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An Alternative to Free Energy for Undergraduate Instruction

Since the publication in 1923 of the book "Thermodynamics and the Free Energy of Chemical Substances" by G. N. Lewis and M. Randall (1) free energy has been a widely used state function in the chemical literature. It serves as a convenient way to represent the equilibrium constant of a reaction and hence to show the extent to which a reaction may proceed under specified conditions. For chemists by far the greater use is made of the free energy function at constant temperature and pressure rather than at constant temperature and volume with the former sometimes called "the Gibbs function" and the latter "the Helmholtz function."

It is the purpose of this paper to question the usefulness of the Gibbs function for the student and to propose an alternative based on the use of entropy functions which will help the student to focus more sharply on the features of a system that relate to its capacity to change. It is not the logic of the Gibbs function that is being questioned, but rather its suitability to the effort of helping students understand the nature of chemical reactions. The structure of the paper will consist of some statements of certain difficulties with the Gibbs function followed by a strategy for replacing the Gibbs function with suitable entropy functions. A concluding section will then present various illustrations that demonstrate ways of applying entropies to practical situations encountered by chemists.

Three major difficulties with the Gibbs function are worth describing. These difficulties are the kind that almost certainly tend to mislead students, and hence can be nearly fatal flaws since the only reason for ever introducing the Gibbs function is the reason of its convenience.

The first difficulty has to do with the implied relation between the Gibbs function and one's mental model of a chemical system. For most students the implication is that there is a single feature of the model related to energy that is identified with the direction of change. However, there are surely two features: one has to do with the difference between ground state energy levels for initial and final states and the other is related to the differing distribution of energy among the accessible energy levels for the two states. It is our intention in this paper to provide a way of emphasizing that there are these two features and evaluating their relative significance in any given system.

The second difficulty has to do with the tendency to regard the Gibbs function as an energy. Of course, it is properly assigned units of energy and widely re-

ferred to as a "free energy." However, it is not truly an energy as can be illustrated by the following example. In the free expansion of an ideal gas the Gibbs function decreases without any accompanying change in enthalpy, temperature, or kinetic energy of the gas molecules. The amount by which the Gibbs function changes is equal to $-T\Delta S$. This latter function has a magnitude that can be calculated as the energy that would have been transferred as heat if the gas expansion had been carried out reversibly. Since the Gibbs function is initially defined by the statement $G \equiv H - TS$ the free expansion case shows a decrease in G that is equivalent to $-T\Delta S$. It is not appropriate to assume that an amount of energy equal to the decrease in ΔG is somehow transferred to something represented by $T\Delta S$. There is no other change within or without the system which permits one to say that the decrease in "free energy" of the expanding gas is accompanied by some equivalent increase in an energy term. Therefore, the Gibbs function does not qualify as a true energy.

Another difficulty with the Gibbs function is that it tends to reinforce students in the notion that changes proceed always from high energy to low energy. Indeed most students seem to have been taught to believe there is an inherent tendency within a system to reduce its energy content. However, so long as we assume energy to be conserved there must be somewhere an energy increase to exactly match each observed energy decrease. Indeed, whether a change in a system is or is not accompanied by an alteration of the energy of that system is determined by how the system is defined. It is always possible to define a system in such a way that no energy change takes place no matter what the other changes may be.

An example to consider is provided by a ball suspended above the earth. It is commonly said that if the ball is released it will only tend to fall toward the earth in order to decrease its gravitational potential energy. However, if the ball-earth system is arranged so there is a hole through the earth, the ball could pass along the hole and travel to the opposite side of the earth and then oscillate back and forth alternately increasing and decreasing its gravitational potential. Releasing the suspended ball does not lead simply to a reduction in potential energy but rather to a system in which the energy is distributed between potential and kinetic energy. This redistribution of energy accompanying a change in state is probably the simplest example of the way energy redistribution accompanies every change. It is energy redistribution that is significant, not any change in the magnitude of the energy.

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The distribution of energy within a system is usually represented by an entropy function. It should be much better for students to get accustomed to thinking about both energy and entropy. "Free energy" seems to serve as a source of confusion because it gives the illusion of focusing all attention on energy to the exclusion of entropy. An illusion is present because in fact the Gibbs function is actually more closely related to entropy than to energy.

