Entropy and the Shelf Model: A Quantum Physical Approach to a Physical Property

Arnd H. Jungermann

Department of Chemistry, Markgräfler Gymnasium, Bismarckstr. 10, D-79379 Müllheim, Germany;
076315245@tiscali.de

Standard entropy values of solids are small, those of gaseous substances are large, and the values for liquids lie in between. What creates a problem is the estimation of comparing pairs of solids, liquids, or gases. One example could be the assessment of whether the molar entropy of helium is smaller, equal, or larger than that of krypton. This article makes a unique contribution to the solution of this problem.

The term "entropy" was first used in the 19th century by Clausius in classical thermodynamic theory and also later in statistical mechanics by Boltzmann. But neither classical thermodynamic theory nor statistical mechanics could solve the problem of a black body. Planck combined entropy considerations of both theories, which resulted in the energy quantization and the correct radiation law. This led to the discipline of quantum physics and with the help of the Schrödinger equation it was possible to calculate the energetic eigenvalues of substances. Thereby a deeper understanding of the thermodynamic term "entropy" was achievable. Kittel and Krömer *(1)* referred to this when they pointed out: *Ohne Quanten-Begriffe gibt es keine diskreten und damit abzählbaren Zustände und ohne abzählbare Zustände bleibt die Entropie unverständlich.* [Transl.: *Without quantum terms there are no discrete and thus countable states and without countable states entropy remains incomprehensibl*e.]

Unlike most other thermodynamic quantities, which have an arbitrarily defined zero level, entropy values are listed in thermodynamic tables *(2)* for specific substances as absolute values $S°$ (not so $\Delta S°$). Therefore, molar entropy values are physical properties of the listed substances and a main task of chemistry is to understand this property from the internal structure of the substances, that is, the particle masses, bonding forces, electronegativity, bond distances, particle volume and so on. Applying three simple rules concerning energy quantization, this article proposes that it is possible to realize that entropy values reflect the differences of particle masses or of chemical bonds.

This article will introduce a model that is easy to apply in order to understand the relation between entropy on the one hand and energy, heat, and temperature on the other. With this new model it is possible to carry out simple calculations showing the systematic trends that are observable from entropy phenomena. Thus it contributes to the understanding of entropy as a quantum physical phenomenon. Former methods of entropy interpretation were rather unconvincing as they tried to understand entropy in terms of order and disorder *(3, 4)*. In recent years entropy has been described in connection with particle motion and dispersal of energy *(5–8)*. But entropy as a physical property, has not yet been discussed. The model introduced in this article has already been successfully applied for some years by the author in chemistry and physics lessons in a secondary school.

The Shelf Model

The Model

In 1901, Max Planck *(9)* discovered that energy does not occur in indefinitely large or small portions but only distinct portions. One of these portions is referred to as an energy quantum. Energy is understood as stored work or stored heat. As the basis for a model of energy storing it is therefore reasonable to choose a tool, which we use for the storage of everyday items: shelves. It is best to use low-cost shelves (Figure 1) that we often find in budget furniture stores because of the numerous analogies between storing items in shelves and storing energy by natural systems (Figure 2).

- The vertical walls constitute the energy scale and correspond to molecular energy levels.

- The shelves cannot be fixed at any height, only distinct positions are allowed depending on the substance
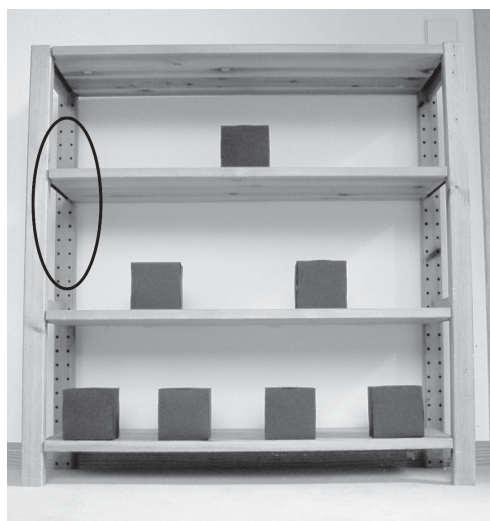

Figure 1. Low-cost shelves, showing that for each shelf only distinct heights are possible.
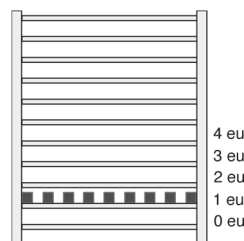

Figure 2. Low-cost shelf model showing the energy scale with equidistant spacing of the shelves and nine particles with nine energy units (eu).

or system. This corresponds to the quantum physical eigenvalues.

- A smallest quantum leap exists.
- The lowest shelf may be fixed at different heights.[1]
- Different widths represent different volumes for the particles (uncertainty of position).
- A few shelves behind each other on the same height represent degenerated energy levels.

Some illustrative examples of how the model is to be used will follow. Figure 3 shows three shelves and, as in Figure 2, there are nine particles with nine energy units (eu's).

Although different distributions are possible, only the particle distribution like that in Figure 3C is of importance. The number of occupied energy levels is greater than in the other cases and only the four lowest levels are concerned. The occupation numbers decrease with increasing height of the energy level. The values shown in Figure 3 had been calculated by

$$\sigma = \frac{S}{k_{B}} = \ln W; \quad W = \frac{N!}{\prod n_i !} \qquad (1)$$

where σ is the entropy, S is the conventional entropy, k_{B} is Boltzmann's constant, N is the total number of particles, and n_i is the occupation numbers.

