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## The Third Law of Classical Thermodynamics

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The third law, or law of limits as  $T \rightarrow 0^\circ\text{K}$ , is expressed as: "for any real phase

$$\lim_{T \rightarrow 0} \left( \frac{\partial S}{\partial x_i} \right)_{x_j, n} = 0,$$

and for any spontaneous isothermal process,

$$\lim_{T \rightarrow 0} \sum_i \nu_i \left( \frac{\partial S}{\partial n_i} \right)_{T, y, n_j} \leq 0."$$

The equality sign applies to reversible processes and the inequality sign to irreversible processes. The  $n$ 's represent composition variables, the  $x$ 's (or  $T$  and the  $y$ 's) a suitable set of state variables, and the  $\nu$ 's the number of moles of the components entering into the reaction (positive for products, negative for reactants). Alternative statements of the third law are given and derived from the above statement. The completeness of this statement as a usable postulate for the further development of classical thermodynamics is briefly discussed.

### INTRODUCTION

LET us begin the discussion of the statement of the third law by a summary of the postulates necessary to form a basis for the development of a practical science of thermodynamics.

(1) There exist single valued functions of the state of the system which are: (a) The internal energy  $U$ ; (b) the absolute temperature  $T$ ; (c) the entropy  $S$ .

(2) These functions are such that: (a) For any infinitesimal change,

$$dU = dQ - dw,$$

where  $dU$  (a perfect differential) represents the change of the function  $U$ ,  $dQ$  is the heat absorbed, and  $dw$  is the work done by the system during the change. (b) A temperature  $T$  may be assigned to any material system which is in thermal equilibrium, and this absolute temperature  $T$  is a function of the empirical temperature  $t$  only.<sup>1</sup> (c) For any infinitesimal change

$$dS \geq dQ/T,$$

where the equality sign applies to reversible processes and the inequality sign to irreversible

processes. Furthermore, the entropy of an isolated system increases spontaneously until the isolated system reaches a state of equilibrium,<sup>2</sup> that is,  $dS \geq 0$ .

(3) The behavior of certain properties of a system as  $T \rightarrow 0^\circ\text{K}$  may be expressed in terms of the following properties of the entropy function:

(a) For any real phase

$$\lim_{T \rightarrow 0} \left( \frac{\partial S}{\partial x_i} \right)_{x_j, n} = 0.$$

(b) For any spontaneous isothermal process

$$\lim_{T \rightarrow 0} \sum_i \nu_i \left( \frac{\partial S}{\partial n_i} \right)_{T, y, n_j} \leq 0.$$

The equality sign applies to reversible processes and the inequality sign to irreversible processes. The  $n$ 's represent composition variables, the  $x$ 's (or  $T$  and the  $y$ 's) a suitable set of state variables and the  $\nu$ 's the number of moles of the components entering into the reaction (positive for products and negative for the reactants).

The statements under (1) and (2) constitute a generally accepted set of postulates: sometimes referred to as the zeroth law, the definition of  $T$ ; the first law, the definition of  $U$ ; and the second law, the definition of  $S$ . We propose the state-

<sup>1</sup> The empirical temperature  $t$  is the temperature as measured on any scale determined only by the choice of the thermometer system. It may, for example, be the temperature as determined by a constant pressure air thermometer.

<sup>2</sup> This may be a state of stable, metastable, or neutral equilibrium.

ments under (3) as a formulation of the third law of thermodynamics<sup>3</sup> which has certain advantages over the formulations now commonly employed.

