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# The Use and Misuse of the Laws of Thermodynamics

I cannot ever remember having sold a book, but I once burned one. It was a text-book of thermodynamics. I have felt a little guilty about that ever since, but only because the particular book that so incensed me at the time was in fact not much worse than nearly all the others in its field. Thermodynamics is incredibly badly presented, for the most part by people who do not understand it. The usual undergraduate course consists more of pretentious pseudo-philosophy than of anything relevant to experimental science. It is hardly surprising that the undergraduate's gorge rises when he is never told what thermodynamics is, or what it is not, or what it is for; or when he rightly suspects that the arguments presented to him are fallacious, or as he would say: "You can prove anything you like by thermodynamics"; or when he is asked as he often is to calculate the results of impossible experiments on imaginary substances.

One of the sources of this muddle is the misguided compulsion most teachers feel to try to introduce thermodynamics historically.[1] Unless the teacher has himself done research on the history, his account is certain to be grossly inaccurate or grossly incomplete or most probably both. Why for example does he never introduce the first and second laws in the order in which they were originally formulated, namely the second before the first? Why, for another example, does his usual account of Carnot's cycle bear so little relation to Carnot's own exposition? But even if the teacher of thermodynamics were a competent historian there would be little to be said for introducing thermodynamics historically. The history of thermodynamics is in fact a much more difficult subject than thermodynamics itself and much less well understood.

Whatever part Carnot's cycle may have played in the history of thermodynamics, its use in undergraduate courses wastes time; unnecessarily introduces considerable conceptual difficulties; hides and obscures the introduction of the new, and in thermodynamics all-important, physical quantity called temperature; and worst, is often used, by way of a stealthy assumption of precisely that which it is proposed to prove, to seem to deduce the second law from the first.[2] Moreover neither Gibbs in the 1870s nor any of the authors of the best modern treatments found it necessary to make use of Carnot's cycle.

Another source of pedagogic muddle is the widely-held misconception that thermodynamics approaches closely the ideal of a purely deductive science, deducible like Euclidean geometry from a small number of axioms which can be expressed in words, though much progress has been made toward the axiomatization of thermodynamics,[3] the mathematical structure has still not been completely separated from the physical content. But none of that need concern the undergraduate. Provided that having made our entry, we then rely quite formally on deduction, we may choose to enter the subject at any level of sophistication, just as we commonly choose to introduce mechanics to students for the first time through Newton's laws of motion rather than through the principle of least action. A rare undergraduate may some day want to interest himself in the logical foundations of thermodynamics. In the meantime he will come to no harm while he listens to us teaching the others, and him, how to *use* thermodynamics in his chemistry. At least in this university I hope that thermodynamics will always be taught as part of an experimental science and never as muddled metaphysics nor bogus history.

Now what *is* thermodynamics? One way of answering that question is by a comparison of thermodynamics with mechanics. In mechanics one deals with three independent basic quantities: mass, length, and time. In electromechanics, by which I mean mechanics plus electricity and magnetism, that number is expanded to four: mass, length, time, and electric current. Thermodynamics includes the whole of electromechanics but

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[2] Briefly,

$$\Delta U = w + q$$

*Assume* that a substance exists for which simultaneously:

(1): $PV = nRT$

and (2): $dU = C_V dT$

i.e., (2a): $(\partial U/\partial V)_T = 0$ and (2b): $(\partial U/\partial T)_V = C_V = C_V(T)$

*Then:*

$$q/T = dU/T - w/T$$
$$= C_V(T)dT/T + nRdV/V + (P_e - P)dV/T$$

so that when $P_e = P$, that is to say when the expansion is reversible,

$$q_{rev}/T = C_V(T)dT/T + nRdV/V$$

Therefore for the reversible expansion of a substance defined by both (1) and (2), $q/T$ depends only on the initial and final temperatures, and on the initial and final volumes, and so for a closed cycle $\Sigma(q/T) = 0$.

[1] GUGGENHEIM, E. A., *Bulletin* of the Institute of Physics, June 1955.

[3] LANDSBERG, P. T., *"Thermodynamics,"* Interscience Publishers, a division of John Wiley & Sons, New York, 1961.

is more general still because it also deals with a fifth basic quantity: temperature.[4]

## The First Law

Having recognized the existence of differences of temperature, we are led to the notion that one of the ways of changing the energy of a body is by placing it in contact with a body at a different temperature. When a hot body is placed in contact with a cold one, energy flows from the hot body to the cold until the temperatures of the two bodies are equal. Such an energy flow is called a flow of heat.