The examples of Figure 3 show three different accessible states of a nine-particle system with the total energy of 9 eu and each of these states consist of a number of microstates. Equation 1 calculates the number of possible permutations of the particles (Figure 4) keeping the occupation numbers of these nine particles on the different energy levels. This number of permutations is the number of accessible mi-

crostates. In the example of Figure 3C, the numbers are $N = 9$, $n_1 = 4$, $n_2 = 2$, $n_3 = 2$, and $n_4 = 1$, so $W = 9!/(4!2!2!1!) = 3780$ (Figure 3B = 1680, Figure 3A = 504). Although in real systems different particle distributions are accessible, only the distribution with the largest number of microstates, W_{max}, is realized. In the example of Figure 3, it is the distribution shown in Figure 3C.

According to the Boltzmann principle the conventional entropy fits the equation $S = k_{B} \ln W$. Because changes of entropy could only derive from the term $\ln W$ and evidently not from the constant k_{B}, it is reasonable to define only $\ln W$ as entropy *(1)*.

The Three Rules

To understand measured values of entropy or entropy changes or to predict or to estimate those values, it is helpful to apply the following three simple rules.

The Basic Rule

Nature distributes the total energy to be stored in the particles always in a way that the number of occupied energy levels is as large as possible and at the same time their energy heights are as low as possible. A distribution that does not follow this rule is not impossible, but very improbable.

Figure 5A shows a typical situation for particles in a shelf model following the basic rule. If one pushes all particles to the right edge of each shelf (Figure 5B), it is possible to recognize a functional connection. By turning the shelf clockwise by 90°, the presentation of a mathematical function becomes visible: the occupation numbers, n, as a function of the level energy, E (Figure 5C).

Using the shelf model it is possible to carry out simple model calculations, especially if one concentrates on cases with constant shelf distances. Equidistant energy levels occur in all substances with chemical bonds, meaning monatomic gases are the only exception. If the entropy values for different total energies are computed with the shelf model a positive association between entropy and the number of occupied levels is the result. Plotting the entropy S/R or the number of microstates as a function of the number of occupied levels n_{occ}, one obtains curves with positive slopes. It is remarkable that the gradients of these curves do not depend on the shelf distances in the shelf. In Figure 6, it can be seen that different level spacing leads approximately to the same curve, which had been calculated for two different, but equidistant, level spacing. The bottom part of Figure 6 shows the analog correlations for two real substances with not equidistant levels. The calculation was carried out with eqs 1 and 6

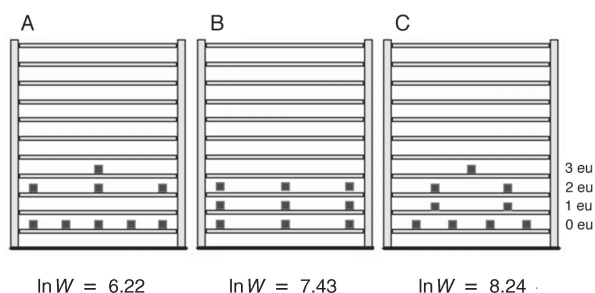ln W = 6.22   ln W = 7.43   ln W = 8.24

Figure 3. Different particle distributions with the same number of particles and the same total energy lead to different values of entropy.
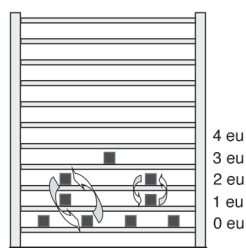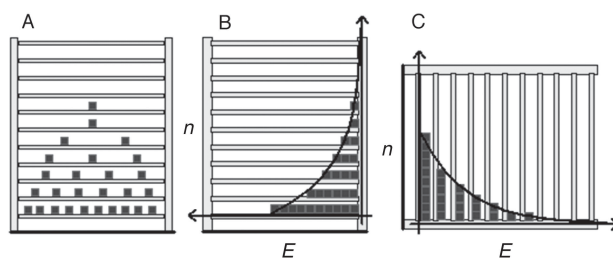

Figure 4. Permutations of the particles lead to different microstates of a system.

Figure 5. Modeling the Boltzmann distribution.

using real values of helium and argon.[2] Different substances, however, differ mainly in the distances between the levels (details will be elaborated later). Independent from the kind of material, one can, therefore, come to the following conclusion:

> **Entropy is a measure of the number of occupied energy levels.**

Entropy is exactly defined as the natural logarithm of the number of energetic microstates belonging to a certain total energy of a system or substance *(1)*. Of course, the above statement can only serve as an approximation.[3] However, the experience with the shelf model shows that in most cases it is sufficient to calculate with equidistant shelves to estimate entropic effects correctly.
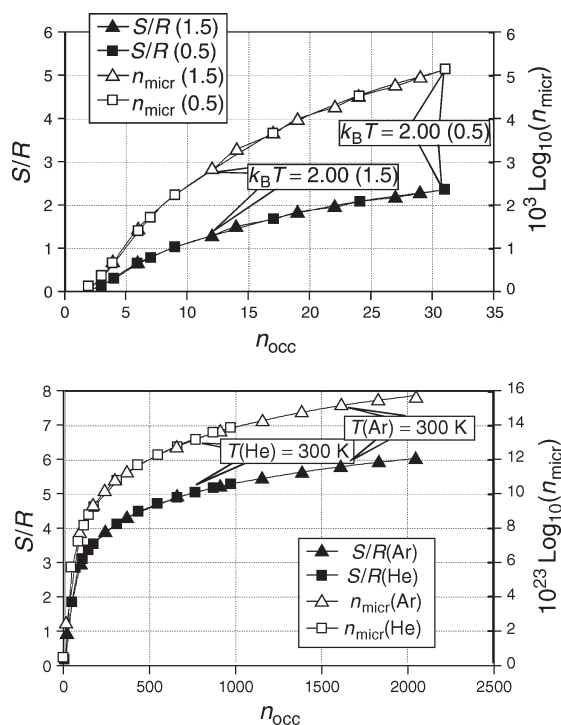