In a system undergoing chemical change there are two important aspects of the change: Why does the change proceed in the observed direction rather than the opposite direction, and why does the change come to a halt before the reagents are exhausted? Any comprehensive view of chemical systems and their changes or indeed of any system should deal with these companion features of change. This point of view can be summarized briefly by *why does a reaction go and then stop?*

Most commonly the Gibbs function is used to indicate the direction of change in state for a system so that a change in state can occur whenever the Gibbs function can decrease and when the only possible value is zero for the change in the Gibbs function then reaction ceases. However, the most general statement appropriate to any observed change in an assembly of materials is that the total entropy of the assembly must increase (2). Or, in symbols, $\Delta S_t > 0$. By the total entropy change is meant the sum of all entropy changes in any way related to the observed change in state for an assembly large enough to encompass all aspects of the change. It is always possible to divide the total entropy change into two terms with one referred to as the entropy change in one part of the assembly called the environment, ΔS_e , and the other referred to as the entropy change in the remainder of the assembly called the system, ΔS_s . Whether and how the total entropy change is divided is a matter of personal judgment corresponding to the arbitrary decision by which some part of the whole assembly is chosen to be the system.

The statement about total entropy change is essentially a formulation of the Second Law of Thermodynamics. It can be summarized as

$$\Delta S_t = \Delta S_e + \Delta S_s > 0$$

The point to emphasize is that this statement is completely general in its application to all conditions of system or environment or process by which any real change in state is accomplished. The crucial distinction at this point is then between total energy change and total entropy change. Since the former is always and everywhere zero in any macroscopic situation, no distinction is provided between a system that changes and one that does not change. Total entropy, however, will always increase as an accompaniment to a real change but remain fixed for a system that does not change. *A reaction proceeds when there is a process available that leads to an increase in total entropy, and the reaction stops when no way is open to total entropy increase.*

From this general statement of total entropy increase various special cases can be developed which help to reveal features applicable to particular kinds of situations. For chemists a system of considerable

interest is one held at constant pressure and constant temperature during a change in state by a process in which the change is totally unopposed so that no work is done other than work (obligatory work) required by any volume change in the system. The work over and above the obligatory work can be referred to as optional work.

When chemicals are mixed in an open container surrounded by a thermostat any change takes place at constant pressure and temperature and without the transfer of any optional work. Such a process for carrying out a change is often said to be one of maximum irreversibility. For these conditions any heat transfer between system and environment, if both are at the same pressure, can be represented by

$$Q_p = \Delta H_s = -\Delta H_e$$

The corresponding entropy change in the environment is given by

$$\Delta S_e = \Delta H_e/T = -\Delta H_s/T = -Q_p/T$$

if the environment is assumed to be so large that its temperature is not altered by the heat transfer. Therefore for this special case where $\Delta P = \Delta T = 0$ and the process is totally unopposed the total entropy change will be

$$\Delta S_{tu} = \Delta S_e + \Delta S_s = -\Delta H_s/T + \Delta S_s$$

The function S_{tu} is identical with the characteristic function, ψ , defined by Planck (3) and will hereafter be referred to as the "Planck function." The subscript "tu" is used as a reminder that ΔS_{tu} refers both to a total entropy change and to a process which is totally unopposed so that no work is done other than work against the atmosphere or in other words the optional work is zero.

Without going through a detailed argument (4) it can be seen that the Planck function change for a process of maximum irreversibility (totally unopposed) at constant temperature and pressure is related to the Gibbs function by

$$\Delta G/T = -\Delta S_{tu}$$

In other words, $-\Delta G/T$ can be considered a measure of the entropy change of the universe for any unopposed change in a system at constant temperature and pressure. Thus we can write

$$\Delta S_{tu} = -\Delta G/T = -\Delta H_s/T + \Delta S_s$$

or the more familiar alternative form

$$\Delta G = \Delta H_s - T\Delta S_s$$

For a single constant pressure throughout system and environment any transfer of heat results in a change in enthalpy in the system, ΔH_s , accompanied by an exactly equal and opposite change in the environment. Whether one focuses attention on the enthalpy change of the system or of the environment is a personal matter determined by convenience or custom. The remainder of this paper will treat ΔH_e as an important quantity because it is directly related to the entropy change in the environment through $\Delta S_e = +\Delta H_e/T$.

Examination of the Planck function reveals several important aspects of the nature of a change in state which can best be shown by considering

$$\Delta S_{tu} = \Delta S_s + \Delta H_e/T$$

In order for ΔS_{tu} to be a positive quantity it is necessary that either ΔS_s or $\Delta H_e/T$ be sufficiently positive. The value of ΔS_s is determined by the change in the energy distribution within the system or, in more pictorial terms, by a change in the organization of the system. The value of $\Delta H_e/T$ is determined by the temperature and by the amount of heat transferred between system and surroundings. The heat transfer is, in turn, determined largely by the making and breaking of bonds within the system, at least for a system undergoing chemical reaction.

