

Are the Concepts of Dynamic Equilibrium and the Thermodynamic Criteria for Spontaneity, Nonspontaneity, and Equilibrium Compatible?

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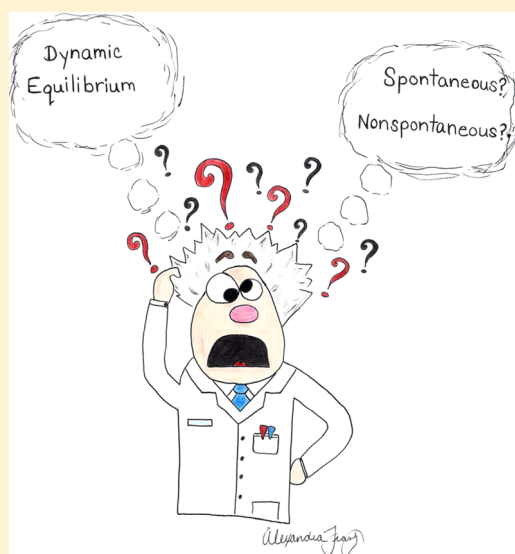
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ABSTRACT: Thermodynamic spontaneity–equilibrium criteria require that in a single-reaction system, reactions in either the forward or reverse direction at equilibrium be nonspontaneous. Conversely, the concept of dynamic equilibrium holds that forward and reverse reactions both occur at equal rates at equilibrium to the extent allowed by kinetic considerations. This paper discusses the resolution of this apparent conundrum. Qualitatively, it is argued that thermodynamics deals only with the macroscopic behavior of large systems, not with the microscopic details that lead to the observed macroscopic events. Since the observed events are measurable changes in the system composition without the necessity to do work on the system, any set of microscopic events that lead to the same macroscopic observations are compatible with thermodynamics. Quantitatively, it is shown that when considered statistically, thermodynamics shows that microscopic reactions in both forward and reverse directions are expected to occur at all points along the reaction coordinate provided only that both reactants and products are present. At equilibrium, the statistical treatment predicts that forward and reverse microscopic reactions have equal probability. Consequently, the concept of a dynamic equilibrium and the spontaneity–equilibrium constraints of thermodynamics are completely compatible.

KEYWORDS: First-Year Undergraduate/General, Second-Year Undergraduate, Upper-Division Undergraduate, Physical Chemistry, Equilibrium, Thermodynamics



INTRODUCTION

Almost all modern textbooks of physical chemistry^{1–3} show that the thermodynamic criteria for spontaneity, nonspontaneity, and equilibrium for single, chemical reactions in closed systems in which the only work done is pressure–volume work are

$$dA < 0 \text{ or } (\partial A / \partial \xi)_{T,V} < 0$$

for reaction spontaneity for increasing ξ (1a)

$$dA > 0 \text{ or } (\partial A / \partial \xi)_{T,V} > 0$$

for reaction nonspontaneity for increasing ξ , and (1b)

$$dA = 0 \text{ or } (\partial A / \partial \xi)_{T,V} = 0$$

for equilibrium when T and V are constant (1c)

$$dG < 0 \text{ or } (\partial G / \partial \xi)_{T,p} < 0$$

for reaction spontaneity for increasing ξ (1d)

$$dG > 0 \text{ or } (\partial G / \partial \xi)_{T,p} > 0$$

for reaction nonspontaneity for increasing ξ , and (1e)

$$dG = 0 \text{ or } (\partial G / \partial \xi)_{T,p} = 0$$

for equilibrium when T and p are constant (1f)

where ξ is a reaction coordinate for the process in question that is defined in terms of the number of moles of one of the reaction products, A is the Helmholtz free energy, and G is the Gibbs free energy.

