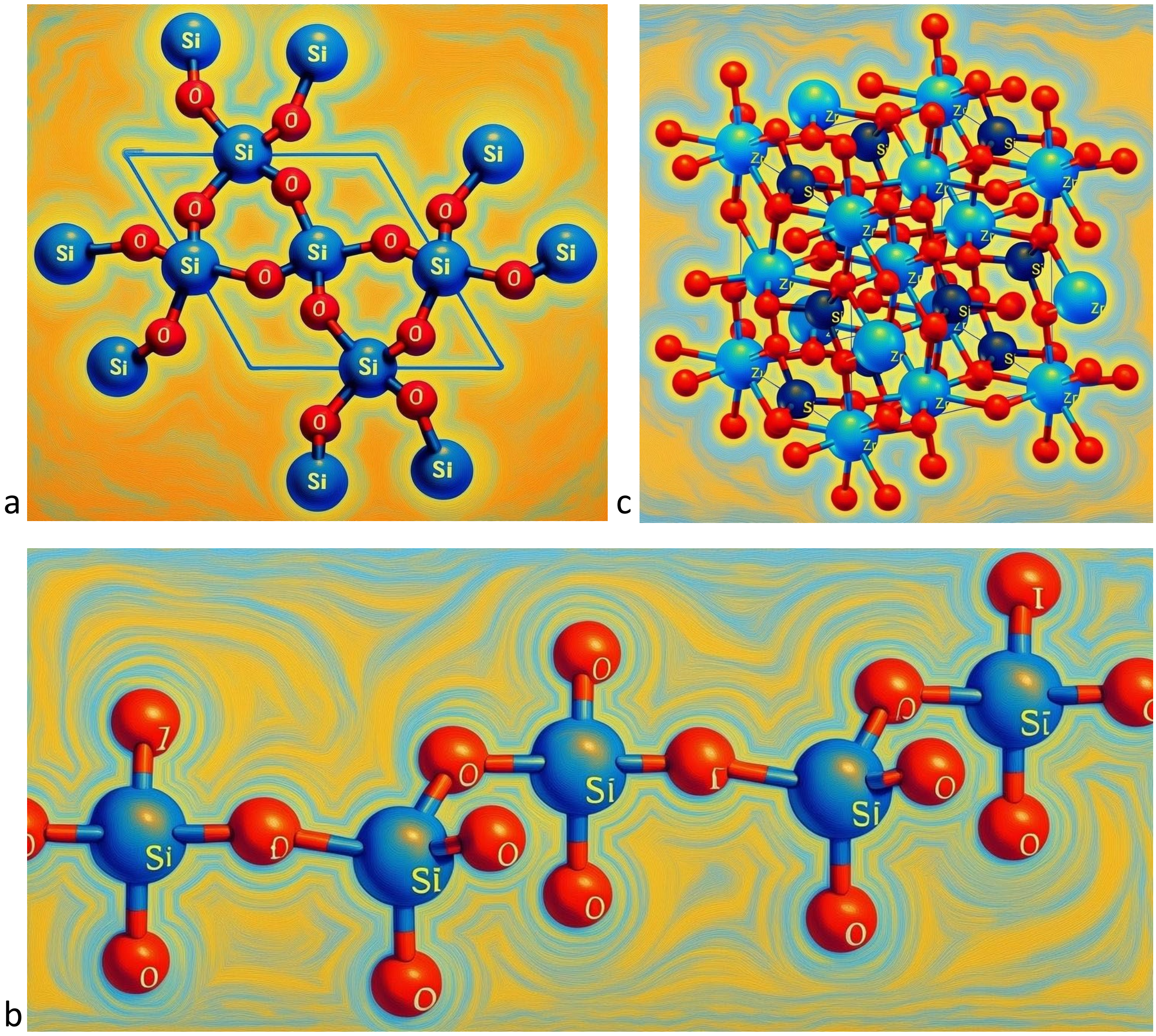

Figure 2. Some silicate motifs: (a) structure of quartz SiO_2, where corner-sharing SiO_4-tetrahedra form a 3D framework, (b) silicate chain from the structure of $MgSiO_3$ enstatite, where corner-sharing SiO_4-tetrahedra form an infinite 1D chain, (c) zircon $ZrSiO_4$, where there are no connections between SiO_4-tetrahedra.