There are three types of situations in which $\Delta S_{tu} > 0$.

Situation 1. $\Delta S_s < 0$ and $\Delta H_e/T > 0$. In this situation the change results in an increase in organization of the system, but there is enough heat transfer to the environment to make $\Delta H_e/T$ sufficiently positive. Thus the entropy increase of the environment more than compensates for the decreased entropy of the system. The system described undergoes an exothermic change. An example would be the reaction of hydrogen and oxygen to form steam for which at 1000°K $\Delta S_s^\circ = -13.2$ eu; $\Delta S_e^\circ = +59.2$ eu; $\Delta S_{tu}^\circ = +46.0$ eu, where eu represents calories/degree.

Situation 2. $\Delta S_s > 0$ and $\Delta H_e/T < 0$. Although in this situation heat is transferred from environment to system with a consequent increased order in the way energy is distributed within the environment, the increased entropy of the system is sufficient to compensate for the decreased entropy of the environment. The system described undergoes an endothermic change. An example would be the evaporation of a liquid above its boiling point or the reaction of solid carbon with steam for which at 1000°K $\Delta S_s^\circ = +34.3$ eu; $\Delta S_e^\circ = -32.5$ eu; $\Delta S_{tu}^\circ = +1.8$ eu.

Situation 3. $\Delta S_s > 0$ and $\Delta H_e/T > 0$. Here both system and environment increase in entropy so the change proceeds no matter what numerical magnitude is associated with either entropy change. An example would be the reaction of solid carbon and oxygen gas to form carbon monoxide gas for which at 1000°K $\Delta S_s^\circ = +21.1$ eu; $\Delta S_e^\circ = +26.8$ eu; $\Delta S_{tu}^\circ = +47.9$ eu.

For most chemical reactions ΔS_s and ΔH_e each vary only slightly with temperature. In the expression

$$\Delta S_{tu} = \Delta S_s + \Delta H_e/T$$

the term $\Delta H_e/T$ will determine the sign of ΔS_{tu} at sufficiently low temperatures while the term ΔS_s will determine the sign of ΔS_{tu} at high temperatures. In other words, exothermic change will be the only reaction feasible at sufficiently low temperatures because the reaction has to increase the entropy of the environment in order to proceed. At high temperatures only those reactions will be feasible that are accompanied by an increase in the entropy of the system. For a high temperature reaction it makes no difference whether it is exothermic or endothermic so far as feasibility is concerned, but it is generally found that when $\Delta S_s > 0$ the reaction is likely to be endothermic because the particles that make up the material of the system are tending to separate from one another.

A summary conclusion is that exothermic reactions are the only generally feasible ones at a sufficiently low temperature. The reason is that only an exothermic

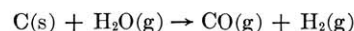
reaction can increase the entropy of the environment. At a sufficiently high temperature feasible reactions are likely to be endothermic because the reaction has to lead to an increase in the entropy of the system. For intermediate temperatures the feasible reaction will be the one for which the relation between the entropy change of the system and its environment is appropriate to an increase in total entropy.

One of the more intriguing experimental illustrations of the main relationships discussed above is provided by an ice calorimeter. If a pair of reagents is assembled without mixing in an ice calorimeter, the entire assembly comes to a constant temperature and pressure. For a pair of reagents such as $\text{CaCl}_2(\text{s}) + \text{H}_2\text{O}(\text{l})$ mixing leads to the formation of a solution and the melting of some ice. On the other hand, with a pair of reagents such as $\text{CaCl}_2(\text{aq}) + \text{Na}_2\text{CO}_3(\text{aq})$ mixing leads to a reaction and the formation of some ice. How is it possible to make any sense out of these two, seemingly different, changes and what is the role played by the ice? In the first system experimental data indicate that mixing leads to an entropy decrease for the $\text{CaCl}_2(\text{s}) + \text{H}_2\text{O}(\text{l})$ while heat is transferred to the ice to produce melting and an entropy increase such that the total entropy change is positive. In the second system the mixing of the reagents leads to an entropy increase for the reagents accompanied by an entropy decrease for the formation of ice so the total entropy change is positive.

