Systems and Processes in Thermodynamics*

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Systems and processes play a vital role in understanding physics, chemistry, and biology. Systems may be of different sizes and they are characterized by their structure, stability, properties, bonding, reactivity, interactions, etc. The state of a classical N-particle system is defined in a $6N$-dimensional phase space, while a related wave function is generated in a $3N$-dimensional configuration (or equivalently momentum) space for a corresponding quantum system. On the other hand, a process takes a system from one state to another, like going from 'being' to 'becoming'. Depending on the different length scales for the former and time scales for the latter, one needs to resort to appropriate theoretical frameworks like classical mechanics, quantum mechanics, molecular mechanics, statistical mechanics, molecular simulation, multi scale-modeling, etc.

A thermodynamic system is a part of the universe in which we have a special interest. The rest of the universe, where observations are made, is the corresponding surrounding. Fortunately, only a handful of state variables like pressure (P), volume (V), temperature (T), number of moles (n_i), *etc.*, define the state of a system.

A thermodynamic space spanned by these variables (see *Box 1* for a geometric representation of thermodynamics) may be constructed. Any state (say A) is defined in terms of the "coordinates" (P_A, T_A, n_1^A, n_2^A, ...) as all thermodynamic properties (potentials) are obtained for this state in terms of those variables. Depending on the possibility of energy (and matter) exchange between the system and the surrounding, we may have isolated, closed, and open systems. In a statistical mechanical description, they are

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respectively analysed through microcanonical (*NVE*), canonical (*NVT*) and grand canonical (μVT) ensembles (see *Box* 2 for an associated information theory).

A thermodynamic process takes a system from state *A* to state *B*. A thermodynamic "trajectory" connecting those states may define a path. Depending on the path taken, the process may be isothermal, adiabatic, isobaric, etc. Any potential difference causes a flow that continues till the difference ceases and an equilibrium is achieved. It is a very general phenomenon. Electric current flows due to electrical potential difference, heat flows due to temperature difference, a body falls from a height due to gravitational potential difference, etc. The direction of a spontaneous (that takes place automatically without using any external device) flow is from the higher potential to the lower potential. Respective equilibria are obtained when the potential difference becomes zero.

A reversible process always keeps a system very close to equilibrium, and the initial states of both the system and the surrounding may be easily retrieved through an infinitesimal change in the conditions. It implies that it is difficult for a natural process to be reversible. The state functions like internal energy does not depend on the path taken during the process, unlike the heat flow and the work done. State functions like internal energy is a property of the system in a given state and accordingly can be defined using the state variables. However, the path functions like heat flow or work done are associated with a process along a given path. In *Figure* 1, a system may move from state *A* to state *B* via different paths in one or several steps. The change in the state function will be the same in all such cases, e.g., $\Delta U = U_B - U_A$. Path functions are different for different paths. Moreover, a path function may be connected to the difference in the state function (and not the state function itself). The former depends on the whole path, whereas the latter depends only on the information regarding the two states lying in the extremes of that path. It is not possible to define the heat or work of a system in a given state. Systems are characterized by the states they are in and ac-
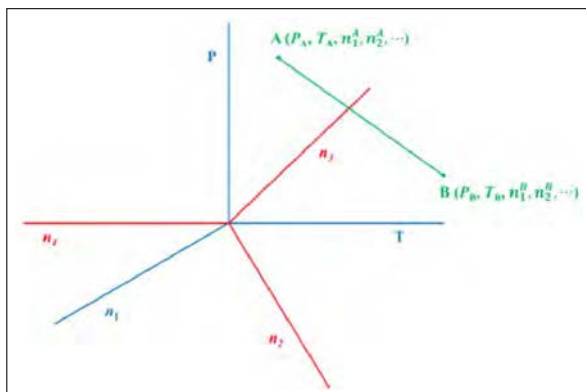
Figure 1. A six-dimensional projection of a thermodynamic vector space.

Systems	Processes
P	dP
V	dV
T	dT
S	dS
μ	$d\mu$
n	dn
U	dU
H	dH
A	dA
G	dG
	$đq$
	$đ\omega$

Table 1. Thermodynamic properties of systems and processes.

cordingly their thermodynamic properties are analysed in terms of various state functions like U, S, H, G, etc. On the other hand, different path functions like $đq$, $đ\omega$, etc. are used to study various processes based on the paths they are involved in. Different thermodynamic properties of systems and processes are presented in *Table* 1.

The nature of a system or a process is better understood through thermodynamic laws:

1. **Zeroth law:** If A and B are in thermal equilibrium, and B and C are also in thermal equilibrium, then C must be in thermal equilibrium with A. It is the working principle behind the use of a thermometer.