Whereas in electromechanics we wrote

$$\Delta E = w$$

where $\Delta E$ is the energy change and $w$ the work done on the body, we must now write

$$\Delta U = w + q \qquad (1)$$

where $q$ is the flow of heat into the body from any bodies at different temperatures with which it is in contact, (its surroundings), and where we have distinguished the old electromechanical energy $E$ from the thermodynamic energy $U$. It is only when $E$ is independent of temperature that $E$ and $U$ are the same.

Equation (1) expresses the first law. It is just the law of conservation of energy expanded so as to include energy changes caused by temperature differences. But is is incomplete until we learn how to measure the quantities in our equation. In thermodynamics we add to the electromechanical armory of measuring devices or meters, such as cathetometers, dynamometers, manometers, and potentiometers, two new ones: thermometers which are used to measure temperature, and calorimeters.

Expositions of calorimetry, especially in textbooks of physics, are still hedged about with antique concepts like the so-called mechanical equivalent of heat which belong, like phlogiston, to the time when the first law of thermodynamics was not yet understood. It is commonly, but wrongly, supposed that in calorimetry one measures heat. On the contrary, the whole art of calorimetry depends on making the heat $q$ as small as possible, or at least as reproducible as possible, and preferably both. In a calorimetric experiment one measures only changes of temperature and amounts of work, and then uses the first law to derive values for energy changes. The key to understanding calorimetry is, as usual in science, to think about exactly what one does in a real experiment in a real laboratory.

Let us use a calorimeter to measure the difference

$$\Delta U = U_P - U_R$$

*between the energy $U_R$ of:*
1. A mixture of 0.01 mole (i.e., 0.02 g) $H_2$ + 0.005 mole (i.e., 0.16 g)$O_2$
            (which we call R for "reactants")
occupying a volume of 200 cm³ at the temperature 25°C *and the energy $U_P$ of:*

2. 0.01 mole (i.e., 0.18 g) $H_2O$
            (which we call P for "products")
also occupying a volume of 200 cm³ at the temperature 25°C

We make up the mixture R in a closed calorimeter of volume 200 cm³ and adjust the temperature to 25°C. We then allow the mixture to react to form water and measure the temperature rise $\delta\theta$.[5] Since no work was done we then have according to the first law:

$$U_P(25°C + \delta\theta, 200 \text{ cm}^3) - U_R(25°C, 200 \text{ cm}^3) = 0 + q'(\text{leak}) \simeq 0$$

where $q'$ is the heat leak, which is kept as small as possible. We now cool the calorimeter back to 25°C and then use ordinary electromechanical methods to measure the work $w$ needed to increase the temperature by $\delta\theta$ so that:

$$U_P(25°C + \delta\theta, 200 \text{ cm}^3) - U_P(25°C, 200 \text{ cm}^3) = w + q''(\text{leak}) \simeq w$$

Then by subtraction we obtain

$$U_P(25°C, 200 \text{ cm}^3) - U_R(25°C, 200 \text{ cm}^3) = -w + (q' - q'') \simeq -w$$

If $(q' - q'')$ is negligible, as it must be in a good calorimetric experiment, then the measured value of $-w$ is equal to the energy difference which we set out to measure. All calorimetric experiments fall into that pattern.

It will be noticed that I have been at pains to specify exactly what the system is, and exactly what are the values of the independent variables. Much of the difficulty students have with thermodynamics stems not from mathematical difficulties, for the mathematics needed in thermodynamics is elementary and easy, but from failure to decide exactly what system is being talked about and exactly what are the values of the independent variables.

When, as is common, the pressure rather than the volume is held constant in a calorimetric experiment $-w$ is equal, not to the energy change $\Delta U$ but to the closely related *enthalpy* change $\Delta H$.

In my experience the student's difficulties with thermodynamics arise as often from his failure to understand the first law as from his failure to understand the second law, to which we now turn.

## The Second Law

We shall state the second law in two parts. First we consider a body which has uniform intensive properties, that is to say a body which has throughout itself the same density and the same temperature and the same dielectric constant and so on. Such a body is called a phase.[6]

The first part of our statement of the second law is that for any phase $\alpha$:

$$dU^\alpha = -P^\alpha dV^\alpha + T^\alpha dS^\alpha + \Sigma_i \mu_i^\alpha dn_i^\alpha \qquad (2a)$$

[4] A sixth basic quantity; luminous intensity (basic unit; the candela) is also needed in physics but only seldom in physical chemistry. It is modern practice to recognize a seventh basic quantity; amount of substance (basic unit; the mole) in physical chemistry.