Figure 6. (Top) Correlation between entropy and number of microstates and the number of occupied energy levels n_{occ}, calculated for 5000 particles with the help of the shelf model for different level distances (ΔE = 1.5 or 0.5 eu), to simulate different substances. (Bottom) Correlation between entropy and number of microstates and the number of occupied energy levels n_{occ}, calculated with eqs 1 and 6 for 1 mole of helium and argon.
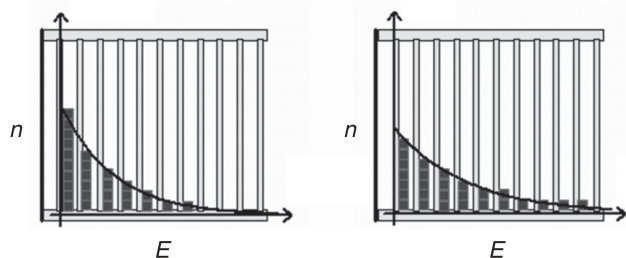

Figure 7. (Left) Low temperature, 7 levels occupied, low entropy. (Right) High temperature, 10 levels occupied, high entropy.

If the temperature of a substance or a system increases the particles will keep a Boltzmann distribution but will be shifted from lower to higher energy levels—the number of occupied levels and the entropy increases (Figure 7).

The definition of temperature T or fundamental temperature, $\tau = k_B T$, in classical thermodynamics is given by the following equations:

$$\tau = \left(\frac{\partial H}{\partial \sigma}\right)_P = \left(\frac{\partial U}{\partial \sigma}\right)_V \tag{2a}$$

or in conventional terms

$$T = \left(\frac{\partial H}{\partial S}\right)_P = \left(\frac{\partial U}{\partial S}\right)_V \tag{2b}$$

$$n_i = n_1 e^{-\frac{E_i - E_1}{k_B T}} \tag{3}$$

$$\tau = \frac{E_i - E_1}{\ln n_1 - \ln n_i} \tag{4}$$

where H is the enthalpy, U is the unternal energy, P is pressure, V is the volume, E_i is the energy of level i, T is the temperature, and τ is the fundamental temperature.

Because the Boltzmann distribution is defined by eq 3, temperature appears as a parameter of this function. The definition of the fundamental temperature *(1)* based on energy quantization fits eq 4.

Because S in the classical definition is incomprehensible without quantum physical terms it becomes necessary to understand temperature as a quantum physical phenomenon. The number of possible values for the numerator $E_i - E_1$, as well as for the denominator $\ln n_1 - \ln n_i$, are countable (i = only natural numbers). As a consequence, the values for the temperature of a certain system correspond to the rational and not to the real numbers. For example if index i indicates the highest occupied level, then increasing i leads to a higher temperature (eq 4) and to more occupied levels, that is, to a larger entropy.

In analogy to the radioactivity phenomenon of half-life, temperature τ may be written, as in eq 5, as a measure of "half-energy" $E_h = E_k - E_j$ with $n_j / n_k = 2$:

$$\tau = \frac{E_h}{\ln 2} \tag{5}$$

Changes in entropy normally do not refer to changes in particle distribution as shown in Figure 3. When exposed to changed conditions of temperature (Figure 6), pressure, number of particles, and so forth, in most cases, natural systems or substances change from one Boltzmann distribution to another. A process linked with entropy production means that the number of energetic microstates increases because of changes in the Boltzmann distribution. Simply speaking this means the number of occupied energy levels increases for three reasons: more particles, higher temperature, or smaller level distances.

The Force Rule

> **If the particles are bound by strong forces to stay in a small space (small uncertainty of position) the distances**

between the energy levels increase. The quantum leaps will be enlarged.

To simulate a liquid, we use a shelf with the level distance of 1.5 eu. The Boltzmann distribution calculated with the shelf model shows that 5000 particles occupy 30 energy levels while having an average particle energy of 5.00 eu/particle and a temperature of 5.75 temperature units (model units). This situation is shown in Figure 8.

We now simulate a solid material, in which the forces between the particles are supposed to be larger. The level spacing therefore increases, for example, to 3.0 eu (Figure 9). Comparing Figures 8 and 9 shows that each even level has been omitted in the second case and the particles on the omitted levels had been additionally placed on the other levels. The occupation numbers are larger in this second case and the number of occupied levels becomes smaller (Figure 9). At the same temperature the average particle energy amounts now to 4.38 eu/particle and only 16 levels are occupied.

Since the number of occupied levels decreases, the entropy of the substance also becomes smaller. At the same temperature and with the same amount of substance the number of occupied levels as well as the entropy is smaller in a system with larger level spacing. This is exactly the situation one would find in a solid material: The forces between the particles are larger than within liquids or gases, which means that the level spacing is larger and the entropy smaller. Thus the shelf model helps to illustrate that normally the entropy of solid materials is smaller than that of liquids or gases where the particles are not forced to stay in such a small space as in the solid state.
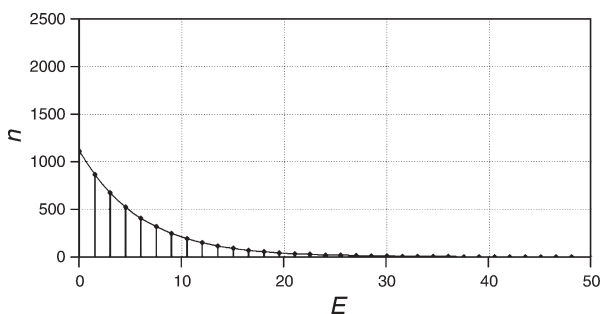