2. **First law:** In an isolated system, internal energy is constant and it can neither be created nor destroyed. If the work done on a system is $đω$, and the amount of heat flow to the system is $đq$, then the change in internal energy dU becomes $dU = đq + đω$. The internal energy stems from the total kinetic energy and potential energy of the constituent atoms, ions, or molecules in a system through their various degrees of freedom like translation, rotation, and vibration. Note that U being a state function, dU is an exact differential, whereas $đq$ and $đω$ are not exact differentials as they explicitly depend on the path taken by the process. In an isolated system, $đq = 0$, $đω = 0$, which imply $dU = 0$, i.e., the internal energy is constant.

3. **Second law:** The first law provides an incomplete picture as it does not have any information on the direction (the so-called "arrow of time") and extent of a change. It is not possible for any process to absorb heat from a reservoir and convert it completely into work. During a spontaneous change, the entropy, S, of an isolated system (universe = system + surroundings is always isolated) always increases. It means that entropy for that system can only be created and never be destroyed.

4. **Third law:** At absolute zero temperature, the entropy is zero for all perfectly crystalline substances. Note that the second law does not allow us to obtain the absolute value of S, but only the change in S (ΔS).

If there is no non-PV work during a reversible process, according to the first law,

$$dU = đq + đω = đq - PdV \,. \tag{1}$$

Therefore, $dU_V = đq_V$ (if the volume remains unaltered during the process).

Similarly, for a constant pressure process, the enthalpy (H) change is given by,

$$dH_P = d(U + PV)|_P = (\text{\dj}q + VdP)_P = \text{\dj}q_P. \qquad (2)$$

From the second law (Clausius inequality), the change in entropy (S) may be written as,

$$dS \geq \frac{\text{\dj}q}{T} \qquad (3a)$$

$$\text{or,} \quad TdS \geq \text{\dj}q \qquad (3b)$$

where the equality sign refers to reversible processes and the inequality sign corresponds to irreversible (spontaneous) processes. In equation (1), the second equality is valid only for the reversible processes, as the external pressure will be infinitesimally close to the internal pressure (so that P_{ex} may be related to V) only in those cases.

Combining the first and second laws (adding equations (1) and (3)) for a reversible process we have,

$$dU = TdS - PdV. \qquad (4)$$

Note that U being a state function, dU is independent of the path and hence equation (4) is valid for both (reversible and irreversible) types of processes. Only for a reversible process can TdS be identified with $\text{\dj}q$ and $(-PdV)$ with $\text{\dj}\omega$. It is established that the sum of two inexact differentials can be an exact differential, which is one of the fundamental (Gibbs) equations of thermodynamics. The corresponding equation involving H is the following:

$$dH = TdS + VdP. \qquad (5)$$

The natural variables for U and H are S and V, and S and P, respectively. As the construction of a process by varying S is

difficult, other thermodynamic potentials whose natural variables are T, P and V may be generated through appropriate Legendre transforms (see *Box* 3). Moreover, T and S are (statistical) thermodynamical conjugates and so are P and V. It is akin to the canonically conjugate variables like position and momentum (in quantum mechanics they cannot be measured simultaneously accurately according to Heisenberg's uncertainty relation).

Two other important thermodynamic potentials are Helmholtz (A) and Gibbs (G) free energies defined as,

$$A = U - TS \tag{6}$$

and

$$G = H - TS = A + PV. \tag{7}$$

Corresponding fundamental equations may be written as,

$$dA = -PdV - S\,dT \tag{8}$$

$$dG = VdP - S\,dT. \tag{9}$$

As $U\,(S,\,V)$ is a state function dU is an exact differential. Therefore,

$$\frac{\partial^2 U}{\partial V \partial S} = \frac{\partial^2 U}{\partial S\,\partial V} \tag{10a}$$

$$i.e., \quad \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \tag{10b}$$

This is called Maxwell's relation. Other associated relations can be derived from other Gibbs equations as,

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \tag{11}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T \tag{12}$$

and

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T . \tag{13}$$

A simple mnemonic to remember the fundamental equations and the Maxwell's relations is provided in *Box* 4.

An associated thermodynamic equation of state may be derived as,

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P = \frac{\alpha T - \kappa P}{\kappa} \tag{14}$$

where α is the expansion coefficient and κ is the isothermal compressibility, given as,

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \tag{14a}$$

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T . \tag{14b}$$

In deriving equation (14), the equations (4) and (12) have been made use of.

Accordingly, $\left(\frac{\partial U}{\partial V}\right)_T$ is called the internal pressure arising out of intermolecular interactions. If we start from the Clausius inequality we arrive at

$$TdS \geq đq \tag{3b}$$

$$i.e., TdS \geq dU + PdV \tag{15}$$

where the inequality sign corresponds to a spontaneous process and when it reaches the equilibrium the equality sign holds good.