[5] In other reactions the temperature may of course fall.
[6] Here we shall ignore the effects of the earth's gravitational field. In a tall enough body some intensive properties such as the density will vary sensibly and continuously from top to bottom. Whenever such variation is important, the body must be regarded as a vertical pile of separate phases.

where we have assumed that any work is pressure $(P)$—volume $(V)$ work,[7] where $T$ is called the thermodynamic temperature and is here introduced for the first time along with $S$ which is called the entropy, and where $\mu_i$ is called the chemical potential of the substance $i$ and $n_i$ is the amount of that substance, and we have summed over all substances present.

Of these quantities $P$ and $V$ can be measured by ordinary mechanical methods and $n_i$ by ordinary chemical methods. But are $T$, $S$, and $\mu_i$ completely and independently defined by this equation? They are if, and only if, we can derive from the equation a recipe for the measurement of each. We find that we *can* derive recipes for measuring ratios of thermodynamic temperatures $T$, by means of a special kind of thermometer called a gas thermometer, and for measuring *differences* of entropy or of chemical potential by means of electromechanical, thermometric, and calorimetric measurements.

It turns out to be convenient to make some new definitions:

$$H = U + PV \qquad A = U - TS \qquad G = H - TS$$

where $H$ is the enthalpy which we mentioned earlier, $A$ is called the Helmholtz function or the Helmholtz free energy, and $G$ is called the Gibbs function.

We can for convenience use these new definitions to transform our fundamental equation to any of the following:

$$dH^\alpha = V^\alpha dP^\alpha + T^\alpha dS^\alpha + \Sigma_i \mu_i^\alpha dn_i^\alpha$$

$$dA^\alpha = -P^\alpha dV^\alpha - S^\alpha dT^\alpha + \Sigma_i \mu_i^\alpha dn_i^\alpha$$

$$dG^\alpha = V^\alpha dP^\alpha - S^\alpha dT^\alpha + \Sigma_i \mu_i^\alpha dn_i^\alpha$$

These equations, though convenient, of course contain nothing new. We might note in passing, however, that the quantity called "energy" in textbooks of physics, such as the "energy" $E = Q^2 l/2\epsilon A$ of charging a condenser is actually a change in free energy and not of energy. The free energy turns out to be the thermodynamic analogue of the electromechanical potential energy, and is both a more familiar and less complicated quantity than the energy $U$.

We must now complete our statement of the second law. Any body can be regarded as being made up of one or more phases. We must now distinguish between such a body which is in internal equilibrium and one which is not. If the body consists of a cup of water with a spoonful of sugar lying at the bottom it is not in internal equilibrium because, without any help from us, the sugar will dissolve in the water. If one part of a body is hot and another cold, the body is not in internal equilibrium because, without any help from us, the hot part will cool and the cold part will warm up. If the body consists of a beaker containing a solution of acidified permanganate at room temperature to which an excess of a solution of an oxalate has just been added then the body is not in internal equilibrium because, without any help from us, a chemical reaction will occur and go on until virtually all the permanganate has been reduced to manganous ion.[8]

The second part of our statement of the second law is that for any body consisting of one or more phases, when the body is isolated from its surroundings, that is to say when $U$ and $V$ are held constant, then the entropy $S$ of the whole body either increases or remains constant according to whether the body as a whole is not, or is, in internal equilibrium. Expressed in symbols we then have for the second part of our statement of the second law:

$$dS(= \Sigma_\alpha dS^\alpha) \geqslant 0 \qquad (U \text{ and } V \text{ constant}) \qquad (2b)$$

Equations (2a) and (2b) together with equation (1) for the first law contain the whole of thermodynamics; the rest is easy algebra.
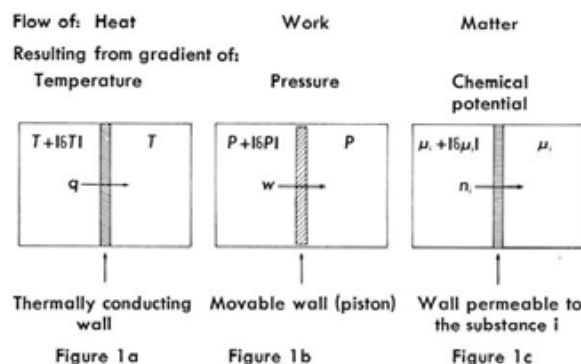
From equation (2b) we can immediately derive a set of other inequalities. In particular

$$dS \geqslant 0 \qquad (H \text{ and } P \text{ constant})$$

$$dA \leqslant 0 \qquad (T \text{ and } V \text{ constant})$$

$$dG \leqslant 0 \qquad (T \text{ and } P \text{ constant})$$

Of these, the last is the most useful because most of our experiments are in fact done at more or less constant temperature and pressure.