Fowler and Guggenheim<sup>4</sup> have discussed objections to the usual statements of the third law, which are essentially modifications of the Nernst heat theorem. Briefly, these objections are based upon the fact that certain reservations must be made in the interpretation of these statements which have the effect of limiting their applicability. One thus encounters the expressions, "exceptions to the third law" and the "so-called third law" which definitely place the third law in an inferior position relative to the other laws of thermodynamics. To avoid this, Fowler and Guggenheim propose the use of the *principle of the unattainability of the absolute zero of temperature* as the third law. Although this is accepted as universally valid, we wish to call attention to the fact that it is not generally useful until supplemented by further postulates. For example, the derivation of the Nernst heat theorem requires the additional postulate of the convergence of the heat capacity integral  $\int_0^T C_{v,n} d \ln T$ . Our above statement is the result of an attempt to express the third law in a form which is: (1) Universally valid; (2) complete as a postulatory basis for further development; (3) capable of yielding any of the other expressions formerly given as statements of the third law.

The expression "spontaneous isothermal process" includes chemical reactions, phase changes, or any change expressible in terms of variations of the amount of any component in any phase of the system. Note especially that in order to apply the third law in the form given above, these processes must be written *in the only direc-*

*tion in which they could possibly occur isothermally at temperatures approaching the absolute zero.*<sup>5</sup>

## APPLICATIONS OF THE THIRD LAW

### The Determination of Some Limits at $T \rightarrow 0^\circ\text{K}$

From part (a) of the third law, it is possible to derive limits for a real phase of fixed composition which lend themselves to experimental verification and to useful application.

First consider only the usual type of thermodynamic system, for which  $S = S(T, p, n_1, n_2, \dots)$ . It follows immediately that the third law requires

$$\lim_{T \rightarrow 0} \frac{C_p}{T} = 0, \quad \lim_{T \rightarrow 0} \left( \frac{\partial v}{\partial T} \right)_{p,n} = 0.$$

If  $S$  is given as  $S(T, v, n_1, n_2, \dots)$ , then

$$\lim_{T \rightarrow 0} \frac{C_v}{T} = 0, \quad \lim_{T \rightarrow 0} \left( \frac{\partial p}{\partial T} \right)_{v,n} = 0.$$

To illustrate the application to other types of systems, consider one for which  $S = S(T, p, \mathcal{H}, n_1, \dots)$ , where  $\mathcal{H}$  represents the homogeneous magnetic field strength in the absence of the system. The third law then requires that

$$\lim_{T \rightarrow 0} \left( \frac{\partial S}{\partial \mathcal{H}} \right)_{T,p,n} = 0.$$

The validity of these consequences of the third law and of other similar expressions is verified by experimental results insofar as the latter supply an adequate test, and may be further confirmed by arguments based upon quantum statistics.

It also follows from part (a) of the third law that for a given amount of a single component, single phase system

$$\lim_{T \rightarrow 0} S = S^\circ,$$

where  $S^\circ$  is finite and independent of all the variables which describe the state of the system.

<sup>3</sup> An equivalent descriptive statement is: "(a) As  $T \rightarrow 0^\circ\text{K}$ , the entropy of any real system becomes independent of all state variables, and: (b) As  $T \rightarrow 0^\circ\text{K}$ , the entropy change for any spontaneous reversible isothermal process becomes equal to zero, and for any spontaneous irreversible isothermal process, becomes negative." The authors prefer the analytic form because its essential equivalent must be deduced from any descriptive form before the latter is of use in the formal development of thermodynamics. For the student of thermodynamics, it is easier to deduce physical behavior from mathematical statements than to formulate the latter from the former.

<sup>4</sup> R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Macmillan, New York, 1939), p. 224.

<sup>5</sup> The impossibility of a reaction, such as  $\text{Si} + \text{O}_2 \rightarrow \text{SiO}_2$  (glass), leading to a metastable state, in the limit  $T \rightarrow 0^\circ\text{K}$  is implied by this statement. This, of course, cannot be confirmed *a priori*, but if such a reaction were possible, one could, in principle, use it to attain  $0^\circ\text{K}$ , in contradiction to the accepted principle of the unattainability of the absolute zero of temperature.