If the process is carried out under constant U and V conditions we have,

$$TdS_{U,V} \geq 0 \qquad (16a)$$

$$\text{or, } dS_{U,V} \geq 0 \qquad (16b)$$

as T cannot be negative. Therefore, under constant U and V conditions entropy of an isolated system increases along a spontaneous process and it reaches its maximum value ($dS = 0$) at the equilibrium.

Equivalently, it is easy to derive,

$$dU_{S,V} \leq 0 \qquad (16c)$$

$$dH_{S,P} \leq 0 \qquad (16d)$$

$$dA_{T,V} \leq 0 \qquad (16e)$$

$$dG_{T,P} \leq 0 \qquad (16f)$$

$$dS_{H,P} \geq 0 \qquad (16g)$$

While comparing these inequalities (valid for spontaneity) and equations (defining equilibrium) with the fundamental equations (4, 5, 8, 9) valid for both reversible and irreversible processes in closed systems with only PV type work, an apparent inconsistency can be observed. As natural spontaneous processes are irreversible, $dU_{S,V} = 0$ as U is a state function and $dU_{S,V} < 0$ for spontaneity (likewise for other state functions). In an isolated system, under certain constraints (say, a specific number of species, volume, and energy) any spontaneous process is accompanied by an increase in entropy until it reaches its maximum at the equilibrium. If the constraints are changed to create a new equilibrium state that spontaneously evolves to the original equilibrium state in an isolated system, variations in constraints will lead to a decrease in entropy as the original state (maximum entropy) may be retrieved through a spontaneous process. When the original constraints are retrieved, δS becomes zero.

This can be better explained as follows:

$$TdS \geq dU + PdV \tag{15}$$

At constant V,

$$TdS \geq dU \tag{15a}$$

which implies that

$$dU - TdS \leq 0 \tag{15b}$$

From equation (6), i.e.,

$$A = U - TS \tag{6}$$

At constant T,

$$dA = dU - TdS \tag{6a}$$

Combining equations (15b) and (6a),

$$dA_{T,V} \leq 0 \tag{16e}$$

Similarly,

$$dG_{T,P} \leq 0 \tag{16f}$$

For a spontaneous process, G will decrease and will attain its minimum value at the equilibrium. At a given T, P condition, the backward reaction is favorable in case $\Delta G > 0$. For instance, we can enjoy both hot coffee and ice cream by changing the T, P condition (being in two different thermodynamic states, e.g., at 1 atm. pressure and 0 °C water may be condensed to ice whereas at the same pressure and 100 °C it may be converted to water vapor), $\Delta G < 0$ (say, vaporization is spontaneous) situation may get changed to $\Delta G > 0$ (condensation becomes spontaneous). It is worth noting that T and P values remain constant in a given state for this analysis and we need to change the state to check the change in the direction of spontaneity. Here ΔG refers to the difference in G in two different phases, say, in a given thermodynamic state. Similarly, the progress of a chemical reaction may be understood (*Figure* 2) in terms of the variation in G. In the case of a multi-component and multi-phase system, it is apt to

Figure 2. Variations in Gibbs free energy as a function of the extent of reaction.
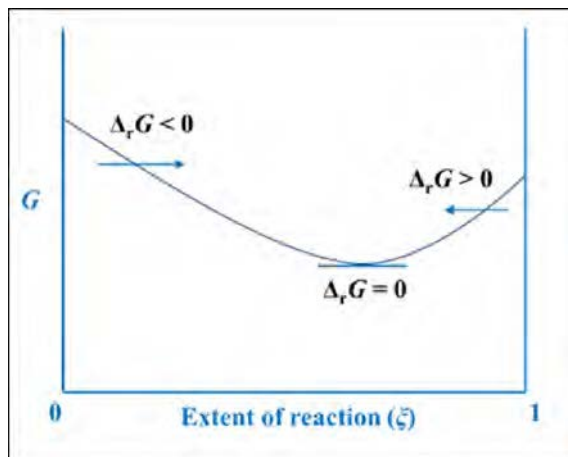
include the variation in the number of moles of various species. The fundamental equations take the following forms:

$$dG(P,T,n_1^{\alpha},n_2^{\alpha},\ldots,n_N^{\alpha},n_1^{\beta},n_2^{\beta},\ldots,n_N^{\beta},\ldots) = VdP - SdT + \sum_{\alpha}\sum_{i}\mu_i^{\alpha}dn_i^{\alpha}$$
$$(17a)$$

$$dA(T,V,\ldots) = -PdV - SdT + \sum_{\alpha}\sum_{i}\mu_i^{\alpha}dn_i^{\alpha} \qquad (17b)$$

$$dU(S,V,\ldots) = TdS - PdV + \sum_{\alpha}\sum_{i}\mu_i^{\alpha}dn_i^{\alpha} \qquad (17c)$$

$$dH(S,P,\ldots) = TdS + VdP + \sum_{\alpha}\sum_{i}\mu_i^{\alpha}dn_i^{\alpha} \qquad (17d)$$