Figure 8. A Boltzmann distribution calculated with the shelf model, simulating low forces between the particles by small level distances.
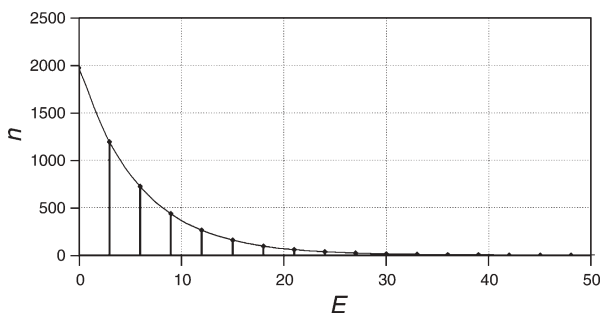

Figure 9. A Boltzmann distribution calculated with the shelf model, simulating strong forces between the particles by large level distances.

The Mass Rule

If the considered particles have large masses, one will find adjoining energy levels at slight distances. Small quantum leaps will occur.

From infrared and Raman spectroscopy we know about the isotopic shift to lower absorption frequencies when one of the vibrating atoms is replaced by a heavier isotope. The lower vibration frequency of the chemical bond with the heavier isotope indicates smaller energy level distances. Likewise this rule helps to understand the different entropy values of substances within the same state of aggregation, for example, the different gases or different salts (2).

The rule works even for the noble gases: The atomic mass increases from period to period. According to the mass rule the energy level distances decrease. Therefore a larger number of energy levels is occupied, which results in a larger entropy value of the heavier noble gases (Figure 10).

The Quantum Physical Principles

Energy quantization forms the basis of the three rules and the energy levels can be calculated with the help of the Schrödinger equation. There are three different ways to store energy according to the classical view of particle motions: translation, rotation, and vibration

$$\text{translation} \quad E^{\mathrm{T}} = \frac{h^2}{8ml^2}n^2 \tag{6}$$

$$\text{rotation} \quad E^{\mathrm{R}} = \frac{h^2}{8\pi^2 mr^2}J(J+1) \tag{7}$$

$$\text{vibration} \quad E^{\mathrm{V}} = \frac{h}{2\pi}\sqrt{\frac{D}{m}}\left(v+\frac{1}{2}\right) \tag{8}$$

where h is Plank's constant, m is the particle mass, l is the uncertainty of position, r is the distance from the rotation axes, D is the force constant, and n, J, and v are quantum numbers. Although quantum physics led to different views about these "movements", the terminology is still in use today.

The main influences on the distances between the energy levels do not come from the quantum numbers but are given by eqs 6–8 derived from the Schrödinger equation (10).
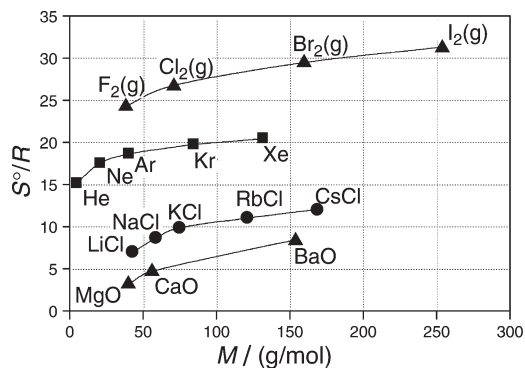

Figure 10. Molar entropy and the influence of particle masses (2).

The force rule and the mass rule can be exemplified in the following way:

> It is easy to recognize the mass rule because the mass always enters the denominators. This means that a large mass leads to a small level spacing. For simulating calculations with the shelf model, the level distance has to be reduced.

In the **vibration term,** the force constant D is found in the numerator. A parabolic potential ($E = 0.5D(\Delta r)^2$, with E = potential energy and Δr = stretching of the bond length) belonging to a small force constant of vibration shows a wide opening and leads to a great uncertainty of position and at the same time to small level distances, that is, low absorption or emission frequencies (Figure 11). For example, the diagrams in Figure 11 help to visualize the difference in infrared spectroscopy; for instance, the C=O double bond of a ketone and the C−O single bond of an alcohol. Figure 11A corresponds to the double bond with a large force constant, large level distance, and a high absorption frequency. Figure 11B corresponds to the single bond with a smaller force constant, smaller level distance, and a lower absorption frequency. Figure 11C shows the situation if the normal oxygen atoms are substituted by ^{18}O atoms in the single bond. A quantum leap downwards (emission of light) is shown in Figure 11A. A quantum leap corresponding to absorption of light is indicated by the arrow in Figure 11B *(11)*.

In the **rotation term** the distance from the rotation axis, r, is found in the denominator. That means for a halogen molecule, X_2, larger values of r (linked to a small vibration force constant) lead to smaller level distances. The molecule needs a larger space (uncertainty of position) to rotate.

In the **translation term** the uncertainty of position l arises in the denominator. In a gas under low pressure a large uncertainty of position l is the result of the weak force, which leads to smaller level distances and larger entropy.

To simulate a stronger force with the shelf model a larger level distance has to be used. Smaller bond distances, larger electronegativity differences, larger polarity, better solubility in water or larger molecular size for organic compounds are effects that lead to stronger forces.

