

Entropy and Disorder

P. G. WRIGHT

Lecturer in Physical Chemistry, The University, Dundee

SUMMARY. A discussion is given of some aspects of the relation between concepts of entropy and intuitive qualitative ideas concerning 'disorder'.

In this connection, a plea is made for moderation in the use of such ideas in teaching.

In particular: (i) They ought not to be so misused as to obscure the status of S as a quantity which can be treated in a purely macroscopic theory. (ii) They do not exhibit a complete correspondence with the concepts of a quantitative treatment on the molecular level.

1. Introduction

It is not uncommon to encounter an inaccurate appreciation of what is the relation between, on the one hand, concepts concerning entropy, and, on the other, intuitive qualitative ideas concerning increased disorder.

In consequence of recent urgings towards the teaching of 'thermodynamics' at earlier stages than those hitherto deemed appropriate, the dispelling of such inaccuracies acquires a new urgency. Among the sponsors of the entry of entropy into school courses, there seem to be many who are unaware that such utterances as "Entropy is a name given to a quantitative measure of disorder" represent, not the received doctrine of physical science, but (to say the least) a highly contentious opinion.

Some points from the literature

The last remark is easily justified by reference to the pertinent literature. Thus Khinchin (1949):

"the statement that 'the entropy of a system is proportional to the logarithm of the probability of the corresponding state' . . . , which is absolutely meaningless in the case of an isolated system, obtains, as we see, some meaning for a system in the larger system. . . All existing attempts to give a general proof of this postulate must be considered as an aggregate of logical and mathematical errors superimposed on a general confusion in the definition of the basic quantities."

After inviting the reader to compare the 'proof' by Planck (1914) with the corresponding critique given by Fowler (1936), Khinchin continues:

"In the most serious treatises . . . the authors refuse to accept this postulate, indicating that it cannot be proved, and cannot be given a sensible formulation even on the basis of the exact notions of thermodynamics.

However, proceeding in this direction we can obtain some reasonable and rather interesting results."

Margenau (1950):

"To many students of science entropy is . . . something closely related to probabilities. This attitude represents an improper approach to thermodynamics. . . The concept would have perfectly good meaning even if probabilities had never been invented—and we beseech the philosophic reader to dismiss at this point all associations with bags of mixed-up marbles and decks of shuffled cards if he desires a correct view of things."

McGlashan (1966):

"When, if ever, has this number anything to do with 'disorder' or 'randomness' or 'mixed-upness'?"

"It does in three very special cases, namely, mixtures of perfect gases, or mixtures of isotopes, or crystals at temperatures near the absolute zero, none of which is commonly studied in the ordinary chemical laboratory . . .

"In all other, and *all* ordinary chemical examples, the entropy change is capable of no simple quasi-geometrical interpretation *even for changes in isolated bodies*. One may not wantonly extrapolate statistical-mechanical results for assemblies of non-interacting particles (that is to say, perfect gases), or for mixtures of almost identical molecules, or for very cold crystals, to one's beakers of liquids at ordinary temperatures."

After a discussion of the deposition of crystals from a supersaturated solution, to which further reference will be made below, McGlashan elaborates:

" . . . chemists commonly behave not only as if entropy increases in *isolated* bodies were a measure of increase of disorder, but also as if this were true of entropy changes at constant temperature and pressure, under which conditions, very different from isolation, most chemical reactions are actually carried out.

"Even if the entropy change *were* a measure of disorder in an isolated body, the corresponding measure in an isothermal and isobaric experiment would be the Gibbs function and *not* the entropy . . . whatever it is that is measured by the entropy increase when a natural process takes place in an isolated body (and we have proved that whatever this is it is *not* an increase of 'mixed-upness'), exactly the same thing is measured by a decrease of the Gibbs function when the same process takes place with the body at fixed temperature and pressure."

Criticism of the "pictures of entropy as disorder" is summarized most concisely and trenchantly by Dingle (1959):

"a most inessential visualization which has probably done much more harm than good".

2. Concepts involved in the discussion

There are three groups of ideas to be considered, and these three are conceptually distinct.

(i) The work of Carnot, on efficiencies of engines in relation to temperature, was followed up, amended and elaborated, by Kelvin and by Clausius in particular, into a thermodynamic theory of physical phenomena. In these studies, Clausius came to the conclusion that a certain integral vanishes when taken around any closed path. By a mathematical theorem, this implies that there exists a function, of which the expression behind the integral sign is the differential. The word "entropy" was invented by Clausius as a name for this function.

All of the arguments necessary to (i) are of a purely macroscopic character.