Here the chemical potential (μ_i^{α}) for the ith component in the α-phase of the system is defined as

$$\mu_i^{\alpha} = \left(\frac{\partial G}{\partial n_i^{\alpha}}\right)_{P,T,n_j^{\beta},j\neq i,\beta=\alpha} \qquad \forall_{j,\beta} = \left(\frac{\partial A}{\partial n_i^{\alpha}}\right)_{V,T,n_j^{\beta},\ldots} = \left(\frac{\partial U}{\partial n_i^{\alpha}}\right)_{S,V,n_j^{\beta},\ldots}$$

$$= \left(\frac{\partial H}{\partial n_i^{\alpha}}\right)_{S,P,n_j^{\beta},\ldots} \qquad (18)$$

In equations (17a–d), thermodynamically conjugate variables (generalized force and displacement, whose product has the

dimension of energy) like (P, V), (S, T), (μ, N) appear in pairs (differential of one is coupled with its conjugate). Three types of thermodynamic potentials appearing on the right-hand side of equations (17a–d) provide information regarding different processes and the corresponding equilibria (thermal, mechanical, and material). Such bilinear forms involving various forces and the associated conjugate fluxes are present in the Onsager relations depicting the explicit time evolution of thermodynamic properties of non-equilibrium systems.

As the chemical reaction proceeds (at constant T and P conditions), the extent of reaction, ξ, increases, G decreases and attains the minimum value at the equilibrium. A similar situation arises for the backward reaction. For an endothermic reaction $dH > 0$ and to have a spontaneous ($\Delta G < 0$) endothermic process under constant T and P conditions, S should increase so much to have $TdS > dH$. Even when the G value of the product is larger than that of the reactant the reaction provides some product as the Gibbs free energy of mixing the reactants and the products is negative.

The chemical equilibrium is dynamic in nature (rates of the forward and the backward reactions are the same). Once we start from the left, G will decrease and will be the minimum at the equilibrium. Similarly, if we start from the other side of the equilibrium, the reaction will run backward until G is a minimum and the rates are equal. The nature of the dynamics in a "dynamical equilibrium" (a combined treatment of kinetics and thermodynamics) may be required to know a dynamic (kinetics) equilibrium (thermodynamics) better. We may start from either side (or even both sides). G will decrease and then reach the equilibrium when $dG = 0$. What next? Is it a dead end as G needs to increase for the reaction to continue to have a dynamical equilibrium? Is it not a dead end in the sense nothing is happening, and the reactions are in balance, but continuing? At equilibrium, what forces the reaction to continue? Actually, G refers to the bulk behavior, not to whether individual events are continuing. Thermodynamics is silent regarding the underlying microscopic processes and

dG being a bulk property has no control over them.

Even if thermodynamics dictates a reaction to be spontaneous, for all practical purposes it may not take place if the rate of that reaction is very small. Only chemical kinetics can provide that information. At ordinary temperature and pressure, the reaction, $2H_2 + O_2 = 2H_2O$, is spontaneous. A catalyst or an electric spark is needed for this reaction to start within a reasonable amount of time. A catalyst actually decreases the activation barrier (*Figure* 3) by following a different route (reaction coordinates are different) depicted by using different colors. For a spontaneous reaction, it is worth searching for a catalyst if the reaction is tremendously slow. It is needless to mention that a similar attempt is not wise for a non-spontaneous process. A non-spontaneous process may, sometimes, be converted to a spontaneous one by coupling it with another favorable process. Catalyst cannot, however, change the yield of a chemical reaction, it can only accelerate the reaction, i.e., it can increase the rate constant (k) with no effect on the equilibrium constant (K).

As shown in *Figure* 3, the reaction Gibbs free energy ($\Delta_r G$) remains the same although the activation Gibbs free energy ($\Delta G^{\#}$) decreases (and hence k increases) in the presence of a catalyst. A linear correlation between $\Delta_r G$ and $\Delta G^{\#}$ for a series of similar reactions is often observed providing the so-called "Linear free energy relationship" connecting thermodynamics and kinetics, one of the first attempts to develop a quantitative structure-activity relationship (QSAR) model.