Thermally conducting wall — Figure 1a
Movable wall (piston) — Figure 1b
Wall permeable to the substance i — Figure 1c

From equations (1), (2a), and (2b), we can also derive the criteria of thermal, mechanical, and material equilibrium. If two parts of a body separated by a thermally conducting wall have different temperatures (Fig. 1a) then heat will flow spontaneously from the part with the higher $T$ to the part with the lower $T$. If two parts of a body separated by a movable wall or piston have different pressures (Fig. 1b) then work will flow spontaneously from the part with the higher $P$ to the part with the lower $P$. If two parts of a body separated by a wall permeable to the substance $i$ have different chemical potentials of the substance $i$ (Fig. 1c) then the substance $i$ will flow from the part with higher $\mu_i$ to the part with lower $\mu_i$.

Among the host of other useful relations which can be derived from these equations is one which is of great importance to engineers. We have seen how one of the ways of increasing the energy of a body is by placing it in contact with a body at a higher temperature, for example by lighting a fire under it. We can now

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[7] If other kinds of work are involved, we merely include the appropriate electromechanical work terms $x\,dX$ along with $PdV$.

[8] A body consisting of more than one phase can thus be in internal disequilibrium from several causes. A body consisting of a single phase can, however, be in internal disequilibrium only because a chemical reaction is taking place spontaneously in the phase.

deduce that when the body is restored to its original state *some* but *not all* of the stored energy can be recovered in a useful form such as can be used to raise water from a well or to drive a washing-machine.

### The Usefulness of Thermodynamics

Now I shall give a different answer to the question "What is thermodynamics?" Thermodynamics is a collection of useful relations between quantities, every one of which is independently measurable. What do such relations "tell one" about one's system, or in other words what do we learn from thermodynamics about the microscopic explanation of macroscopic changes? Nothing whatever. What then is a thermodynamic theory? There is no such thing. What then is the *use* of thermodynamics? Thermodynamics is useful precisely because some quantities are easier to measure than others, and that is all.

I shall now give three examples of such useful relations, all of which I happen to have used recently in my own work.

*First example:*

$$\Delta_e H = T(V^{g\sigma} - V^{l\sigma})\, dP^\sigma/dT \qquad \text{(Clapeyron's relation)}$$

In connexion with a certain statistical mechanical theory of fluid mixtures, I recently needed the latent heats of vaporization $\Delta_e H$ over wide ranges of temperature for simple substances like argon and methane. Unfortunately $\Delta_e H$ is difficult to measure accurately and has in fact been measured only at one temperature for each of these substances. However, the orthobaric pressure $P^\sigma$ and the orthobaric volumes $V^{g\sigma}$ of the gas and $V^{l\sigma}$ of the liquid are easier to measure and have been measured accurately over wide temperature ranges. So I was able to use these results with Clapeyron's relation instead.

*Second example:*

$$\Delta_{mV}U \simeq \Delta_{mP}U - T(\alpha/\kappa)\Delta_{mP}V$$

Another statistical mechanical theory of liquid mixtures leads to predictions about the energy of mixing $\Delta_{mV}U$ at constant *total volume*. This is a difficult quantity to measure. When liquids mix, the total volume changes. Not, it is true, by much, but the pressures needed to prevent such changes are nevertheless often hundreds of atmospheres. In other words we should need a very strong calorimeter to measure $\Delta_{mV}U$ directly. The quantity we can and do measure is $\Delta_{mP}U$ the energy of mixing at constant *pressure*. Provided we know also the expansivity $\alpha$ and compressibility $\kappa$ and the volume change on mixing at constant pressure $\Delta_{mP}V$, all of which quantities are relatively easy to measure, then we can use the equation to calculate values of $\Delta_{mV}U$ which we can then compare with the theory.[9]

*Third example:*

$$V - T(\partial V/\partial T)_P = (\partial H/\partial P)_T$$

Any pair of molecules interacts with an energy which dies away rapidly as the molecules are separated. At very short distances the energy is positive (repulsive). If it were not so, molecules could occupy the same space, and matter would cease to exist. At greater distances the energy is negative (attractive). If it were not so all gases would be perfect and no gas would ever condense to a liquid or solid. Of the various ways of studying this pair-interaction energy, the most direct is through measurements of the dependence of the volume of a gas on temperature and pressure, that is to say, of the deviations from Boyle's law, which can be related via statistical mechanics to the dependence of the pair-interaction energy on intermolecular distance. At temperatures far below the critical, where the results of such measurements are most informative, however, the measurements become increasingly inaccurate because of the adsorption of the gas on the walls of the apparatus. At such temperatures we can study, instead, the quantity on the right-hand side of the equation, namely the dependence of the enthalpy on pressure at constant temperature, which we can measure[10] in a flow-calorimeter fitted with a throttle, like that shown in Figure 2, without any errors due to adsorption.
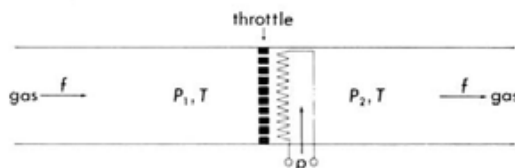


Figure 2. Flow-calorimeter fitted with a throttle. When a steady state has been achieved, and in the absence of heat losses, $p/f = \int_{P_1}^{P_2} (\partial H/\partial P)_T dP$ where $f$ is the flow-rate of the gas and $p$ is the (electric) power required to restore the gas to the temperature $T$ after it has passed through the throttle.