Let us look at other classes of compounds. For example, carbonates at ambient pressure contain CO_3-triangles and (since carbon has valence 4) the valence of each C-O bond is equal to 4/3. If two such triangles share an oxygen, the oxygen will receive 8/3 = 2.67 valences from its neighboring carbons, which is much greater than oxygen's valence. Hence, Pauling's second rule forbids polymerization of CO_3-triangles, demanding that they be isolated from each other. The exceptions from this are extremely rare. At high pressures, however, coordination numbers increase and carbonates are based on CO_4-tetrahedra (e.g., [4]), the C-O bond valence is 4/4=1, just like in silicates, and polymerization of CO_4-tetrahedra is perfectly possible. All these expectations are fully consistent with both experimentally determined and predicted crystal structures.

Table 1 shows conclusions based on Pauling's second rule for various classes of compounds. This rule correctly predicts that borate ions (both BO_3-triangles and BO_4-tetrahedra) can polymerize, but nitrate-groups cannot (the only exception is the very reactive N_2O_5 molecule). This is again highly consistent with experiment. It is amazing how powerful this simple rule turns out to be.

Table 1. Inferences on crystal chemistry of various inorganic compounds from Pauling's second rule.

Class of compounds	Anionic group /cation-anion bond valence	Allowed to polymerize? /sum of bond valences on oxygen	Is polymerization observed?
Silicates	SiO_4 /1	Yes / 2	Yes, widely
Carbonates	CO_3 /1.33	No / 2.67	Almost never
High-pressure carbonates	CO_4 /1	Yes / 2	Yes, widely
Borates	BO_3 /1, BO_4 /0.75	Yes / 1.5-2.0	Yes, widely
Nitrates	NO_3 /1.67	No / 3.33	No, except N_2O_5
Phosphates	PO_4 /1.25	No / 2.5	Yes, sometimes
Sulfates	SO_4 /1.5	No / 3	Seldom
Chromates	CrO_4 /1.5	No / 3	Seldom
Perchlorates	ClO_4 /1.75	No / 3.5	No, except Cl_2O_7
Permanganates	MnO_4 /1.75	No / 3.5	No, except Mn_2O_7

Now let us step into a very interesting gray zone, going from the already discussed silicates (with SiO_4-groups) to phosphates (PO_4-groups) to sulfates (SO_4-groups) to perchlorates (ClO_4-groups). Along this series the valence of the central cation increases, and so does the bond valence, making polymerization of these tetrahedral ions more and more in violation of Pauling's second rule – by 0.5, 1.0, 1.5 valence units, respectively. Polymerization of MO_4-tetrahedra is unfavorable for M = P, S, Cl, progressively increasing in this series and making the polymeric structures highly reactive. For example, Cl_2O_7 molecule, the only known case of polymerization of ClO_4-groups, has a notoriously high enthalpy of formation from the elements, +238.1 kJ/mole in the liquid and +272.0 kJ/mole in the gaseous state [5], meaning that its formation from the elements is highly unfavorable. Cl_2O_7 exothermically reacts with water forming perchloric acid:

$$Cl_2O_7 + H_2O = 2HClO_4 \tag{3}$$

This can be viewed as hydrolytic cleavage of the Cl-O-Cl brigde. The experimental enthalpy of reaction (3) at room temperature is -33.43 kJ/mole [5]. Pyrosulfate-ion $S_2O_7^{2-}$ is well known, but is prone to hydrolysis similar to (3) and also exothermic by 68.55 kJ/mole [5]:

$$H_2S_2O_7 + H_2O = 2H_2SO_4 \tag{4}$$

Phosphate tetrahedra more easily polymerize forming well-known pyrophosphoric acid $H_4P_2O_7$, numerous oligophosphoric acids such as $H_5P_3O_{10}$ and $H_6P_4O_{13}$ and others, and metaphosphoric acid HPO_3 where corner-sharing PO_4-tetrahedra form infinite chains akin to metasilicate chain shown in Fig. 2b. Another limiting case is phosphoric anhydride P_4O_{10}, the structure of which is shown in Fig. 3a.