The significance and implications of these criteria for both single and multiple reaction systems have been discussed at length in several recent publications in this Journal.^{4–7} Among other points, these publications note that G and $(\partial G/\partial \xi)_{T,p}$ are functions of ξ , and dG depends upon both ξ and $d\xi$. These quantities are not defined for a finite interval over a reaction process but rather vary continuously as the reaction proceeds. Consequently, the issue of spontaneity or nonspontaneity is a question that must be addressed at each point along the reaction path. A similar statement is true for A , dA , and $(\partial A/\partial \xi)_{T,V}$. Since $(\partial A/\partial \xi)_{T,V} = (\partial G/\partial \xi)_{T,p} = \Delta_r\mu$, where $\Delta_r\mu$ is the difference between the chemical potentials of the reaction products weighted by their stoichiometric coefficients and the same quantity for the reactants, it is seen that the chemical potentials play the central role in determining spontaneity and equilibrium.^{4–6}

Spontaneity

In thermodynamics, the terms “reaction spontaneity” or “reaction nonspontaneity” refer to the question of whether or not the reaction system will move spontaneously toward products or reactants without the necessity to do work on the system and thereby produce a measurable change in the chemical composition of the system.

The gas-phase reaction of two moles of $\text{NO}_2(\text{g})$ to produce one mole of $\text{N}_2\text{O}_4(\text{g})$ at 298.15 K under constant T and V conditions provides a simple, clear example. Since T and V are constant, the Helmholtz free energy, A , is the thermodynamic potential that gives the criteria for spontaneity and equilibrium. Figure 1 shows the variation of A as a function of the reaction

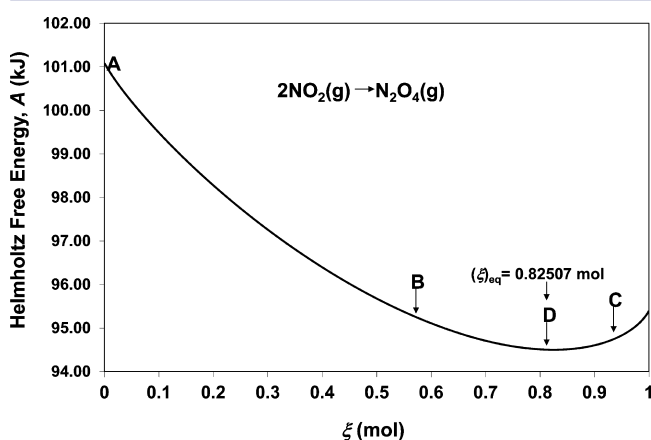


Figure 1. Variation of the Helmholtz free energy, A , with ξ , where ξ is the number of moles of $\text{N}_2\text{O}_4(\text{g})$ formed in the reaction $2\text{NO}_2(\text{g}) \rightarrow \text{N}_2\text{O}_4(\text{g})$ at 298.15 K in a closed container of volume 24.788 L and $n_0 = 2$ mol. Point D is the equilibrium point for the reaction at this temperature. The value of ξ at this point was determined by equating $(\partial A/\partial \xi)_{T,V}$ to zero, eq 1c, and solving for the resulting algebraic equation for ξ_{eq} . Points A, B, and C are for discussion purposes in the text. All values of A are relative to those of the chemical potentials of the elements, which are assigned the value of zero at 298.15 K and one bar pressure. The computational details are given in ref 4.

coordinate, ξ , which is taken to be the number of moles of $\text{N}_2\text{O}_4(\text{g})$ formed in the reaction. The derivation and details of the calculations leading to Figure 1 are given in ref 4. At points A and B, it is clear that $(\partial A/\partial \xi)_{T,V} < 0$. Therefore, eq 1a shows that the reaction will proceed spontaneously in the forward direction to increase the concentration of $\text{N}_2\text{O}_4(\text{g})$ and decrease that of $\text{NO}_2(\text{g})$. At point C, $(\partial A/\partial \xi)_{T,V} > 0$.