(ii) In the course of work on the rigorous kinetic theory of ideal monatomic gases, Boltzmann noticed that a certain quantity related to the distribution of molecular velocities had all the observable properties of Clausius' entropy (for such a system). In subsequent extensions of this formulation, by generalizations due to Planck and others, the fundamental quantity is

$k \log_e W$, where k is a universal constant (Boltzmann's constant), and W is the number of microscopically distinct ways (i.e. ways distinct on the molecular level) in which, compatibly with the specification of the energy of the system, a given macroscopic state can be realized.†

In some quantitative treatments on the molecular level, W does not appear as such. Other quantities, defined in the statistical mechanics of Gibbs, are fundamental; and these other quantities may be looked upon as implicitly defining a quantity which replaces $k \log_e W$.

(iii) There are intuitive qualitative ideas of disorder, or (Gibbs 1906) of 'mixed-up-ness'.

Between concepts of types (i) and (ii), there is a precise and quantitative correspondence. A $k \log_e W$ in a statistical molecular theory is the precise microscopic analogue of the function whose existence was inferred in Clausius' macroscopic theory. (The two sorts of concept are nevertheless clearly distinct, and failure to distinguish them—whether by ignorance or by design—can result only in misunderstanding.)

However, between concepts of types (i) and (ii) on the one hand, and concepts of type (iii) on the other, it is not reasonable to expect any more than a rough correspondence. No exact correlation should be expected between precise quantitative concepts and imprecise qualitative concepts.

3. Entropy and disorder: illustrative examples, more obscure examples, and 'counter-illustrative' examples

In considering the extent to which there is a correspondence between entropy and intuitive qualitative ideas concerning disorder, or 'mixed-up-ness', it may first be noted that there is one trivial sense in which greater S , and greater W , assuredly do *not* correspond to greater disorder. For a given temperature and pressure, S and $\log W$ are twice as great for 2 mole of a gas as for 1 mole, but the specimen of double size would not be said to be any more disordered than the smaller one. It is, if anything, the entropy *per mole* that might be considered a measure of disorder; or a change of entropy *in a closed system* a change in the extent of disorder.

In saying that, of two macroscopic states, the one which can exist in a greater number of ways is the more disordered, such situations as the following are envisaged.

... AAA	BBB ABA	ABB ...
... AAA	BBB BBA	BAA ...
... AAA	BBB BAA	ABB ...
... AAA	BBB ABA	BBA ...
one possibility only: ordered state		many possibilities: disordered state	

'Perfect ordering' is realizable in one way only; but there are many ways in which the A's and B's can be jumbled up together.

† W is sometimes mistakenly assumed to refer to a single energy level. It refers, rather, to the quantum levels in a certain short range of energy. No more precise specification of the energy of a macroscopic system may properly be given.

It is easy to find examples of processes for which $\Delta S > 0$, and there is an intuitively recognizable increase of disorder. Such can be furnished by:

- (i) the mixing of two gases (at constant temperature and pressure)
- (ii) the vaporization of a solid (, , , ,)

There may also be noted the 'residual entropy' of ice: a contribution to the entropy, due to the disordered arrangement of H_2O units in the crystal (even at the lowest temperatures).

Some instances, however, are less straightforward, and any intuitively recognisable increase of disorder may be harder to find, or even non-existent.

(i) Consider (Bridgman 1941) a specimen of supercooled water, so enclosed that no heat passes between it and other bodies. A spontaneous change is possible in which some of the water freezes. A thermodynamic theorem requires that, since no heat has passed, the entropy has increased. However, the most obvious change, formation of crystalline ice, looks like increase in *order*. What has happened is that the final temperature is greater than the initial temperature, and it could be said that the more violent thermal motions of H_2O units at the higher temperature correspond to an increased disorder which more than counterbalances the more obvious "ordering" involved in the deposition of crystals.

(ii) Consider (McGlashan 1966) a specimen of a supersaturated solution, so enclosed that no heat passes between it and other bodies. Again, there is a possible spontaneous change, deposition of crystalline solute, with increase of entropy. This case is more 'awkward' than the preceding one in that, depending on the thermochemistry of solution of the solute, the final temperature may be either greater or less than the initial temperature. The entropy S has certainly increased, and with it W ; but, if along with deposition of crystals there has been a *decrease* in temperature, it is not very obvious where to find any increase in disorder.

The final state (of greater entropy) is certainly less, and not more, 'mixed up' than the initial state (McGlashan 1966): there has been separation of solute from the solution.