Hydrolysis reactions

$$H_4P_2O_7 + H_2O = 2H_3PO_4 \tag{5}$$

$$P_4O_{10} + 6H_2O = 4H_3PO_4 \tag{6}$$

have experimental enthalpies of -16.27 kJ/mole and -368.62 kJ/mole, respectively [5], at normal conditions, so both are exothermic. Unfavorable P-O-P linkages can be viewed as storing chemical energy. The former reaction corresponds to a hydrolysis of only one P-O-P linkage (carrying 16.3 kJ/mole worth of energy), whereas the latter has six (each one storing 61.4 kJ/mole worth of energy). The much greater value in the case of P_4O_{10} is due to its strained geometry. One can recall that P_4O_{10}

is widely used in chemical laboratories as a powerful dehydrating agent – precisely because of its highly exothermic reaction with water.

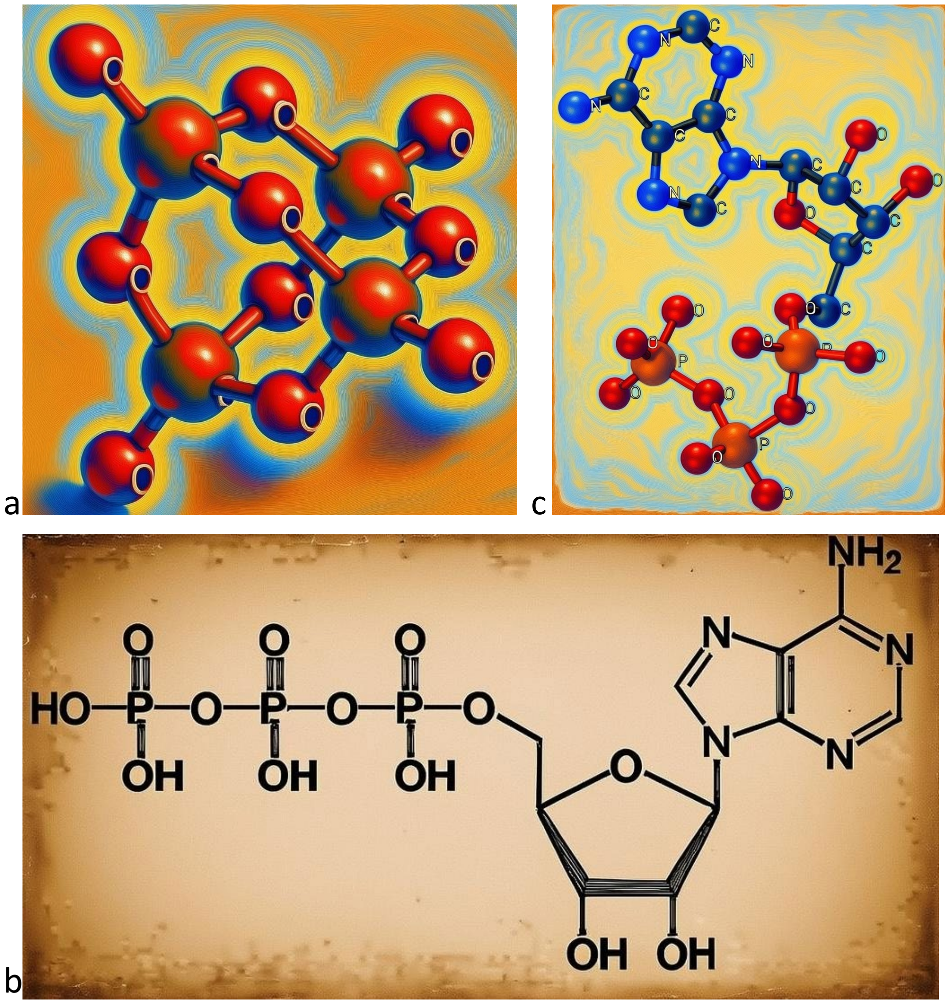

Figure 3. Polymerization of PO_4 tetrahedra: (a) in P_4O_{10}, (b,c) in adenosine triphosphate (ATP). (b) is a classical structural scheme of ATP, which does not reflect all aspects of 3D structure, (c) 3D-structure of ATP. The P-O-P angles in P_4O_{10} molecule and in ATP are 123° and 132-139°, respectively, reflecting the more strained bonding in P_4O_{10}. Note that hydrogen atoms are omitted in (c), as their positions were not reported in the experimental paper [6] (from which I plotted the structure) as X-ray is not sensitive to hydrogen atoms.