### The Dependence of the Entropy upon Temperature

For any system,  $S$  may be taken as  $S=S(T, y_1, y_2 \dots n_1, n_2 \dots)$ . The following important result is readily derived from the above analytical form of the third law:

$$S = \int_0^T \left( \frac{\partial S}{\partial T} \right)_{y,n} dT + S^\circ(n) = \int_0^T \frac{C_{y,n}}{T} dT + S^\circ(n), \quad (1)$$

where  $S^\circ(n)$  is a function of composition variables only.<sup>6</sup>

Since the conditions for stability of a thermodynamic system require  $C_{y,n}$  always to be positive and not zero for any temperature  $T \neq 0^\circ\text{K}$ , it follows that  $\int_0^T C_{y,n} d \ln T$  approaches zero positively as  $T \rightarrow 0^\circ\text{K}$  and that  $S - S^\circ(n) \geq 0$ .

### The Nernst Heat Theorem

From part (b) of the third law one may readily obtain the Nernst heat theorem. Let us introduce the notation

$$\left( \frac{\partial S}{\partial n_i} \right)_{T, y, n_j} = \bar{S}_i.$$

Where  $y=p$  and no other external forces are acting,  $\bar{S}_i$  is the usual *partial molal entropy* of the  $i$ -component. Hence

$$\sum_i \nu_i \left( \frac{\partial S}{\partial n_i} \right)_{T, y, n_j} = \sum_i \nu_i \bar{S}_i = \Delta S.$$

From the third law

$$\lim_{T \rightarrow 0} \sum_i \nu_i \bar{S}_i = \sum_i \nu_i \bar{S}_i^\circ \leq 0.$$

<sup>6</sup> If  $S=S(T, y, n)$  one obtains upon integration over the state variables

$$S = \int_0^T \left( \frac{\partial S}{\partial T} \right)_{y,n} dT + \int_{y_1^\circ}^{y_1} \left( \frac{\partial S}{\partial y_1} \right)_{T, y_2 \dots n} dy_1 + \int_{y_2^\circ}^{y_2} \left( \frac{\partial S}{\partial y_2} \right)_{T, y_1, y_3 \dots n} dy_2 + \dots + S^\circ(n).$$

The third law requires that

$$\left( \frac{\partial S}{\partial y_1} \right)_{T, y_2 \dots n} \Big|_{T=0} = \left( \frac{\partial S}{\partial y_2} \right)_{T, y_1, y_3 \dots n} \Big|_{T=0} = \dots = 0$$

and the above relation (1) follows at once.

Now neglect the irreversible processes. For any *reversible* process, then

$$\sum_i \nu_i \bar{S}_i^\circ = \lim_{T \rightarrow 0} \Delta S = 0. \quad (2)$$

For a process to be reversible, the phases entering into the reaction at any given temperature must be in states of equilibrium at that temperature. If the state of equilibrium for any phase is one of frozen metastable equilibrium, then the process must not disturb this state of equilibrium. It can readily be seen that this statement (2) is equivalent to the statement of the Nernst heat theorem as given by Fowler and Guggenheim: "For any isothermal process involving only phases in internal equilibrium or, alternatively, if any phase is in frozen metastable equilibrium, provided the process does not disturb this frozen equilibrium  $\lim_{T \rightarrow 0} \Delta S = 0$ ."

$T \rightarrow 0$

### The So-Called Absolute Entropy

In any experimental determination of the entropy of a given substance only *entropy differences* can be determined. It follows that an entropy scale can be constructed for each substance by assigning an arbitrary value to  $S^\circ$ . However, because of the requirement that  $\sum_i \nu_i \bar{S}_i^\circ = 0$  (for reversible isothermal processes) the values of the  $S^\circ$ 's are not all independent. For the construction of a useful scale upon which to represent entropies it is necessary to specify in some convenient way the arbitrary values of  $S^\circ$  for a complete set of independent substances. As long as nuclear processes and isotopic separations are neglected, it is obvious that the chemical elements form such a complete independent set. By convention, therefore, the value zero is assigned to  $S^\circ$  for each element in its state of stable equilibrium. This requires that  $S^\circ = 0$  for all pure substances in their states of stable equilibrium, and that  $S^\circ > 0$  for these substances in any other state. These conclusions were expressed by Lewis and Gibson in the following statement now commonly quoted as the third law. "If the entropy of each element in some crystalline state be taken as zero at the absolute zero of temperature, every substance has a finite positive entropy, but at the absolute zero of temperature the entropy may become zero,

and does so become in the case of perfect crystalline substances."