Another aspect of the description of a reaction grows out of the entropy consideration. For a reaction in which each component of the system is in its standard state it is possible to show that the standard Planck function change, ΔS_{tu}° , is related to the equilibrium state composition of the system by

$$\Delta S_{tu}^\circ = R \ln K = \Delta S_s^\circ - \Delta H_s^\circ/T$$

where the dimensionless constant K is defined by the equilibrium composition in relation to a standard state for each component. To the extent that ΔS_s° and ΔH_s° are independent of temperature, a plot of $R \ln K$ versus $1/T$ should give a straight line whose intercept at infinite temperature gives ΔS_s° and whose slope gives $-\Delta H_s^\circ$. In any event, the slope of the curve at any one temperature will give $-\Delta H_s^\circ$ at that temperature (5). Such plots are a convenient way of displaying equilibrium constant data. An example is given in Figure 1 for the water gas reaction (6)



The curve is nearly linear which implies that ΔS_s° and ΔH_s° are nearly, but not entirely, independent of

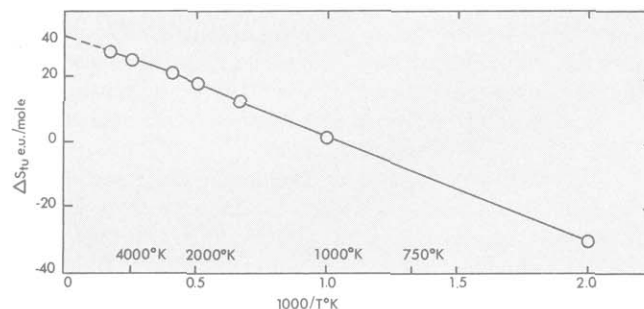


Figure 1. Total entropy change as a function of temperature for the reaction $\text{C}(\text{s}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{CO}(\text{g}) + \text{H}_2(\text{g})$. Data from reference (6).

temperature. Presumably this means that the equilibrium constant varies with temperature because ΔH_s° is a non-zero quantity and changes slightly with temperature.

Consideration of the feasibility of a reaction, such as the water-gas reaction, leads to questions about what aspects of the system and its environment are important in determining the feasibility. The sign of the Planck function indicates the general criterion of feasibility. Beyond the sign, we can also compare the entropy changes in the system and its environment. By this comparison it is possible to decide whether further interpretation efforts should concentrate on the ability of the system to alter its environment ($\Delta S_e = -\Delta H_s/T$) or the energy distribution within the system (ΔS_s). This comparison is facilitated by a plot of ΔS_s versus ΔS_e .

The entropy relations for the water-gas reaction system with each component in its standard state can be shown by plotting ΔS_e° versus ΔS_s° for various temperatures as is done in Figure 2 (curve III). In the

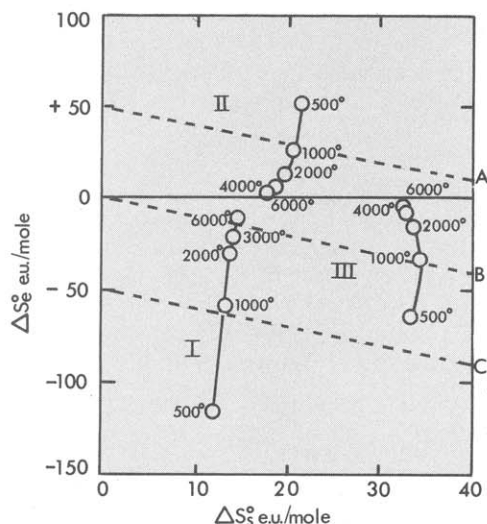


Figure 2. Entropy changes for water-gas system: I, $\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2} \text{O}_2$; II, $\text{C} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}$; III, $\text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2$. The diagonal dotted lines represent constant ΔS_{tu}° values of A, +50 eu; B, 0 eu; C, -50 eu.

plot the diagonal dotted lines represent constant values of ΔS_{tu}° and hence also constant values of $\Delta G^\circ/T$ or of K . The variation in ΔS_{tu}° with temperature for the water-gas reaction is seen to be almost entirely a consequence of the variation in ΔS_e° since the system entropy change varies only slightly from 500°K to 6000°K. With increasing temperature the transfer of heat from the environment to the system as a consequence of bond breaking and making produces less and less change in the entropy of the environment. Since ΔS_s° is fairly large and positive for all temperatures, the Planck function change becomes more and more positive with increasing temperature. Thus the equilibrium constant is less than unity at low temperatures and greater than unity at high temperatures.