(iii) Consider the isothermal expansion of a gas. It is known from a thermodynamic calculation, based on the equation of state, that the entropy of the gas has increased. It is less obvious that by occupying a greater volume the gas has become more disordered (except perhaps in the sense that when allowed to occupy a greater volume, the gas is 'ordered about' less drastically). It is more informative to go back to the fundamental significance of W as the number of microscopically distinct ways in which (compatibly with the specification of the energy) a given macroscopic state can be realised. Now for a particle in a box, the energy levels become closer together if the volume of the box is increased; and thereby the number of energy levels in a given range of energy is increased. It is possible along these lines to understand the increase in W for the isothermal expansion of a gas.

(iv) For the first three inert gases, the changes in entropy on heating up from a very low temperature (close to 0 K) to 25°C and 1 atm, evaluated from calorimetric data as

$$\sum \int \frac{C_p}{T} dT + \sum \frac{L}{T_{eq}}$$

come to the following (values in joule mole⁻¹ K⁻¹):

He 127 Ne 147 Ar 154

The trend in these values can be given a precise microscopic interpretation, along the lines of that appropriate in (iii), in that the translational energy levels become closer together as the mass of the molecule increases. (This interpretation is made quantitative in the Sackur-Tetrode equation.) While this is clear-cut, a correlation with intuitive ideas of disorder is not easy to find. Argon has the greatest value of $\log W$, but it is hard to see that the more sluggish thermal motions of the molecules of argon are in any meaningful way more *disordered* than the more rapid thermal motions of the molecules of helium.

4. Crystallization

Since a number of people have found it puzzling that there could in certain cases be a *deposition* of crystals attended simultaneously by an *increase* in entropy and a *decrease* in temperature (when it can no longer be argued that the 'necessary' increase in disorder results from disordering due to an increase in temperature 'over-riding' the effect of the decreased mixing-up associated with deposition of ordered crystals), this possibility perhaps merits closer examination.

Let a supersaturated solution be kept, at a constant pressure, in an enclosure such that no heat passes between it and other bodies. Then thermodynamic theorems require that in the possible process of deposition of crystals of solid solute:

(i) The initial and final values of H (\equiv energy + pV) are equal.

(ii) The final value of S will be greater than the initial value.

Consider, for simplicity, a solution that was initially only slightly supersaturated. Then

$$\text{change in } H \approx (C_p \text{ for the solution}) \cdot \delta T - \left[\begin{array}{l} \Delta H \text{ per mole, for dis-} \\ \text{solving solid solute in} \\ \text{saturated solution at} \\ \text{constant } T \text{ and } p \end{array} \right] \cdot \delta n_s$$

$$\text{change in } S \approx \frac{(C_p \text{ for the solution})}{T} \cdot \delta T - \left[\begin{array}{l} \Delta S \text{ per mole, for dis-} \\ \text{solving solid solute in} \\ \text{saturated solution at} \\ \text{constant } T \text{ and } p \end{array} \right] \cdot \delta n_s$$

(where δn_s denotes the quantity of solid solute deposited).

Since the first of these is zero, and C_p for any physical system is positive, it follows that the change in temperature δT necessarily has the same sign as the ΔH for dissolving solid solute in the solution. That is: In such an experiment there is a *decrease* in temperature if the particular solute and solvent are such that ΔH for dissolving solid solute in a saturated solution, at constant temperature and pressure, is *negative*. (This condition is equivalent to: in such an experiment there is a decrease in temperature if the particular solute and solvent are such that the solubility decreases with increase in temperature.)

Now consider the change in S . When the change in temperature is a *decrease*, the directly associated change in S (the first term in the expression given above) is necessarily negative. The fact that, overall, S must *increase* then requires that ΔS for dissolving solid solute in a saturated solution, at constant temperature and pressure, is negative. (This ΔS and the corresponding ΔH are related by the equation $\Delta S = \Delta H/T$, and so in any case are necessarily of the same sign.)

There are presumably those who would insist on saying that "the solute particles and surrounding solvent in solution must, then, be so strongly ordered as to be more ordered than the solid". It is, however, hardly uncharitable to suggest that such a statement is not so much 'explaining' the facts as *explaining them away*; or that it 'explains' disorder in terms of entropy, rather than entropy in terms of disorder.

The point is that here there is no clear correlation between propositions about entropy and anything *intuitively obvious* about disorder.

It ought not really to occasion surprise that such instances can be found (even in such familiar elementary contexts as the deposition of crystals from supersaturated solutions). It is not to be expected that there will be any exact correlation between precise quantitative concepts and intuitive qualitative ideas which cannot be other than imprecise.