As the reaction advances, G changes and passes through a maximum at the transition state (TS) (*Figure* 3). When a system moves towards a TS from the reactant side or the product side its enthalpy generally increases and entropy decreases. A proper balance between these two trends guarantees the maximum of G in the TS. Along the x-axis, there is the reaction coordinate (projection along the minimum energy path) which connects reactants and products (*via* TS(s), intermediate(s), *etc.*). On the other hand, as the reaction proceeds, G changes and attains a minimum value at the equilibrium. Along the x-axis, there is the extent of reaction
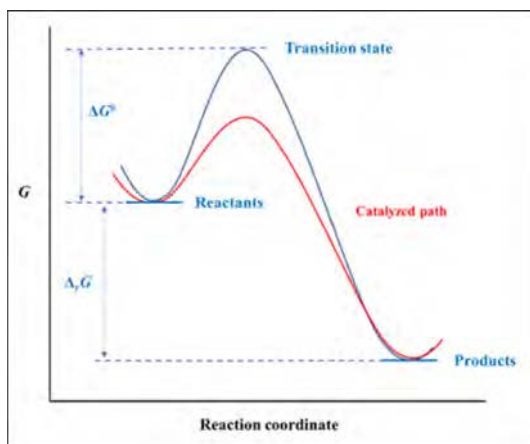
Figure 3. The free energy profile of the uncatalyzed (blue) and catalyzed (red) paths of a reaction.

that varies between 0 (pure reactant) and 1 (pure product). If we follow the variation of G accompanied by the advancement of a reaction, why there is a maximum in the former case (*Figure* 3) and a minimum in the latter case (*Figure* 2)? In the former case, it is the process of reactant molecules getting transformed into the product molecules explained in terms of the transition state theory of chemical kinetics. In the latter case, it is the variation of the relative concentrations of the reactants/products to reach the relative equilibrium concentrations in thermodynamics, *albeit* attaining a dynamical equilibrium.

In summary, an understanding of any macroscopic system and the process it takes part in, in terms of only a few state variables is the hallmark of thermodynamics. Four laws and four fundamental equations (including four Maxwell relations) provide the guiding light in this endeavor. The direction of a spontaneous process and the condition for the associated equilibrium under a given set of constraints can be analysed through the judicious choice of appropriate thermodynamic potential and its variation. The "coordinates" in a "thermodynamic space" describe a system and the connected "trajectory" defines the path attached to a process. Variation in the natural variables of any thermodynamic potential dictates the conditions for a spontaneous journey of a system along a prescribed path toward the related equilibrium.

Box 1. Understanding Thermodynamics through a Geometric Route

Any thermodynamic potential can be written as a differentiable function of thermodynamic state variables (extensive, viz., S, V, n_1, n_2, ...).

For example,

$$U = U(S, V, n_1, n_2, \ldots). \tag{1.1}$$

Corresponding partial derivatives may be considered as generalized forces (see *Box* 3):

$$F_j = \left(\frac{\partial U}{\partial R_j}\right)_{R_1, R_2, \ldots, R_{j-1}, R_{j+1}, \ldots} \tag{1.2}$$

where $\{R_j\}$ are the state variables (generalized displacements) and $\{F_j\}$ are the associated generalized forces. We may conceive of a vector space spanned by $\vec{F}$ and $\vec{R}$ with components as $\{F_j\}$ and $\{R_j\}$, respectively.

One may define a scalar product $\langle j\,|\,k \rangle$ as

$$\langle j\,|\,k \rangle = \left(\frac{\partial F_j}{\partial R_k}\right)_{R_1, R_2, \ldots, R_{k-1}, R_{k+1}, \ldots} \tag{1.3}$$

and conventional linear algebra will provide us with the essence of equilibrium thermodynamics.

1. Any thermodynamic potential, say U, is a differentiable function of a few state variables.

2. $(\mathrm{d}U)$ is an exact differential. Therefore,

$$\frac{\partial^2 U}{\partial R_j \partial R_k} = \frac{\partial^2 U}{\partial R_k \partial R_j} \qquad \forall_{j,k} \tag{1.4}$$

   which may be interpreted as the first law of thermodynamics where the internal energy is an exact differential and hence a state function.

3. The internal energy is minimized at constant entropy (or entropy is maximized at constant U), i.e.,

$$\frac{\partial^2 U}{\partial R_j^2} \geq 0 \qquad \forall_j \tag{1.5}$$

   which is nothing but the second law of thermodynamics.

Now, we analyse the above three conditions in terms of the properties of vectors in a linear vector space, viz.,

Contd.

Box 1. *Contd*.

$$\langle F_j | \chi F_k + \lambda F_l \rangle = \chi \langle F_j | F_k \rangle + \lambda \langle F_j | F_l \rangle \tag{1.6}$$

$$\langle F_j | F_k \rangle = \langle F_k | F_j \rangle \tag{1.7}$$

$$\langle F_j | F_j \rangle \geq 0 \quad \text{(equality sign for } |F_j\rangle = 0) \tag{1.8}$$

Equations (1.2) and (1.7) together imply equation (1.4).