Further interpretation of the water-gas reaction can be developed by considering the entropy data for the formation of $\text{H}_2\text{O}(\text{g})$ and $\text{CO}(\text{g})$ with the reminder that the elements $\text{C}(\text{s})$, $\text{H}_2(\text{g})$, and $\text{O}_2(\text{g})$ are, by definition, in their standard states at each temperature and hence represented only by zeros insofar as entropies of formation are concerned. Since in the water-gas re-

action, water disappears, the reaction for the dissociation of water is included in Figure 2 (curve I) by $\text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g})$, while carbon monoxide is formed and therefore (curve II) the reaction $\text{C}(\text{s}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{CO}(\text{g})$ is included. The conversion of water to its elements at a low temperature is accompanied by a large decrease in the entropy of the surroundings. However, as the temperature rises the disappearance of the water has less and less effect on the entropy of the environment although there is little alteration in the effect on the entropy of the system. Presumably converting 1 mole of water to 3/2 mole of products raises the entropy of the system about the same amount whether the temperature is 500°K or 6000°K. For the formation of carbon monoxide from its elements the entropy of the system is raised considerably, presumably because of the highly ordered solid carbon being replaced by gaseous carbon monoxide with a corresponding increase in translational entropy. But, as the temperature rises the formation of carbon monoxide has less and less effect on the environment. Around 1000°K the effect on the environmental entropy of the water disappearing and the carbon monoxide being formed just about balances the entropy change in the system so the water-gas system in its standard state at 1000°K is essentially at equilibrium. Around 6000°K the environmental entropy changes are close to zero and just about cancel one another so the water-gas reaction is dominated by the sum of the entropy increases in the system for the disappearance of water and the formation of carbon monoxide. Thus, at temperatures above 1000°K solid carbon and water vapor convert to carbon monoxide and hydrogen gases in a spontaneous endothermic process at standard state conditions.

Another example of the use of a plot of ΔS_e° versus ΔS_s° is provided by data for proton transfer from an acid in aqueous solution at 25°C. Data for several proton transfer reactions are displayed in Figure 3 (7). As in Figure 2 the diagonal dotted lines represent constant values of ΔS_{tu}° and hence constant pK 's. Comparison of protonated glycine, (point 3) $^+\text{NH}_3\text{CH}_2\text{COOH}(\text{aq}) \rightarrow ^+\text{NH}_3\text{CH}_2\text{COO}^-(\text{aq}) + \text{H}^+(\text{aq})$ ($pK = 2.35$ at 25°C), with propionic acid, (point 1) CH_3-

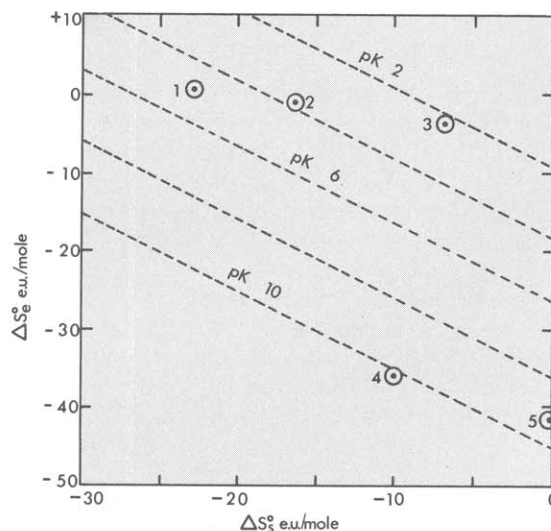


Figure 3. Entropy changes for proton transfer aqueous solution at 25°C for: 1, $\text{CH}_3\text{CH}_2\text{COOH}$; 2, HOCH_2COOH ; 3, $^+\text{NH}_3\text{CH}_2\text{COOH}$; 4, $^+\text{NH}_3\text{CH}_2\text{COO}^-$; 5, NH_4^+ . Data from reference (7).

$\text{CH}_2\text{COOH}(\text{aq}) \rightarrow \text{CH}_3\text{CH}_2\text{COO}^-(\text{aq}) + \text{H}^+(\text{aq})$ ($pK = 4.37$ at 25°C), indicates the substantial difference in pK to arise largely because of differences in ΔS_s rather than ΔS_e . In other words, any attempt to interpret the observed differences in pK values should be based on examining changes in energy level distribution within the system as a consequence of proton transfer rather than changes in the bonds. On the other hand comparison of protonated glycine with glycine itself, (point 4) $^+\text{NH}_3\text{CH}_2\text{COO}^-(\text{aq}) \rightarrow \text{NH}_2\text{CH}_2\text{COO}^-(\text{aq}) + \text{H}^+(\text{aq})$ ($pK = 9.78$ at 25°C), indicates the difference in pK to be largely a consequence of differences in ΔS_e rather than ΔS_s . In other words, any attempt to interpret the observed differences in pK values for these two successive ionizations of glycine should be based on examining the bond changes rather than energy level distribution changes.