But none of these examples has much to do with chemical reactions. What useful result does thermodynamics lead to when applied to chemical equilibrium?

Let us take as an example the important reaction by which atmospheric nitrogen is converted into ammonia.

| | $\frac{1}{2}N_2$ | $+$ | $\frac{3}{2}H_2$ | $\rightleftharpoons$ | $NH_3$ |
|---|---|---|---|---|---|
| Amounts present before introduction of catalyst: | $a$ | | $b$ | | $c$ |
| Amounts present at some time after introduction of catalyst: | $a - \frac{1}{2}\xi$ | | $b - \frac{3}{2}\xi$ | | $c + \xi$ |

Here we start with amounts $a$, $b$, and $c$ of nitrogen, hydrogen, and ammonia respectively, and suppose that at a time $t$ after the introduction of a catalyst the amount of ammonia has been increased by the chemical reaction shown from $c$ to $c + \xi$. What if anything does thermodynamics tell us about the equilibrium value of $\xi$?

[9] McGLASHAN, M. L., MORCOM, K. W., AND WILLIAMSON, A. G., *Trans. Faraday Soc.*, **57**, 581, 588, 601, 907 (1961); DIAZ-PENA, M. AND McGLASHAN, M. L., *Trans. Faraday Soc.*, **57**, 1511 (1961).

[10] FRANCIS, P. G., McGLASHAN, M. L., AND WORMALD, C. J., *NEL Report*, 1963, no. 122: and forthcoming publications.

From equations (2a) and (2b) it follows immediately that

$$\ln(\lambda_{N_2}^{1/2}\lambda_{H_2}^{3/2}/\lambda_{NH_3})d\xi/dt \geqslant 0$$

according as the phase is not, or is, in internal equilibrium, so that at equilibrium

$$\lambda_{NH_3}(T, P, \bar{\xi}) = \{\lambda_{N_2}(T, P, \bar{\xi})\}^{1/2}\{\lambda_{H_2}(T, P, \bar{\xi})\}^{3/2} \quad (3)$$

where $\bar{\xi}$ is the equilibrium value of $\xi$, and $\lambda_i$ is defined by

$$\mu_i = RT \ln \lambda_i$$

Equation (3) is the thermodynamic equilibrium law for this chemical reaction.

Thermodynamics does not, however, tell us how to solve equation (3) for $\bar{\xi}$. To do that we must appeal to statistical mechanics or to experiment from which we learn that, provided that the gases are perfect which is a good approximation at high temperatures and low pressures, then for each gas:

$$\lambda_i(T, P, x_i) = \lambda_i\dagger(T)x_iP/P\dagger \quad (4)$$

where $x_i$ is the mole fraction of the gas, $P\dagger$ is a chosen standard pressure, and $\lambda_i\dagger$ depends only on $T$.

By substitution of equation (4) in equation (3) we then obtain:

$$\frac{\bar{x}_{NH_3}}{\bar{x}_{N_2}^{1/2}\bar{x}_{H_2}^{3/2}P} = \frac{(a+b+c-\bar{\xi})(c+\bar{\xi})}{(a-{}^1/_2\bar{\xi})^{1/2}(b-{}^3/_2\bar{\xi})^{3/2}P} = \frac{\{\lambda_{N_2}\dagger(T)\}^{1/2}\{\lambda_{H_2}\dagger(T)\}^{3/2}}{\{\lambda_{NH_3}\dagger(T)\}P\dagger} = K(T,P\dagger) \quad (5)$$

and we notice that the right-hand side depends only on temperature. We call it the equilibrium constant and have now derived the famous equilibrium law. I repeat that the *thermodynamic* equilibrium law is equation (3), and that equation (4), and hence (5), cannot be derived without recourse to statistical mechanics or to experiment. Nearly all textbooks get this wrong. The so-called thermodynamic deduction of (5) by use of van't Hoff's "equilibrium box" is sufficiently complicated to hide the stealthy introduction of the non-thermodynamic equation (4).