It is to be noted that their expression "perfect crystalline substances" should be interpreted as the substance in its state of stable equilibrium as  $T \rightarrow 0^\circ\text{K}$ .

It is obvious from the foregoing discussion that the values  $S^\circ = 0$  for the elements and the resulting "absolute" entropy scale have no theoretical significance. In fact, this convention may indeed have to give way in the future to one which assigns  $S^\circ = 0$  for pure isotopes of the elements in their stable states. The chemical elements would then have a finite positive entropy, the entropy of mixing of their isotopic constituents, at  $T = 0^\circ\text{K}$ .

### Apparent Exceptions to the Nernst Heat Theorem

The phenomena often discussed as "exceptions of the third law" should now more properly be described as "apparent exceptions to the Nernst heat theorem." Experimentally, the only means of studying the applicability of the Nernst heat theorem is to evaluate the heat capacity integrals  $\int_0^T C_{v,n} d \ln T$  for the substances involved in the given process. This necessitates a knowledge of the heat capacity of these substances in states of stable equilibrium, or of undisturbed frozen metastable equilibrium, from  $0^\circ\text{K}$  to  $T^\circ\text{K}$ . Part of this "knowledge" must be obtained by an extrapolation from the lowest available temperature to  $0^\circ\text{K}$ . The two main experimental causes of apparent exceptions to the Nernst heat theorem are: (1) Failure of the system to maintain the proper state of equilibrium (for the process in question) during the heat capacity measurements; (2) failure of the extrapolation of the heat capacity measurements to predict correctly the true heat capacity in the region of extrapolation.

### The Unattainability of the Absolute Zero of Temperature

The limiting cases of the methods by which the temperature of a system may be lowered are: (1) The removal of heat from the system by transfer to a colder body; (2) the occurrence within the system of a spontaneous process yielding a state of lower temperature.

Obviously the first method cannot be used to lower the temperature of a system to  $0^\circ\text{K}$  because it would require the existence of an infinite heat reservoir at  $0^\circ\text{K}$ .

That the process of the second method must be spontaneous can be deduced from arguments concerning the stability of real systems. In general this method implies the occurrence of a process capable of decreasing the energy of the system by the performance of work, and such a process must necessarily be spontaneous.

Let any conceivable process for lowering the temperature of any conceivable system be represented by

$$A(T'y'n') \rightarrow B(T''y''n''),$$

where  $T'y'n'$  are the values for the initial state of a set of variables capable of completely describing the system and  $T''y''n''$  the corresponding values for the final state.  $T'$  is any temperature, however low, but not  $0^\circ\text{K}$ . Let us now show that  $T''$  cannot be  $0^\circ\text{K}$  by showing that the assumption  $T'' = 0^\circ\text{K}$  leads to a contradiction of the third law.

Since the process must be spontaneous, the entropy change must be  $\geq 0$ .

$$\Delta S = S_B - S_A = \int_0^{T''} C_B d \ln T + S_B^\circ - \int_0^{T'} C_A d \ln T - S_A^\circ \geq 0.$$

From the third law

$$S_B^\circ - S_A^\circ = \lim_{T \rightarrow 0} \Delta S \leq 0.$$

If now we were to set  $T'' = 0^\circ\text{K}$

$$0 \geq S_B^\circ - S_A^\circ \geq \int_0^{T'} C_A d \ln T.$$

But the integral is always positive for any value of  $T' \neq 0^\circ\text{K}$ , and we are forced to conclude that  $T'' \neq 0^\circ\text{K}$ . This is true even for the most idealized case, that of an adiabatic reversible process, where the equality signs apply. Hence, "it is impossible by any procedure, no matter how idealized, to reduce the temperature of any system to the absolute zero in a finite number of operations." This is the principle of the unattainability of the absolute zero of temperature.