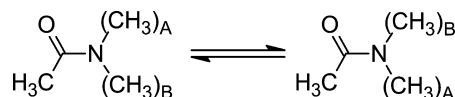
Consequently, the forward reaction is nonspontaneous. Instead, the reaction will proceed spontaneously in the reverse direction to decrease the number of moles of $\text{N}_2\text{O}_4(\text{g})$ in the system. Equation 1c demonstrates that equilibrium will occur when the relevant thermodynamic potential, A in this case, attains a minimum value. This occurs at point D. At this point, the chemical force on the system, $-(\partial A/\partial \xi)_{T,V}$, is zero.⁴ Consequently, the reaction will not proceed spontaneously either toward reactants or products. There will be no net change in the composition of the system with time.

Dynamic Equilibrium

Instead of describing the $2\text{NO}_2(\text{g}) \rightarrow \text{N}_2\text{O}_4(\text{g})$ reaction from a thermodynamic point of view, the concept of “dynamic equilibria” may be usefully employed. In this view, both the forward and reverse reactions are occurring on the microscopic scale at all points in the reaction process without respect to the spontaneity or equilibrium criteria provided by eqs 1a, 1b, and 1c. Therefore, at points B, C, and D in Figure 1, microscopic reactions are proceeding in both directions provided only that both $\text{NO}_2(\text{g})$ and $\text{N}_2\text{O}_4(\text{g})$ are present.

At point B during a given time interval, more NO_2 molecules are changing to N_2O_4 molecules than N_2O_4 molecules to NO_2 molecules. At point C, the reverse is true. At the equilibrium point D, forward and reverse microscopic reactions are occurring at equal rates so that there will be no net change in the composition of the system. Chemistry textbooks frequently use this concept to equate the forward and reverse rates at equilibrium and thereby obtain the equilibrium constant in terms of the ratio of the rate constants for the forward and reverse reactions. This is achieved by assuming that the kinetics follow a simple, mass-action rate law in both directions.

There is ample experimental evidence in the form of isotope exchange reactions and temperature-dependent NMR studies to support the concept of dynamic equilibrium. For example, two groups have reported NMR measurements of the rotational barrier for the *cis*–*trans* isomerization of *N,N*-dimethylacetamide (DMAC).^{8,9} This molecule exhibits the two chemically equivalent equilibrium structures as shown below



with a rotational barrier of about 17 kcal mol^{–1} that hinders the internal rotation.^{8,9}

If no carbonyl–nitrogen bond rotations are occurring at equilibrium, the NMR spectrum of DMAC would be expected to comprise three singlets, two for methyl groups A and B attached to nitrogen and a third peak for the carbonyl methyl group. When the temperature was 279 K or less, this is exactly what was observed by Gasparro and Kolodny.⁸ At lower temperatures, only a small fraction of the molecules have enough energy to overcome the activation energy (i.e., rotation barrier) and so the rate of *cis*–*trans* conversion is slow relative to the frequency separation, $\Delta\nu$, of the A and B protons (~10 Hz). Consequently, the lifetime of each equivalent structure is very long. This extended lifetime leads to very sharp NMR bands and the appearance of two singlets in the spectrum. At higher temperatures, however, the *cis*–*trans* rate constant, k_{c-t} , increases rapidly. The resulting rapid rotation shortens the lifetime of both isomers, which causes a broadening of the NMR bands, and when the rate constant becomes much greater

than $\Delta\nu$, the two singlets merge into a single absorption band at an intermediate frequency. Gasparro and Kolodny observed that at 331 K, the two peaks had merged into one broad peak, and at 368 K, the peak was sharp.⁸

The NMR experiments on DMAC clearly demonstrate that chemical equilibrium will be dynamic, not static, although the combination of an activation barrier and a low temperature can make the interconversion of the equilibrium forms very slow.