Equation (5) still cannot be used to calculate an absolute value of $\bar{\xi}$ but now if we know the yield at one pressure then we can calculate the yield at another pressure and the same temperature.

### Calculation of Equilibrium Constants

I shall now deal with two famous questions about equilibrium constants which occupied the minds of scientists at the end of last century and at the beginning of this century. The first is: *"Can equilibrium constants be determined from calorimetric measurements alone?"* The answer is yes, provided that we use some statistical mechanical results as well as thermodynamic ones.

Equation (5) is a statistical mechanical one. Once having it, can we relate the right-hand side, which contains only properties of the *pure* substances, to other quantities all of which can be measured calorimetrically? It turns out that from pure thermodynamics we can write

$$-RT \ln K(T,P\dagger) = \Delta H(T,P\dagger) - T\Delta S(T,P\dagger)$$

where $\Delta H$ is the enthalpy change and $\Delta S$ is the entropy change which occur when $^1/_2$ mole of pure $N_2$ and

$^3/_2$ mole of pure $H_2$ combine to form 1 mole of $NH_3$ all at the standard pressure $P\dagger$ and the temperature $T$.

The $\Delta H$ cannot be measured *directly* in a calorimeter because the reaction does not go to completion. However, we *can* measure values of $\Delta H$ for various reactions involving nitrogen, hydrogen, and ammonia which *do* go to completion and then add and subtract the results so as to get the $\Delta H$ we need.

We are then left with the question whether we can measure $\Delta S$ calorimetrically. Thermodynamics tells us how to measure the difference

$$S(T,P\dagger) - S^r(T \to 0)$$

for any substance by making calorimetric measurements of heat capacity and enthalpy of transition from a very low temperature, usually about $10°K$, on the solid, up through any change to liquid or gas, to the temperature $T$ and pressure $P\dagger$. Having done such measurements for each of the substances we can add and subtract and obtain

$$\Delta S(T,P\dagger) - \Delta S^r(T \to 0)$$

Statistical mechanics tells us that $\Delta S^s(T \to 0)$ is often zero and if it is not zero how to calculate it. (It is not zero in the ammonia synthesis.) This is sometimes called the third law of thermodynamics but it is better to regard it as a statistical mechanical result.

We can now calculate $\Delta S(T,P\dagger)$ and hence $K$. In Figure 3 a value $(+)$ of $K(700°K, 1$ atm$)$ so calculated from calorimetric results is compared with the directly measured results $(\circ)$ of Larson and Dodge. The agreement is certainly within experimental error. (The curve drawn in Figure 3 will be discussed later.)

We now turn to the second question which is: *"Can equilibrium constants be calculated according to the methods of statistical mechanics by making use only of measurements of the mechanical properties of individual molecules?"* The answer is: almost but not quite.
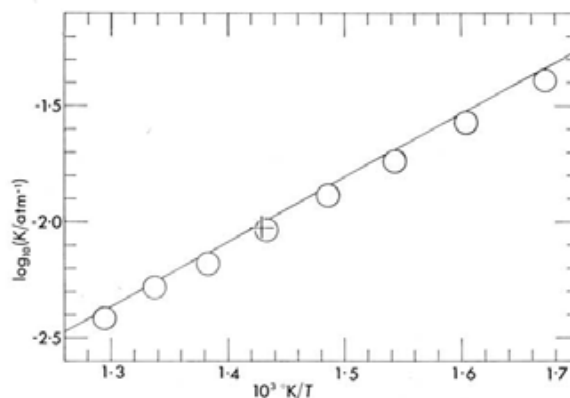


Figure 3. The equilibrium constant for the ammonia synthesis. ○ direct measurements at 10 atm [Larson and Dodge, J. Amer. Chem. Soc., **45**, 2918(1923); **46**, 367(1924)]. + calculated as described in the text for 700°K from calorimetric measurements only. The curve was calculated as described in the text from spectroscopic measurements plus one calorimetric result.

By investigating the quantally allowed energies of molecules we can use statistical mechanics to derive a formula for the equilibrium constant of a perfect gas reaction, which contains only spectroscopically measurable properties of the motions of individual molecules

*plus one* calorimetrically measured macroscopic quantity. The need for this one calorimetric quantity arises because, in the case of enthalpies, in contrast to entropies, we do not have a reliable way of calculating the difference of enthalpy from the enthalpies of the separate substances each measured from some "base camp."