A variety of other comparisons can be made as steps toward the interpretation of the details of proton transfer. To this end glycollic acid, (point 2) HOCH_2COOH ($pK = 3.83$ at 25°C), and ammonium ion, (point 5) NH_4^+ ($pK = 9.24$ at 25°C), are also included in Figure 3. The various acids: propionic, glycine, protonated glycine, and glycollic have been chosen for comparison here because they are isoelectronic and hence the main differences among them reside in the nature and arrangement of the nuclei. Transferring a proton from a carboxyl group to a water molecule is a change accompanied by only small effects on the entropy of the environment; however, the entropy change of the system is quite sensitive to the way charge is distributed close to the carboxyl group as shown by comparing propionic acid, glycollic acid, and protonated glycine. It is rather remarkable that the entropies are not greatly different for loss of a proton from $^+\text{NH}_3\text{CH}_2\text{COO}^-$ and from NH_4^+ .

A rather different example of an entropy plot makes use of data for the formation of the alkane hydrocarbon gases, butanes through octanes, from their elements at 25°C and 1 atm pressure. Standard entropies of formation for these hydrocarbons and some of their isomers are displayed in Figure 4 (8). Among the features to remark are such ones as the fact that each set of isomers from the pentanes to the octanes occupies a nearly constant interval on the plot (about $15 \Delta S_e$ units). Any one type of isomer, for example the normal alkanes, lies along a straight line tilted so that ΔS_{tu}° becomes more negative with increase in chain length. Both ΔS_e° and ΔS_s° alter as chain length increases but in opposite directions and with ΔS_s° decreasing somewhat more than ΔS_e° increases so that the larger hydrocarbons are less stable with respect to the separated elements than are the smaller hydrocarbons. One can conclude that big hydrocarbon molecules tend to change into smaller highly branched hydrocarbons.

The relationships among the alkanes are revealed more clearly in Figure 5 where each set of isomers has been plotted to show the amount by which ΔS_e for a particular isomer differs from the normal, straight chain isomer. Since the isomers of a given alkane can be regarded as more compact than the straight chain isomer, a general conclusion is that increased compactness raises ΔS_e but has comparatively little effect on ΔS_s . The largest increase for ΔS_e from the normal

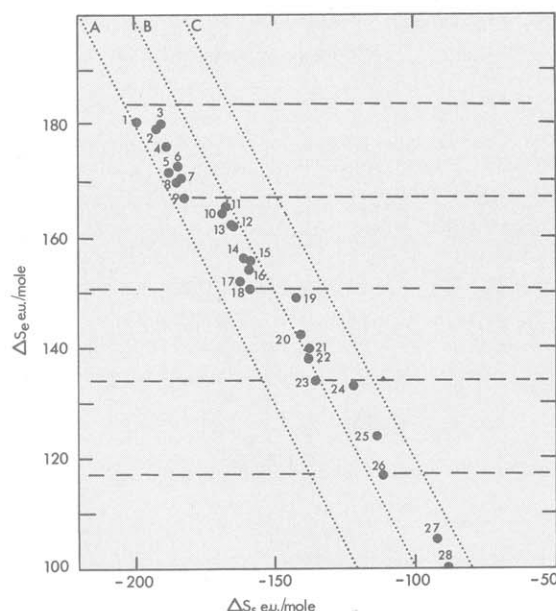


Figure 4. Entropies of formation for alkane hydrocarbons at 25°C , 1 atm. The dotted diagonal lines represent constant ΔS_{tu}° values of A, -20 eu; B, 0 eu; C, $+20$ eu. Data from reference (8).