It is a quantum physical result (eqs 6–8) that the effects of translation, rotation, and vibration show qualitatively similar trends. Therefore, in all three cases the shelf model calculations with equidistant levels lead to good approximations showing these trends.
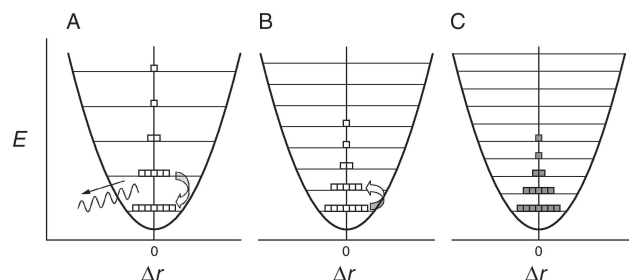

Figure 11. (A) Parabolic potential of a strong force (small opening) and large level distances. (B) Parabolic potential of a weaker force (wide opening) and small level distances. (C) Parabolic potential of a weak force like in (B) (wide opening) but between heavier atoms as in (B) and therefore smaller level distances.

Entropy as Physical Property

Entropy Is Absolute

With the help of the shelf model it is possible to understand that entropy indicates the number of occupied energy levels in a system or in a substance. Molar entropies belong to the thermodynamic quantities, which are given as absolute values $S°$ and not relative to an arbitrarily defined zero level. We are only free to elect the unit of entropy, because each phenomenon is invariant in relation to the used unit.

According to the third law of thermodynamics 0 K is regarded as the zero level for entropy. The entropy of any system reaches its minimum value at this temperature. The value will be zero unless the lowest energy level is degenerated *(10)*. But 0 K is a phenomenon and cannot be freely defined at a different point of the temperature scale. Furthermore the number of energetic microstates belonging to a certain total energy stored in a specific set of eigenvalues is not free for an arbitrary definition. It would inevitably lead to contradiction if a positive number would be defined as zero.

Similar to the density of a substance molar entropy is a physical property that depends on temperature. The way in which a material stores supplied heat or work is characteristic of its internal structure and is reflected in its molar entropy value. It is a result from the Boltzmann distribution (especially for vibrational motion) that the same quantity of total energy leads to different temperatures in systems with different spacings of energy levels, that is, with different entropy.[4] At the same temperature a system with small entropy stores less energy than a large one. Thus, a high value of entropy indicates a large storage system for energy.[5]

The Concept of Atomic Entropy

Thermodynamically measured entropy values of the elements are carried out with samples that consist of the natural isotopic mixture. Therefore, these values include all effects deriving from the mixture of the masses, the mixture of the chemical bonds within these samples, and the mixture of possible particle motions. For example different bonds occur within the layers and between the layers of the hexagonal carbon ring systems of a graphite lattice. Two different bonds occur as well in phosphorus and sulfur: within the molecules P_4 or S_8 and between those molecules. The molar entropy values of the elements represent average values per atom, because entropy is divided by the number of atoms. Unfortunately there are some exceptions: The values for the diatomic gases are average values per molecule, that is, double the number of atoms. It is obvious that a larger number of atoms will occupy a greater number of energy levels and thus will store more energy. The comparison of different elements is therefore unnecessarily complicated.

To avoid this complication, it is reasonable to treat all substances equally. Consequently, the molar entropies were converted and related to the number of atoms for the following statements. For these values this article introduces the symbol S_{at} as a designation for atomic entropy. The molar standard entropy $S°$ of a substance $A_hB_iC_k...$ must be divided by ($h + i + k + ...$) to get the value of the atomic entropy S_{at}. Atomic entropies are more meaningful than the molar entropies especially if one intends to compare substances with different stoichiometry. For most elements atomic entropies

are identical with the molar entropies (apart from the exceptions mentioned above). To apply the three rules it is reasonable to calculate average atomic masses and average atomic distances (as a measure of the internal forces). The three rules are tools for the qualitative interpretation of measured entropy values. Calculations based on the shelf model are used to confirm the following qualitative interpretations or estimations of real data *(2)*, not to approximate the listed measured entropy values.

Atomic Entropy of Elements

The Noble Gases
and the Gaseous Halogens in Comparison

Figure 12 shows that the entropies of the noble gases increase from period to period. We assume that the noble gas atoms do only exert almost negligible attractive forces under standard conditions. So only the increasing mass is responsible for the increasing entropy values within the elementary group of the noble gases. The forces really affecting the noble gas atoms come from repulsion against the walls of the system and we consider them to be equal as long as the gases are under the same conditions of temperature and pressure.

The halogens, bromine and iodine, are not gaseous at 298 K. Because the thermodynamic tables *(2)* list the entropy values for both gaseous bromine and iodine at 298 K, we are able to compare the gaseous halogens with the noble gases.
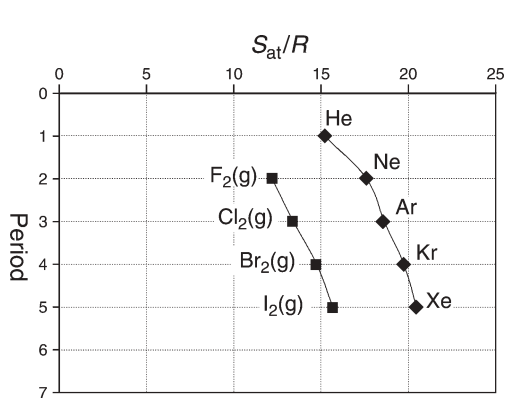
The elementary groups behave similarly in increasing entropy values within the group because of the increasing mass of the atoms or the molecules. However, the curve of the halogens is at considerably lower values. From these data we conclude that the motion of each halogen atom is reduced by the force of the nonpolar atomic bond. According to the force rule larger forces lead to smaller entropies. The mass rule and force rule make these phenomena understandable.

The Alkali Metals and Alkaline Earth Metals in Comparison

At first sight the diagram in Figure 13 looks familiar as its two curves run nearly parallel from period to period with increasing values. The increasing mass however is only partially responsible for the development of the entropy values. With increasing period the atomic diameter becomes larger and the distances between the metal ions in the lattice increase. This means that the forces decrease in strength and the entropy becomes larger additionally.