Equation (1.8) implies equation (1.5).

The dimensionality of this vector space is governed by the degrees of freedom (n_F) according to Gibbs phase rule:

$$n_F = n_C - n_P + 2 \tag{1.9}$$

where n_C and n_P are the number of components and number of phases, respectively. As equation (1.8) guarantees $\langle F_j | F_j \rangle = 0$ only if $|F_j\rangle = 0$, it automatically guarantees the validity of the phase rule (1.9). Moreover, it ensures that C_v cannot be finite at $T = 0$. It should tend to zero as fast as T which is the third law of thermodynamics.

$$\langle T | T \rangle = \left(\frac{\partial T}{\partial S} \right)_V = \frac{T}{T} \cdot \frac{1}{\left(\frac{\partial S}{\partial T} \right)_V} = \frac{T}{C_V} \,. \tag{1.10}$$

In order to have $\langle T | T \rangle \neq 0$ (unattainability of absolute zero vide the third law of thermodynamics and equation (1.8)) both T and C_V should approach zero at the same rate.

The nature of the thermodynamic conjugate variables (see *Box* 3) may be better appreciated through the following biorthogonality condition:

$$\langle F_j | R_k \rangle = \delta_{jk} \tag{1.11}$$

where

$$|R_k\rangle = \left(\frac{\partial U}{\partial F_k} \right)_{F_1, F_2, \ldots, F_{k-1}, F_{k+1}, \ldots} \tag{1.12}$$

and

$$\langle R_j | R_k \rangle = \left(\frac{\partial R_j}{\partial F_k} \right)_{F_1, F_2, \ldots, F_{k-1}, F_{k+1}, \ldots} \,. \tag{1.13}$$

Therefore, the conjugate variables can interchange their characteristics of being generalized forces and generalized displacements (compare equations (1.2) and (1.12)).

Box 2. The Second Law of Thermodynamics and the Shannon Information Measure

The temperature alone can determine the most probable distribution of molecules over its available energy levels subject to some constraints dictated by the nature of the system. If it is an isolated system (N, V, E) there is no dialogue between the system and the surrounding as there is no exchange of mass and energy. Due to this ignorance in a corresponding microcanonical ensemble in statistical thermodynamics, one resorts to the principle of equal *a priori* probabilities which states that the system is equally likely to be in any of its allowed quantum states. It is akin to paying equal respect to everyone in an assembly in case their actual status is unknown. Moreover, a temperature (in the thermodynamic sense) cannot be defined (zeroth law of thermodynamics) as the system cannot attain thermal equilibrium by exchanging heat with the surrounding. A formal temperature is defined to obtain the associated Boltzmann distribution.

A statistical entropy was defined by Boltzmann as

$$S = k_B \ln W \qquad (2.1)$$

where k_B is the Boltzmann constant and W is the weight of any configuration or the number of ways it can be achieved. It may be noted that as W increases, disorder increases and so does the entropy. Therefore, equation (2.1) can be connected to the thermodynamic entropy. A most probable distribution provides the maximum entropy and a system (assuming to be in thermal equilibrium) prefers to attain the most probable distribution vide the second law of thermodynamics. Considering the system to behave classically, at $T \to 0K$, all the molecules will be in the zero-energy state and $W \to 1$ will imply $S \to 0$ for that "perfectly crystalline solid" as prescribed by the third law of thermodynamics.

The key quantity in information theory is Shannon information measure (also popularly known as Shannon entropy or von Neumann entropy) given by

$$S_S = -\sum_i p_i \ln p_i \qquad (2.2)$$

where p_i is the probability of the ith outcome of a random process. Originally, base 2 was used for the logarithm in Equation (2.2) as it was expressed in terms of bits. For a continuous distribution, it may be written as

Contd.

Box 2. *Contd*.

$$S_S = -\int \rho(\vec{r}) \ln \rho(\vec{r}) \, d\vec{r} \qquad (2.3)$$

where $\rho(\vec{r})$ may be the single particle density for an N-electron system defined as

$$\rho(\vec{r}) = N \int \cdots \int \psi^*(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) \psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) \, d\vec{r}_2 \, d\vec{r}_3 \ldots d\vec{r}_N \qquad (2.4)$$

and it contains all information about the ground state of the system according to density functional theory.

Shannon information measure provides information regarding the total distribution and not of the probabilities associated with individual events. The distribution that maximizes S_S is the equilibrium distribution. The maximum value of S_S may be connected to the thermodynamic entropy (and also Boltzmann statistical entropy, equation 2.1). Therefore, this entropy is a special case of S_S. So, S_S may increase (vide second law) but S and W in equation (2.1) are defined for the equilibrium state only and neither of them will increase with time.