Octanes, C_8H_{18} . 1: 1,1,2,2-tetramethylbutane; 2: 2,2,4-trimethylpentane; 3: 2,2-dimethylhexane; 4: 3,3-dimethylhexane; 5: 2,3-dimethylhexane; 6: 2-methylheptane; 7: 3-methylheptane; 8: 4-methylheptane; 9: *n*-octane.
 Heptanes, C_7H_{16} . 10: 2,2,3-trimethylbutane; 11: 2,2-dimethylpentane; 12: 3,3-dimethylpentane; 13: 2,4-dimethylpentane; 14: 2,3-dimethylpentane; 15: 2-methylhexane; 16: 3-methylhexane; 17: 3-ethylpentane; 18: *n*-heptane.
 Hexanes, C_6H_{14} . 19: 2,2-dimethylbutane; 20: 2,3-dimethylbutane; 21: 2-methylpentane; 22: 3-methylpentane; 23: *n*-hexane.
 Pentanes, C_5H_{12} . 24: 2,2-dimethylpropane; 25: 2-methylbutane; 26: *n*-pentane.
 Butanes, C_4H_{10} . 27: 1-methylpropane; 28: *n*-butane.

isomer is obtained with the 2,2-dimethyl isomer with the only exception being that of tetramethyl butane, which lies slightly higher than 2,2-dimethyl hexane. Within any one set of isomers the fact that changes in ΔS_e are considerably larger than changes in ΔS_s implies that the isomers differ mainly in bond energy rather than in entropy. The more compact isomers have greater bond energies than the straight chain isomer of each set. Therefore any attempt to interpret the relative stabilities of the various hydrocarbons should be directed toward the effect of compactness on bond energies rather than on system entropies. On the face of it this is a somewhat surprising conclusion.

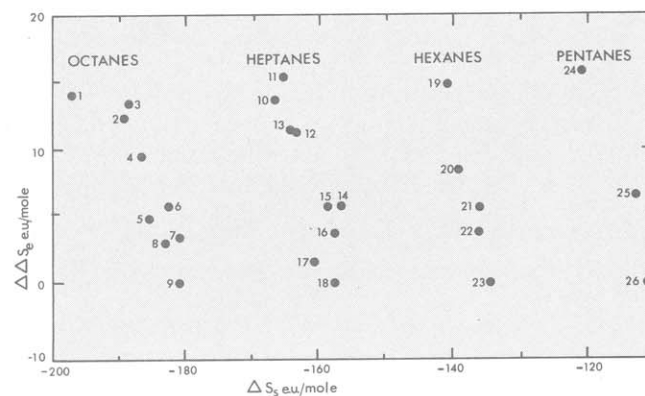


Figure 5. Entropies of isomerization for alkane hydrocarbon gases at 25°C and 1 atm. Numerical key to hydrocarbons same as for Figure 4. For octanes $\Delta S_e = -166.9$; heptanes, -150.4 ; hexanes, -134.0 ; pentanes, -117.3 .

Data available include only nine of the seventeen octane isomers. Clearly it will be of considerable interest to see where the other octane isomers fit in once data become available.

As a final illustration a biochemical system will be presented. This choice will serve to underscore the proposition that entropy changes are really much more significant than energy changes in biological systems. This proposition has been rather eloquently stated by Schrödinger (9). Here the illustrative systems concern the reactions of aqueous adenosine triphosphate (ATP) with aqueous protons and aqueous magnesium ions. Entropy data (10) are plotted in Figure 6. Their

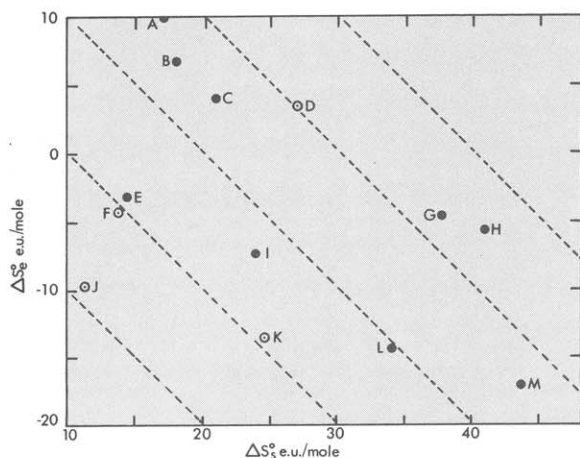


Figure 6. Entropies of reaction for ATP, ADP, and related ions in aqueous solution at 25°C. The dotted diagonal lines represent constant ΔS_{tu}° values of 0–40 eu in 10 eu increments. The points represent the values for the following reactions