5. Schrödinger and Bohr; and entropy and disorder

Bohr's treatment of atomic hydrogen is certainly still taught (though I know people who think that it ought not to be, and also people who think that it ought not to be taught until *after* students have become familiar with the treatment based on Schrödinger's equation). However, is it not usually taught along the lines "Bohr postulated that an atom of hydrogen consists of an electron revolving about the nucleus....., whence it follows that....." (all of which is true), rather than along the lines "an atom of hydrogen consists of an electron revolving about the nucleus in one or another of certain definite orbits....."? The latter could, I think, justly be condemned for implanting false conceptions in the minds of those taught.

To teach that "entropy is a name given to a quantitative measure of disorder" is also open to objection (and with elementary classes at least as much as anywhere else: the impression first assimilated is often the one which persists the most strongly). Entropy is a name given to the function, in macroscopic thermodynamic theory, whose differential is dq_{rev}/T ; or to the microscopic quantity $k \log_e W$. Intuitive qualitative ideas of 'disorder' correlate closely with these quantities in many cases, and this fact is important and informative—but it is a matter of CORRELATION and not of IDENTITY.

Entropy 'is' a function S such that $dS = dq_{\text{rev}}/T$; or the quantity $k \log_e W$; and not a name given to disorder.

6. Some points concerning 'probability'

With insufficient understanding of relations of entropy to disorder, some misconceptions concerning probability are often associated. These perhaps arise from a misinterpretation of a remark by Lewis and Randall (1923):

"When therefore the gas is at first enclosed in one of [two] flasks, and the stopcock is then opened to allow it to distribute itself between the two flasks, it is legitimate to say that immediately after opening the cock the system passes from a state of very small probability to a state of very large probability."

The grossly improbable state is that in which, *with the tap open*, the gas has not left the flask in which originally it was contained. It is *not* the original state in which the gas is enclosed in one flask, with the tap shut.

In a variant of the experiment, in which a partition is removed, the gross improbability appears in the situation of fig. 1, not in that of fig. 2.

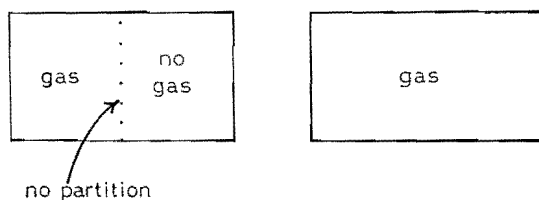


Fig. 1. Situations one of which may be characterized as grossly improbable.

This difference in probability has nothing to do with the increase in S associated with a simple increase in volume, an increase to which it is the situations of fig. 2 that are relevant. In each of the states of fig. 2 it is a matter not of probability but of certainty that the gas is confined to that volume wherein it is confined, and the microscopic interpretation proceeds as in (iii) above, as follows. The number of microscopically distinct ways in which, compatibly with the specification of the energy, the system can exist (W) is much greater for a gas confined to the larger volume than for the gas *confined to* the smaller volume. The counting of W is concerned with a counting of translational quantum states, and each quantum state is represented by a wave function which extends throughout the vessel wherein the gas is contained.

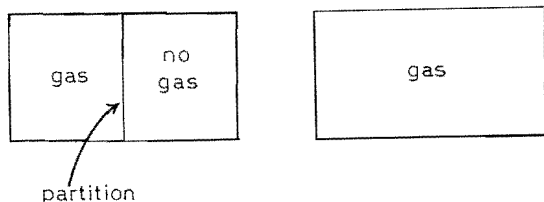


Fig. 2. Situations for which S , or W , may be compared.

Certain correct arguments in terms of probabilities can be given (especially in the classical form of the theory), based on the proposition that for any one molecule there is an equal chance of being in each of the halves of the total accessible volume. Such arguments are to be distinguished from the misconceptions considered above.

Another possible source of misunderstanding lies in the unfortunately chosen (Fowler 1936; Kennard 1938) name 'thermodynamic probability' sometimes given to W (a number of ways, and not a probability).

C.P.

Guggenheim (1949) has argued that some popular views on 'entropy and probability' stretch the word 'probable' beyond its recognised meaning, and he commends instead the interpretation of W [his Ω] as measuring the extent to which a system is spread over its various quantum states consistent with the prescription of its energy.

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The Author:

P. G. Wright, M.A., Ph.D. (Cambridge). After three years on a research fellowship at Leeds, has held various posts at Dundee. Principal research interests: transport phenomena in gaseous systems, and thermodynamic theory.