According to Jaynes' maximum entropy principle, the probability distribution that closely reflects the actual knowledge about a system is associated with the maximum information entropy. It connects statistical mechanics with information theory. It may, however, be noted that the steady state of an irreversible process is characterized by the minimum value of the entropy production.

A local temperature and the related entropy have been defined in terms of the electronic kinetic energy density. They vary from point to point and serve the purpose of indicators of structure, stability, bonding, and reactivity.

Box 3. Legendre Transformation

Any mathematical function may be equivalently represented in two different ways, *viz.*, (i) locus of points $y = f(x)$ when plotted against x and (ii) envelope of its tangent curves drawn at each point (x, y). Each tangent curve will have a unique intercept. If we write the equation of the tangent as $y = mx + c$ we may equivalently write the intercept (c) as a function of m for a given (x, y), *i.e.*,

$$c(m) = y - mx = y - \frac{dy}{dx} \cdot x \tag{3.1}$$

$c(m)$ is the Legendre transform of y, and m is its argument and not x.

We may start from $U(S, V)$ where the natural variables of U are S and V

Recall,

$$dU = TdS - PdV. \tag{3.2}$$

Suppose we search for a thermodynamic potential whose natural variables are T and V. We know that, $\left(\frac{\partial U}{\partial S}\right)_V = T$ (from (3.2))

$$A(T, V) = A\left(\left(\frac{\partial U}{\partial S}\right)_V, V\right) = U - \left(\frac{\partial U}{\partial S}\right)_V S = U - TS \quad \text{(from (3.1))}$$

$H(S, P)$ and $G(T, P)$ can be equivalently derived. It may be generalized in case there are several variables $\{x_i\}$

$$c(\vec{\mathbf{m}}) = y - \sum_i m_i x_i = y - \vec{\mathbf{m}} \cdot \vec{\mathbf{x}} \tag{3.3}$$

where $\vec{\mathbf{m}} = (m_1, m_2, \ldots)$ and $\vec{\mathbf{x}} = \begin{pmatrix} x_1 \\ x_2 \\ \vdots \end{pmatrix}$.

In case we allow the variation in the number of moles in different phases/components, we have,

$$dU = TdS - PdV + \sum_j \mu_j \, dn_j \tag{3.4}$$

and similarly, for the other three thermodynamic potentials.

Remember,

$$\mu_j = \left(\frac{\partial U}{\partial n_j}\right)_{S,V,n_i \neq n_j} = \left(\frac{\partial H}{\partial n_j}\right)_{S,P,\ldots} = \left(\frac{\partial A}{\partial n_j}\right)_{T,V,\ldots} = \left(\frac{\partial G}{\partial n_j}\right)_{T,P,\ldots}. \tag{3.5}$$

Contd.

Box 3. *Contd.*

It is interesting to note that

$$\left(\frac{\partial U}{\partial S}\right)_V = T \tag{3.6}$$

$$\left(\frac{\partial U}{\partial V}\right)_S = -P \tag{3.7}$$

$$\left(\frac{\partial H}{\partial S}\right)_P = T \tag{3.8}$$

$$\left(\frac{\partial H}{\partial P}\right)_S = V \tag{3.9}$$

$$\left(\frac{\partial A}{\partial T}\right)_V = -S \tag{3.10}$$

$$\left(\frac{\partial A}{\partial V}\right)_T = -P \tag{3.11}$$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \tag{3.12}$$

$$\left(\frac{\partial G}{\partial P}\right)_T = V \tag{3.13}$$

In the above relations, we notice that when S varies we have T constant (and vice-versa) whereas when P varies we get V constant (and vice-versa). It is the reason S and T (and also P and V) are called thermodynamic conjugate variables ($\{\mu_j, n_j\}$ are also conjugate). These thermodynamic conjugate variables are akin to a generalized force (an intensive variable) and the corresponding generalized displacement (an extensive variable) caused by that force and their product has the dimension of energy (an extensive variable), e.g., an application of pressure causes a volume change. The force is related to the derivative of the energy with respect to displacement (like, Force = $-\nabla$ (potential energy)), e.g., $\left(\frac{\partial A}{\partial V}\right)_T = -P$, where P acts as the force and dV as the displacement. Notice the striking resemblance with the canonically conjugate variables $\{q_j, p_j\}$ of classical mechanics through the following Hamilton's equations of motion:

$$\left(\frac{\partial H}{\partial p_j}\right) = q_j \quad \forall_{j=1,2,\ldots,3N} \tag{3.14}$$

$$\left(\frac{\partial H}{\partial q_j}\right) = -p_j \quad \forall_{j=1,2,\ldots,3N} . \tag{3.15}$$