For the reaction $\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightleftharpoons NH_3$ the formula takes the form:

$$
\begin{aligned}
-\ln\{K(T,P\dagger = 1\text{ atm})/\text{atm}^{-1}\} = \\
\frac{T^*}{T}\Bigg[\frac{\Delta_f H(T^*,P\dagger = 1\text{ atm})}{RT^*} + 3 - \sum_{i=1}^{6}\left\{\frac{\theta_i/T^*}{\exp(\theta_i/T^*)-1}\right\}_{NH_3} \\
+ \frac{1}{2}\left\{\frac{\theta/T^*}{\exp(\theta/T^*)-1}\right\}_{N_2} + \frac{3}{2}\left\{\frac{\theta/T^*}{\exp(\theta/T^*)-1}\right\}_{H_2}\Bigg] \\
-\frac{3}{2}\ln(M_{NH_3}/\text{g mol}^{-1}) + \frac{3}{4}\ln(M_N/\text{g mol}^{-1}) + \\
\frac{9}{4}\ln(M_{H_2}/\text{g mol}^{-1}) \\
+ \frac{3}{2}\ln(\Theta_{NH_3}/°K) - \frac{1}{2}\ln(\Theta_{N_2}/°K) - \frac{3}{2}\ln(\Theta_{H_2}/°K) \\
+ \sum_{i=1}^{6}\ln\{1-\exp(-\theta_i/T)\}_{NH_3} \\
-\frac{1}{2}\ln\{1-\exp(-\theta/T)\}_{N_2} - \frac{3}{2}\ln\{1-\exp(-\theta/T)\}_{H_2} \\
+ \ln\sigma_{NH_3} - \frac{1}{2}\ln\sigma_{N_2} - \frac{3}{2}\ln\sigma_{H_2} \\
+ 3\ln(T/°K) - \frac{5}{2}\ln 4.333 - \frac{1}{2}\ln\pi \qquad (6)
\end{aligned}
$$

where $T^*$ is the temperature at which a value of the molar enthalpy of formation $\Delta_f H$ of ammonia is available, $\theta$ is the vibrational characteristic temperature, $M$ is the molar mass, $\Theta$ is the rotational characteristic temperature, and $\sigma$ is the symmetry number of the molecule.

The values needed for the calculation of $K$ from equation (6) are given in the following table.

Table 1. Results Needed for the Calculation of $K$ from Equation (6)

| | $M$/g mol$^{-1}$ | $\Theta$/°K | $\sigma$ | $\theta$/°K |
|---|---|---|---|---|
| $N_2$ | 28.01 | 2.88 | 2 | 3350 |
| $H_2$ | 2.016 | 85.3 | 2 | 5980 |
| $NH_3$ | 17.03 | 12.3 | 3 | 1370, 2340[2]; 4800, 4910[2] |

The values of $\Theta$ and of $\theta$ were taken from G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," van Nostrand, 1945, and "Molecular Spectra of Diatomic Molecules," van Nostrand, 1950.

For $NH_3$:[11]

$$\Delta_f H(T^* = 298.15°K, P\dagger = 1\text{ atm})/298.15\, R°K = -18.63$$

The curve in Figure 3 is that calculated according to equation (6) with the values given in Table 1. The agreement is probably within experimental error though the discrepancies at the lowest temperatures are a little surprising.

It would be fair to expect a final-year honors candidate in chemistry to discuss these discrepancies. First he would have to examine all the approximations made in the derivation of equation (6), such as the use of Boltzmann statistics, the separability of the several modes of motion, the treatment of the translational modes and especially the rotational modes as effectively classical, the assumption that all the vibrations are harmonic, and the omission of contributions from electronic and nuclear modes. He would then have to examine the difference to be expected between values of $K$ measured on the real gas mixture at 10 atm and those for an ideal gas mixture. Finally he would have to examine critically the accuracy of the measured spectroscopic quantities, of the calorimetric quantity (which is probably the main culprit), and of Larson and Dodge's direct measurements of the equilibrium constant. If he has a good grasp of both the theoretical and the experimental aspects of chemical thermodynamics and statistical mechanics he will be able to make a good job of this, but not otherwise.

The answers to the two questions we asked about chemical equilibrium constants form the principal achievement of thermodynamics and statistical mechanics in chemistry.

## What Entropy Does Not Mean

It is tempting, but in my opinion a complete waste of time, to inquire into the "meanings," as it were, of thermodynamic functions like the enthalpy, or the Gibbs function, or (especially) the entropy. Thermodynamics reveals nothing of any microscopic or molecular meaning for its functions. Statistical mechanics *does* provide a severely quantum-mechanical microscopic interpretation for the thermodynamic functions but leads to no general easy quasi-geometrical picture. Nevertheless it is widely assumed by chemists and others that increase of entropy measures increase of "disorder" or of "randomness" or of "mixed-upness." When, if ever, is this assumption justified?