The alkaline earth atoms are approximately 9% heavier than those of the alkali metals. On the other hand the distance between the atoms is approximately 19% smaller. This leads to the assumption that the forces will be larger. We therefore expect that the force influence is larger than the effect of the mass. The chart confirms this expectation. This further corresponds with our experience about the properties of these metals: Sodium and potassium can be cut with
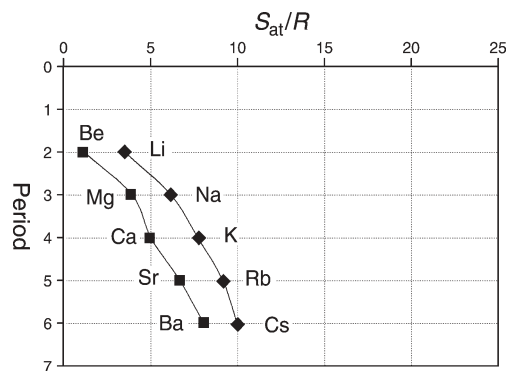

Figure 12. Atomic entropy of gaseous elements *(2)*.

Figure 13. Atomic entropy of alkali metals and alkaline earth metals *(2)*.

Table 1. Systematical Development of Entropy Values within the Main Group Elements of the Periodic Table

H(g) 7.86								He(g) 15.17
Li(s) 3.50	Be(s) 1.15	B(s) 0.79	Cgr 0.68	N(g) 11.53	O(g) 12.34	F(g) 12.20	F(g) 12.20	Ne(g) 17.60
Na(s) 6.15	Mg(s) 3.93	Al(s) 3.41	Si(s) 2.26	Pwhite 5.34	S(s) 3.85	Cl(g) 13.42	Cl(g) 13.42	Ar(g) 18.62
K(s) 7.72	Ca(s) 5.01	Ga(s) 5.13	Ge(s) 5.13	As(s) 4.22	Se(s) 5.03	Br(l) 9.16	Br(g) 14.76	Kr(g) 19.74
Rb(s) 9.15	Sr(s) 6.69	In(s) 7.00	Sn(s) 6.19	Sb(s) 5.28	Te(s) 5.99	I(s) 6.99	I(g) 15.88	Xe(g) 20.45
Cs(s) 9.96	Ba(s) 8.05	Tl(s) 7.75	Pb(s) 7.80	Bi(s) 6.84				

NOTE: The values for the atomic entropy, S_{at}/R, are from ref *2*. The following conditions wre used: 298 K; 101.3 kPa

a knife, but not magnesium and calcium. Alkaline earth atoms deliver in each case 2 electrons to the electron gas. This means that smaller metal ions with larger charge will develop larger forces. This corresponds with the higher melting temperatures of the alkaline earth metals.

The Main Groups of the Periodic Table of Elements

The atomic entropies of the main group elements are shown in Table 1. The values apply to 298 K and 101.3 kPa. Two values for bromine and iodine are listed (2): Br(l) and Br(g) and I(s) and I(g), all under standard condition. That is why Table 1 contains two versions of the 7th main group. Some of the data presented here have already been published in (12).

Inorganic Compounds

We start our discussion of compounds with the nonmetals and try to compare the hydrogen halides with the halogens. Both kinds of substances consist of diatomic molecules and the tables contain the standard entropies for both in the gaseous state. This makes the comparison simple and the two important differences are (i) the kinds of chemical bonding and (ii) the particle masses.

Because of the electronegativity difference in the hydrogen halogen bonding, polar atomic bonds arise. In this case the particles are influenced by stronger forces than in the case of the pure halogens with nonpolar bonds.[6] Since hydrogen atoms have smaller masses than the halogen atoms, the particle mass decreases compared to the respective halogens. Both effects cause the entropy values of the hydrogen halides to be smaller than those of the pure gaseous halogens (Figure 14).

We now focus on simple compounds of the metals such as salts, for example, the chlorides of the alkali metals and alkaline earth metals. Some of these substances are well-known such as sodium chloride. All these substances are solid and crystalline under standard conditions. The crystals are hard and brittle. Because of this characteristic property sodium chloride is also called rock salt. This property indicates large forces and smaller entropies rather than the gaseous materials discussed above.

Again we will have to answer two questions:

1. Which forces arise?
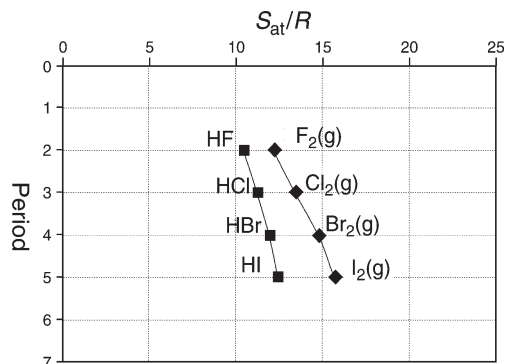2. How large are the particle masses?

Atomic entropies were already discussed. It is therefore easy to compare substances with different stoichiometry. Since the alkaline earth atoms form doubly charged ions one can expect larger Coulomb forces than with the chlorides of the alkali metals and thus smaller entropy values. The diagram (Figure 15), however, shows one exception: beryllium chloride.

In order to understand this deviation two further diagrams will be introduced. Figure 16 shows the electronegativity differences, ΔEN, of these salts and Figure 17 the bond distances.

For the chlorides of the second main group it is obvious that the electronegativity differences will be smaller than those of the alkali metal chlorides (Figure 16). With the beryllium chloride the value of 1.5 is already so small that we can no longer call it an ionic bond. This causes smaller forces and therefore a larger entropy value. The masses of the alkaline earth atoms are approximately. 9% larger than those of the alkali metals. Therefore the influence of the mass is not so important and the smaller entropy values are mainly a consequence of the larger forces.