Box 4. Fundamental Equations of Thermodynamics and Maxwell's Relations

For a closed system (with constant composition) not having any non-expansion work the fundamental (Gibbs) equations of thermodynamics are given by:

$$dU = T\,dS - P\,dV \tag{4.1}$$

$$dH = T\,dS + V\,dP \tag{4.2}$$

$$dA = -P\,dV - S\,dT \tag{4.3}$$

$$dG = V\,dP - S\,dT \tag{4.4}$$

and the corresponding Maxwell's relations are written as:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \tag{4.5}$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \tag{4.6}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T \tag{4.7}$$

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T . \tag{4.8}$$

The above two sets of equations may be memorized through a simple mnemonic involving a thermodynamic square, also known as Born square, named after Max Born.

$-S$	U	V
H		A
$-P$	G	T

Figure A: The Born square.

"Good (Great) Physicists Have Studied Under Very Able (Accomplished) Teachers" (G, P, H, S, U, V, A, T).

Contd.

Box 4. *Contd.*

1. Alternatively, thermodynamic potentials (G, H, U, A along the sides (middle) of the square) and thermodynamic conjugate variables (see *Box* 3) ($-P$, $-S$, V, T along the corners; conjugate variables (S, T), (P, V) along the opposite corners; left corners with negative sign).

2. Put G in the bottom side (middle) and approach clockwise.

3. No negative sign for differentials or derivatives.

4. Suppose we want to know dU in terms of the exact differentials of its natural variables (S, V).
   i) Draw two downward arrows starting from U towards the corners ($-P$ and T).
   ii) Now, connect P and T along the diagonals.
   iii) $-P$ connects to dV and T connects to dS (see point 3 above). So, $dU = TdS\text{-}PdV$ (4.1)

5. Follow likewise for the other three equations.

Maxwell's relations involve only the corners (thermodynamic conjugate variables).

1. Start from any corner and move clockwise.

2. Where it ends, go to the next corner and move anticlockwise.

3. Include signs (only for constant, we have a negative sign). (S and P) and not for the derivatives.

4. For example,

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \, .$$

5. Similarly, for the remaining three equations.

6. One may remember the sequence (anticlockwise) of conjugate variables, alternatively, through the word "SPorTiVe".

Acknowledgements

Suggested Reading

[1] P W Atkins and J de Paula, *Atkins' Physical Chemistry*, Oxford University Press, Oxford, UK, 2014.

[2] G W Castellan, *Physical Chemistry*, Wesley Publishing Company, Massachusetts, USA, 1983.

[3] R S Berry, S A Rice and J Ross, *Physical Chemistry*, John Wiley & Sons Incorporated, New York, USA, 1980.

[4] P C Rakshit (Revised by S. C. Rakshit), *Physical Chemistry*, Sarat Book Distributors, Kolkata, India, 2001.

[5] F Weinhold, Geometric Representation of equilibrium thermodynamics, *Accounts of Chemical Research*, Vol.9, No.6, pp.236–240, 1976.

[6] E T Jaynes, Information theory and statistical mechanics, *Physical Review*, Vol.106, No.4, p.620, 1957.

[7] C E Shannon and W Weaver, *The Mathematical Theory of Communication*, Vol.1, University of Illinois Press, Urbana, Illinois, USA, 1949.

[8] D A McQuarrie, *Statistical Mechanics*, Harper & Row Publishers, New York, USA, 1975.

[9] P K Chattaraj and S Sengupta, Dynamics of chemical reactivity indices for a many-electron system in its ground and excited states, *Journal of Physical Chemistry A*, Vol.101, No.42, pp.7893–7900, 1997.

[10] P K Chattaraj and E Chamorro and P Fuentealba, Chemical bonding and reactivity: A Local Thermodynamic Viewpoint, *Chemical Physics Letters*, Vol.314, No.1–2, pp.114–121, 1999.

[11] C Guo, X He, C Rong, T Lu, S Liu and P K Chattaraj, Local Temperature as a Chemical Reactivity Descriptor, *Journal of Physical Chemistry Letters*, Vol.12, No.23, pp.5623–5630, 2021.

[12] S K Ghosh, M Berkowitz and R G Parr, Transcription of Ground-state Density-functional Theory Into a Local Thermodynamics, *Proceedings of the National Academy of Sciences*, Vol.81, No.24, pp.8028–8031, 1984.

[13] K G Denbigh, *Thermodynamics of the Steady State*, Methuen, London, England, 1951.

[14] S R de Groot, *Thermodynamics of Irreversible Processes*, Vol.242, North-Holland Publishing Comp., Amsterdam: North-Holland, Netherlands, 1951.

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