The entropy change which occurs when an *isolated* body moves spontaneously toward equilibrium is, according to thermodynamics, always positive. By the methods of statistical mechanics, the entropy increase in such an *isolated* body can be simply related to the increase in the number of independent eigenstates to which the isolated body has access. 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 each of these special cases the number of independent accessible eigenstates *is* simply related to the purely geometrical or spatial mixed-upness, and so, therefore, is the entropy. But *only* in these special cases.

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.

The Dewar flask shown in the first photograph in Figure 4 contains a mixture of sodium thiosulfate and water—thoroughly mixed-up—dissolved in fact—and more or less isolated. If anything happens of itself in that flask then it will certainly do so with an increase of entropy, and if the view widely held by chemists were

[11] *Circular 500* (U.S. National Bureau of Standards, 1952).

correct, therefore with an increase of mixed-upness. Yet when a catalyst is introduced, for example in the form of a few small crystals of sodium thiosulfate, so that the body hitherto "frozen" is "thawed," the process which takes place is, as we can see, the partial *sorting* of sodium thiosulfate on the one hand and of water on the other. If such a process of sorting can be described as an increase of "mixed-upness" then I do not understand the meaning of words.
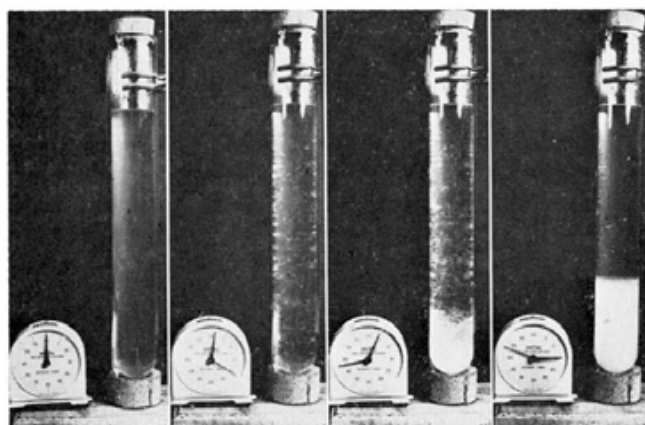


Figure 4

But the situation is even worse than this, for 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. Expressed in symbols[12]

$$(\partial S/\partial \xi)_{U.V} = -T^{-1}(\partial G/\partial \xi)_{T.P} \geqslant 0$$

where we use $\xi$ to mean the extent of any natural process such as a chemical reaction or the crystallization of sodium thiosulfate from a supersaturated solution. Thus, 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.[13]

One cannot so easily opt out of the game. One must try to invent a model, use statistical mechanics to deduce experimentally refutable consequences, and then test them against experiment. And different models

will lead to quite different values and even signs for the entropy changes of ordinary reactions.

Some of this kind of misunderstanding has even rubbed off on the layman. I suspect that Lord Snow's choice of the second law of thermodynamics as a test of scientific literacy for the humanist (he said[14] it was "about the scientific equivalent of: *Have you read a work of Shakespeare's?*") derives from just such a misunderstanding about the meaning of entropy, and especially from its supposed implications with respect to the Fate of the Universe.

Since I regard these supposed implications as nonsensical I can hardly be expected to give a coherent account of them, but I think the argument runs something like this. Any process which actually takes place in the universe increases the entropy of the universe. Increase of entropy implies increase of mixed-upness. Ergo the inevitable fate of the universe is a state of more and more mixed-upness. In the end there would be neither sea nor dry land, but I suppose a kind of porridge. But then there would be no earth and no heavens but just some species of structureless particle distributed uniformly throughout space. Then the universe would have suffered the so-called "heat-death," and chaos would be come again.

Now I suppose that if thermodynamics could be shown (but how?) to be applicable to the universe, and if the universe were known to be a bounded and isolated body (whatever that might mean in the case of the universe), then we might deduce that the universe would eventually reach a state of complete thermal, mechanical, and chemical equilibrium. But there is no scientific reason to suppose that the universe *is* a bounded isolated body. Isolated? Isolated from what indeed? And even if it were, there is no reason to suppose that thermodynamics, which is an experimental science, can be applied to bodies as large as the universe. Clausius's famous statement: "Die Entropie der Welt strebt einem Maximum zu" is, to say the least, misleading. The pessimistic idea that the fate of the universe is chaos no doubt has an appeal to a certain kind of mind but it is a matter of faith which has no support from the science of thermodynamics.

### Acknowledgment

[12] GUGGENHEIM, E. A., "Thermodynamics," North-Holland Publishing Company, Amsterdam, 3rd ed., 1957, p. 45.
[13] GUGGENHEIM, E. A., *Research*, 2, 450 1949.

[14] SNOW, C. P., "The Two Cultures and a Second Look," Cambridge University Press, 1964, p. 15.