Another case is the sequential hydrolysis of adenosine triphosphate, ATP $(C_{10}H_{16}N_5P_3O_{13})^{4-}$ to adenosine diphosphate, ADP $(C_{10}H_{15}N_5P_2O_{10})^{3-}$ to adenosine monophosphate, AMP $(C_{10}H_{15}N_5P_2O_{10})^{2-}$:

$$\mathrm{ATP} + H_2O = \mathrm{ADP} + H_3PO_4 \tag{7}$$

$$\mathrm{ADP} + H_2O = \mathrm{AMP} + H_3PO_4 \tag{8}$$

The former reaction is exothermic by 30.5 kJ/mole, the latter by 15.1 kJ/mole [7]. Note that reactions (5) and (8) are directly analogous to each other, and their exothermic effects are very close.

Pauling's second rule not only explains structural chemistry of entire classes of inorganic compounds, but sheds light onto biological phenomena. All living cells share a small number of common, universal molecules – among them are ATP (the universal energy currency of all cells in all organisms), five nucleobases (building blocks of DNA and RNA), phospholipids (materials of cell membranes), twenty amino acids (building blocks of proteins), carbohydrates (structural polymers and fuel for cells). The most surprising thing in this list is the importance of phosphorylated organic molecules – ATP, nucleobases, phospholipids. Life is very economic and parsimonious, trying to use and reuse the same building blocks whenever possible. ATP and nucleobase adenosine have very different functions in the cell, but their sole chemical difference lies in the fact that ATP contains an inorganic triphosphate "tail". It is this triphosphate group that enables the energy storage/release function of ATP, as I discussed above. Why did nature choose phosphorus for that? Because abundant alternatives – silicon, carbon, sulfur, - are unsuitable. SiO_4-groups easily polymerize, but as the result of their polymerization is stable, no energy is stored. On the other hand, SO_4- and CO_3-groups tend not to polymerize at all, and whenever they do, the result is too unstable - yes, there is a great deal of energy stored in such compounds, but creating and keeping them is too difficult, as they are too easily hydrolyzed. Thus, the extraordinary biochemical role of phosphate is a result of a compromise. This extends even further: when nucleobases form a DNA or RNA molecule (which happens with direct participation of ATP), they join via phosphate PO_4-groups by means of phosphodiester linkages that act as a "glue" to hold DNA or RNA together. Each of these linkages is in slight violation of Pauling's second rule (with the sum of bond valences on the oxygen equal to 2.25), which makes it easier for enzymes to cleave DNA and RNA whenever needed. Once again, nature found a compromise – phosphodiester linkages are stable enough to be formed and maintained for a long time, but their small degree of instability (due to a slight violation of Pauling's rule) makes them suitable targets for enzymatic cleavage. DNA and RNA are thus easy to assemble and easy to disassemble, like a Lego constructor.

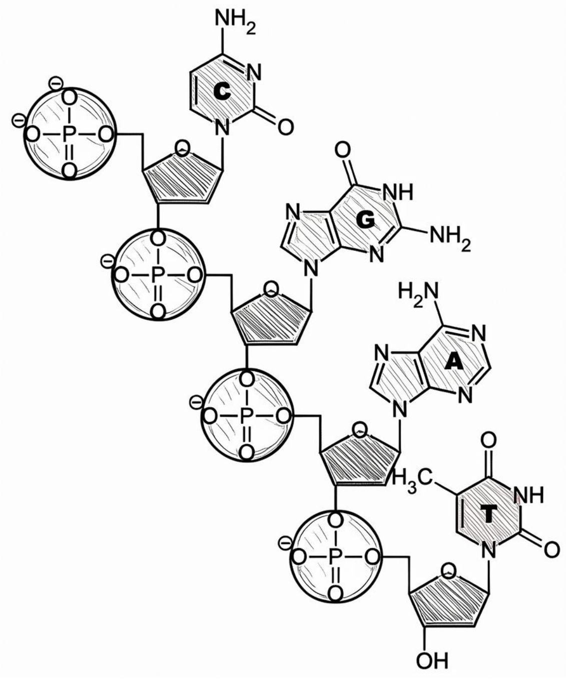

Figure 4. Four nucleobases (C = Cytozine, G = Guanine, A = Adenine, T = Thymine), joined by PO_4 tetrahedra to form a strand of DNA. RNA strand is made of the same nucleobases, except that instead of thymine it contains uracil.

I believe that this view, inspired by inorganic crystal chemistry, will prove fruitful in biochemistry and other fields. Such simple and universal rules have always been fruitful in science.

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