- A, $\text{ATP} + \text{H}_2\text{O} \rightarrow \text{ADP} + \text{HPO}_4^-$
- B, $\text{H}^+ + (\text{ADP})\text{Mg}^- \rightarrow (\text{ADP})\text{HMg}^-$
- C, $\text{H}^+ + (\text{ATP})\text{Mg}^{2-} \rightarrow (\text{ATP})\text{HMg}^-$
- D, $\text{H}^+ + \text{HPO}_4^{2-} \rightarrow \text{H}_2\text{PO}_4^-$
- E, $\text{Mg}^{2+} + (\text{ADP})\text{H}^{2-} \rightarrow (\text{ADP})\text{HMg}^-$
- F, $\text{H}^+ + \text{H}_2\text{PO}_4^- \rightarrow \text{H}_3\text{PO}_4$
- G, $\text{H}_3^+ + \text{ADP}^{3-} \rightarrow (\text{ADP})\text{H}^{2-}$
- H, $\text{H}^+ + \text{ATP}^{4-} \rightarrow (\text{ATP})\text{H}^{3-}$
- I, $\text{Mg}^{2+} + (\text{ATP})\text{H}^{3-} \rightarrow (\text{ATP})\text{HMg}^-$
- J, $\text{Mg}^{2+} + \text{HPO}_4^{2-} \rightarrow \text{MgHPO}_4$
- K, $\text{Mg}^{2+} + \text{SO}_4^{2-} \rightarrow \text{MgSO}_4$
- L, $\text{Mg}^{2+} + \text{ADP}^{3-} \rightarrow (\text{ADP})\text{Mg}^{2-}$
- M, $\text{Mg}^{2+} + \text{ATP}^{4-} \rightarrow (\text{ATP})\text{Mg}^{2-}$

Data based on reference (10) Data for H_3PO_4 ionization from reference (7); for MgSO_4 , from reference (11).

interpretation is left to the readers. However, the authors won't resist pointing out that the evidence indicates that the reaction in which a phosphate bond is broken in ATP to form ADP is largely controlled by entropy change in the system rather than by effects on the environmental entropy. In other words, energy transfer and bonding are not the main controlling features of the reaction. Hence this is a significant argument from the evidence against the use of the term "high energy phosphate bond" since it can easily mislead students and possibly even some biochemists. The great significance of biological systems is the tremendous organization they exhibit which in thermodynamics is described by entropy.

Summary

It is proposed that chemical reactions at constant temperature and pressure carried out by a process that

is totally unopposed be described in terms of ΔS_{tu}° rather than ΔG° where $\Delta S_{tu}^\circ = -\Delta G^\circ/T$. A major advantage lies in the fact that $\Delta S_{tu}^\circ = \Delta S_s^\circ + \Delta S_e^\circ$ where ΔS_e° and ΔS_s° describe the entropy changes of environment and system, respectively, and ΔS_{tu} refers to the total entropy change for the totally unopposed reaction at constant temperature and pressure. For a reaction to be a feasible one ΔS_{tu}° must be a positive quantity. Since for many reactions of interest to chemists ΔS_s° is negative, this means that feasibility depends on ΔS_e° being positive and sufficiently large in magnitude to provide for $\Delta S_{tu}^\circ > 0$. The related equation $\Delta S_{tu}^\circ = \Delta S_s^\circ - \Delta H_s^\circ/T$ shows how ΔS_{tu} is controlled by temperature since both ΔS_s° and ΔH_s° are nearly independent of the temperature. For high temperatures, reaction feasibility is controlled by ΔS_s° , while at low temperatures, reaction feasibility is controlled by ΔS_e° , or in other words by the ability of the system to increase the entropy of the environment. The function S_{tu} is a characteristic function defined and used by Planck, and it is here proposed that S_{tu} be called the Planck function.

The advantage for students lies in the emphasis given to entropy. Presumably every observed change must be accompanied by an increase in the total entropy. Unopposed changes at constant pressure and temperature are no exception and for these changes the total entropy can be divided into two parts. It is then appropriate to ask and find answers to the question as to whether the more important feature controlling the change is what happens to the energy distribution within the system or the energy distribution between the system and its environment. On the basis of these answers the student has an improved notion of where to direct his efforts toward interpretation of the behavior of a chemical system.

A further development of relationships between ΔH_s and ΔS_s has recently been made by Larson and Hepler (12). Their discussion centers on the thermodynamics of proton transfer reactions and they present a rather comprehensive and critical summary of available data. In some personal correspondence with Dr. Karl Bloss at Batelle Institut e.V. in Frankfurt, Germany, he has pointed out a rather similar discussion by him some years ago (13). What has here been referred to as the Planck function he proposed calling "lability."

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