Since Coulomb forces become larger with smaller ion distances the average particle distances of the salts were calculated and are depicted in Figure 17. The diagram shows the different bond distances and confirms the given interpretation of the entropy values including the exception of the beryllium chloride. The bond distance is relatively large in comparison with the other substances (Figure 17). There-
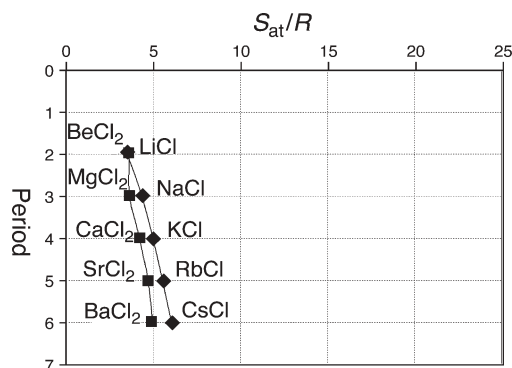

Figure 15. Atomic entropy of saltlike compounds, chlorides of alkali metals and alkaline earth metals (2).

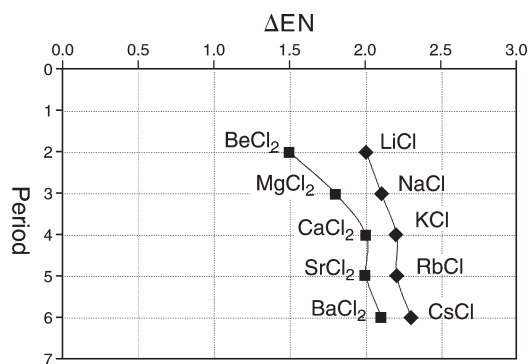Figure 14. Atomic entropy of diatomic gaseous molecules, halogens and hydrogen halides (2).

Figure 16. Electronegativity difference ΔEN of the chlorides of alkali metals and alkaline earth metals (13).

fore the forces are unsystematically small and the entropy value is found to be large.

Organic Compounds

The atomic entropies of organic compounds and those of saltlike materials show a clearly different behavior. One of the causes for it is the force of covalent bond. In the case of the salts strong Coulomb forces between the ions increase with decreasing diameter of the ions. In organic substances atomic bonds lead to van der Waals forces between permanent or induced dipoles. Van der Waals forces however increase with expanding volume of the molecules. Figure 18 shows the atomic entropies for some organic liquid compounds: hydrocarbons, primary alcohols, and mono carboxylic acids. It shows that the entropies decrease within the homologous series with increasing number of carbon atoms, that is, with increasing van der Waals forces. The curve belonging to the primary alcohols is typical for substances with covalent bonds as well. One alcoholic group added to the five C-atoms of pentane leads to pentanol and reduces the entropy value:

$$\text{pentane} \quad \frac{S_{at}}{R} = 1.86$$
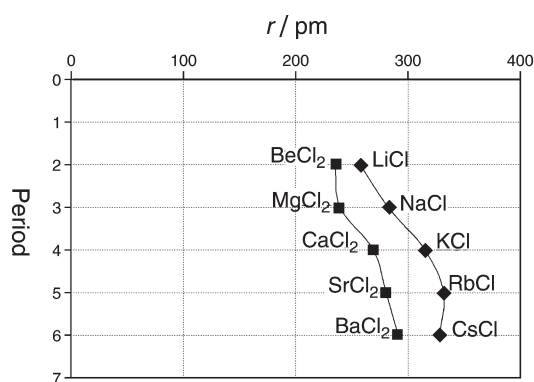
$$\text{pentanol} \quad \frac{S_{at}}{R} = 1.70$$

The one added polar OH-group slightly enlarges the van der Waals force and lowers the entropy. The changes in polarity and in solubility in water corresponds to changes of these two entropy values. This effect decreases if the main carbon chain increases, which means that there is less influence of one hydroxyl group on a longer chain.

Although the difference is obvious the organic compounds follow the three rules as well as the elements or the inorganic compounds. As pointed out above atomic entropies are average values. To apply the three rules it is helpful to calculate the average atomic volumes V_{at} and the average atomic masses m_{at} of these compounds by dividing the molecular volumes and masses by the number of atoms per molecule. The molecular volume can be calculated from the density (13). Smaller atomic volume means that the atoms come closer together and the forces increase, so it is possible to understand the decreasing entropy within a homologous series (Figure 18 and 19) as a result of the force rule.

The relatively high values of atomic entropy for the mono carboxylic acids (Figure 18) may be astonishing because one normally supposes strong forces related to the large polarity of these substances. In comparison to the primary alcohols with the same number of carbon atoms two light and small hydrogen atoms are substituted by one heavy and large oxygen atom: CH_4O to CH_2O_2 According to the mass rule the enlarged average atomic mass (73.6% for methanoic acid) leads to a greater entropy value (Figure 20).

Figure 17. The average particle distance of alkali metals and alkaline earth metals (13).