## CONCLUSION

There are numerous ways, both descriptive and analytic, in which the basic principles of the third law may be satisfactorily expressed. The expression here advocated is favored because:

(1) Partial derivatives enter directly in most applications of the third law.

(2) The convergence of integrals of the type

$$\int_0^T \left( \frac{\partial S}{\partial T} \right)_{y,n} dT$$

becomes a part of the postulatory basis of classical thermodynamics.

(3) It includes the limiting behavior, as  $T \rightarrow 0^\circ\text{K}$ , of the entropy as a function of both state and composition variables.

(4) It gives information relating to both reversible and irreversible isothermal processes for any real system.

(5) It is universally valid, thereby permitting it to rank as a *law* of thermodynamics.

(6) It leads naturally to the definition of an arbitrary zero of entropy such that (a) no system ever has a negative entropy, and (b) the zero of entropy could be obtained by a system only at the absolute zero of temperature.

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## On the Strength of Carbon-Hydrogen and Carbon-Carbon Bonds

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Electron impact critical potentials are combined with thermochemical data to obtain values for the heats of the dissociation reactions,  $\text{CH}_4 = \text{CH}_3 + \text{H}$ ,  $\text{C}_2\text{H}_6 = \text{C}_2\text{H}_5 + \text{H}$ ,  $\text{C}_2\text{H}_6 = 2\text{CH}_3$ , and  $n\text{C}_4\text{H}_{10} = 2\text{C}_2\text{H}_5$ . The values found are:  $D(\text{CH}_3-\text{H}) = 101$  kcal./mole,  $D(\text{C}_2\text{H}_5-\text{H}) = 96$  kcal./mole,  $D(\text{CH}_3-\text{CH}_3) = 82.6$  kcal./mole and  $D(\text{C}_2\text{H}_5-\text{C}_2\text{H}_5) = 77.6$  kcal./mole. These values are compared with estimates based on kinetic and photochemical data.

VARIOUS estimates of the kinetically important energetic quantities,  $D(\text{CH}_3-\text{H})$  and  $D(\text{CH}_3-\text{CH}_3)$ , made by combining thermochemical data with either kinetic or photochemical data are not in good agreement. In this communication we shall discuss the application of still another source of energetic data, electron impact critical potentials, to this problem. It will be shown that certain reasonable assumptions as to the nature of the potential energy surfaces for the aliphatic ions,  $\text{C}_n\text{H}_{2n+2}^+$ , permit estimates of  $D(\text{CH}_3-\text{H})$  and  $D(\text{C}_2\text{H}_5-\text{H})$  to be made. In particular, data on ethane, propane, and the two isomeric butanes will be discussed.

The interpretation of electron impact data involves two difficulties. The first of these evolves from the necessity of correcting the voltage scale for contact potentials associated with the filament (source of bombarding electrons). The

usual procedure is to compare the ionization efficiency curves for the processes of interest with that of a monatomic gas (usually argon), taken under similar conditions of sensitivity.<sup>2</sup> It is then assumed that the difference between the energies at which the first upward breaks of the two curves (process of interest and argon) occur gives the difference ( $\delta$ ) between the desired critical potential and the ionization potential ( $I^z$ ) of argon. Since the latter quantity is known accurately from spectroscopic data, the critical potential is given by  $I^z - \delta$ . The assumption that the form of the ionization efficiency curves for the simple ionization of an atom and the ionization and dissociation of a complex molecule will be the same in the vicinity of the critical energy is without theoretical justification. Pronounced differences are to be noted in the experimental curves. It has been found, however, that the

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<sup>2</sup> L. G. Smith, Phys. Rev. **51**, 263 (1937).