Figure 19. Average atomic volume V_{at} of the homologous series of hydrocarbons, primary alcohols, and mono carboxylic acids (13).
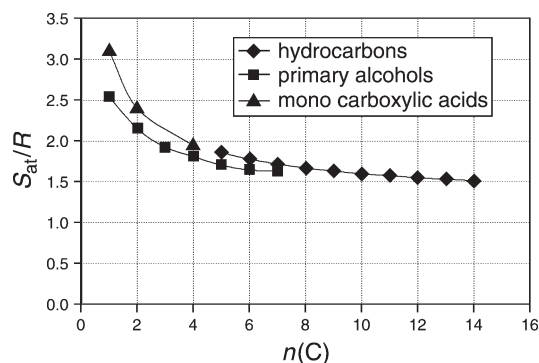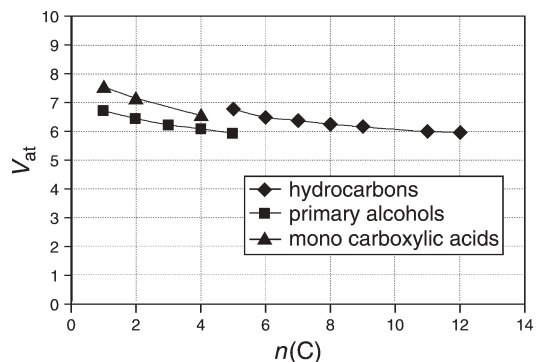

Figure 18. Entropy decreases with increasing number of carbon atoms (molecular volume); a typical effect linked to van der Waals forces (2).
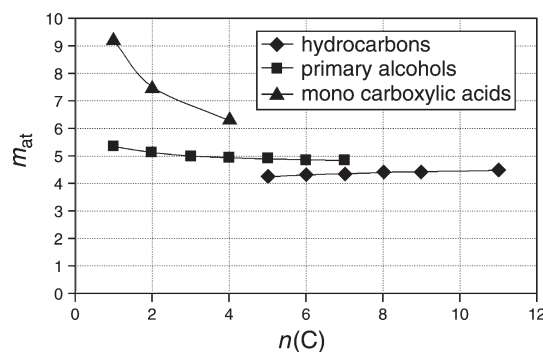

Figure 20. Average atomic mass m_{at} of the homologous series of hydrocarbons, primary alcohols, and mono carboxylic acids (13).

Because of the greater diameter of the oxygen atom the average atomic distances are enlarged (12.3% s. Figure 19). According to the force rule this leads to an additional entropy increase.

Conclusions

The ability to carry out reasonable interpretations of the thermodynamically measured entropy values of all kinds of substances is the key for understanding all kinds of phenomena in which entropy and entropy changes are involved: chemical reactions, chemical equilibrium, change of the state of aggregation, temperature, refrigeration, steam engines, laser beams, black bodies, and more. This is because all these phenomena are linked to substances and changes in substances. If one accepts that in all cases quantum phenomena constitute the basis, a deeper comprehension is possible and not difficult to achieve. Entropy as a physical property describes the way energy is stored on the energy levels that are characteristic for each substance.

It is indeed surprising, that only very little mathematical quantum physics is necessary to carry out good interpretations. The three rules and the assumption of equidistant energy levels as an approximation are sufficient in most cases. For several years this had been practiced successfully by the author with students at the age of 16 to 19 years in chemistry as well as in physics lessons in a secondary school.

Notes

1. This analogy is important when chemical reactions, chemical equilibrium, and entropy maxima are discussed.

2. Equation 6 describes the translational eigenvalues only in one direction. So the calculated entropy is about one third of the standard value. The calculation of occupation numbers is described in the textbook by P. W. Atkins *(10)*.

3. The number of microstates in a real system is so large, that no one is able to get a realistic perception about it. The natural logarithm of this number is smaller, but it still surpasses our imagination. The number of occupied energy levels, however, is of a size that allows a vivid and concrete idea about it. Since the number of microstates increases when the number of occupied energy levels increases (see Figure 6) the statement may be accepted as a good working simplification. The shelf model proves to work properly even for the exception "noble gas".

4. Monatomic gases may be possible exceptions because no vibration is present.

5. From this experimental result a description of entropy may be: Entropy is a measure of the extent of the storage system for energy. Considering the mass rule this definition appears to be more general because the dispersal of energy *(5, 7)* cannot be a mere geometric effect. Larger entropy means that the stored energy is more dispersed on a larger number of occupied energy levels.

6. If van der Waals forces occur the entropy values may be affected by the size of the molecules because these forces increase with the molecular surface. In the gaseous state this effect may be considered to be small, since the particle distances are rather large and the van der Waals forces rapidly decrease in this case. Molecular size is more important in organic liquids, but not within salts.

Literature Cited

1. Kittel, Ch.; Krömer, H. *Thermodynamik,* 5th ed.; Oldenbourg: München, 2001.
2. *Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik und Technik,* 6th ed.; II/4; Landolt, H., Börnstein, R., Eucken, A., Eds.; Springer: Berlin, 1961.
3. Laird, Brian B. *J. Chem. Educ.* **1999,** *76,* 1388–1390.
4. Lambert, Frank L. *J. Chem. Educ.* **2002,** *79,* 187.
5. Lambert, F. L. *J. Chem. Educ.* **2002,** *79,* 1241–1246.
6. Jensen, William B. *J. Chem. Educ.* **2004,** *81,* 639–640.
7. Bindel, Thomas H. *J. Chem. Educ.* **2004,** *81,* 1585–1594.
8. Kozliak, Evguenii I. *J. Chem. Educ.* **2004,** *81,* 1595–1598.
9. Planck, Max. *Annalen d. Physik* **1901,** *4* (Folge, Bd. 4)*,* 553–563.
10. Atkins, P. W. *Physikalische Chemie,* 2nd ed.; VCH Verlagsgesellschaft: Weinheim, Germany, 1996.
11. Williams, Dudley H.; Fleming, Ian. *Spektroskopische Methoden zur Strukturaufklärung,* 3rd ed.; Thieme, Georg, Ed.; Verlag: Stuttgart, 1975; pp 40–80.
12. Jungermann, A. H. *PdN-Ch* **2000,** *49/5,* 34.
13. *Chemiker Kalender,* 3rd ed.; Synowietz, C., Schäfer, K., Eds.; Springer Verlag: Berlin, 1983.