Dynamic Equilibrium versus Spontaneity

At first glance, it would appear that the existence of dynamic equilibria invalidates the thermodynamic criteria for spontaneity, nonspontaneity, and equilibrium given in eqs 1a–1f. These equations unequivocally predict that both the forward and reverse reactions at equilibrium will be nonspontaneous, but the presence of dynamic equilibrium shows that both forward and reverse microscopic reactions are, in fact, taking place. Similarly, at point B in Figure 1, eqs 1a and 1b clearly predict that only the forward reaction will be spontaneous. In contrast, dynamic equilibrium predicts that microscopic reactions in both directions will be occurring. The resolution of this conundrum is addressed in the next section.

DISCUSSION

Microscopic and Macroscopic Views

Thermodynamics is a science that deals with the observable behavior of macroscopic systems in which the number of atoms or molecules, N , is very large. At the microscopic level, each molecule has a set of different positions, internal energy states, and velocities (i.e., kinetic energy). If each molecule may be in any of s different states, there will be an extremely large number of different distributions of molecules among the s possible states. Moreover, the probability of a given distribution of molecules among the s states will vary with temperature. Each of these distributions is generally called a microstate. Any macroscopic property of the system at temperature T , $X(T)$, will be the sum of the values of $X(T)$ of each microstate weighted by the probability that a given microstate will exist. In other words, the observed value of $X(T)$, $\langle X(T) \rangle$, will be given by

$$\langle X(T) \rangle = \sum_{\alpha}^{N_{\alpha}} P_{\alpha}(T) X_{\alpha} \quad (2)$$

where $P_{\alpha}(T)$ is the probability that microstate α will exist, and N_{α} is the total number of microstates. As previously noted, $P_{\alpha}(T)$ is expected to depend upon the temperature.

If eq 2 actually had to be used to predict the macroscopic properties of a system, thermodynamics would be intractable. Fortunately, this is not the case. When N is much larger than s , it is possible to show that the only distribution of measurable importance is the most probable distribution. This reduces eq 2 to a single term, $\langle X(T) \rangle = X_{mp}$, where X_{mp} is the value of $X(T)$ for the most probable distribution. The determination of the most probable microstate at temperature T leads to the Boltzmann distribution for which

$$P_{\alpha}(T) = C \exp \left[-\frac{\Phi_{\alpha}}{k_b T} \right] \quad (3)$$

where C is a constant that can be shown to be the reciprocal of the partition function of the ensemble comprising the microstate, Φ_{α} is the relevant energy of the microstate, k_b is

the Boltzmann constant, and T is the absolute temperature. Derivations of eqs 2 and 3 may be found in many modern physical chemistry textbooks.^{1–3} Specifically, the reader is referred to chapter 17 of ref 2, where it is shown that if 2×10^{15} molecules are distributed between two states, the probability of observing a 0.0001% deviation from the most probable distribution is on the order of 10^{-435} .

Consequently, the resolution of the apparent conundrum discussed in the previous section lies in the scale of the system being considered. Thermodynamics applies only to the most probable behavior of macroscopic systems involving a large number of molecules. In contrast, the concept of individual reactions proceeding in both directions at all points during a chemical process involves microscopic systems such as those that might be examined in a molecular dynamics study, where thermodynamics does not apply.

In thermodynamics, the statement that a reaction is spontaneous in a given direction at some point along the reaction coordinate means that the overall behavior of the macroscopic ensemble of molecules will be such that the measurable, macroscopic composition of the system will be altered in that direction without the necessity to do work on the system. Thermodynamics does not state that every reaction must proceed in that direction. It only requires that the net change in the composition of the system be in the spontaneous direction. Conversely, a thermodynamically nonspontaneous reaction is one that cannot occur in a specified direction to a sufficient extent to produce a measurable change in the system composition without work being done on the system.

Thermodynamic equilibrium is characterized by having $dG = 0$ at constant T and p or $dA = 0$ at constant T and V . In this case, a measurable, finite reaction in either direction will be characterized by having either ΔG or $\Delta A > 0$, and therefore, reactions in either direction will be nonspontaneous.^{1–4} This means there can be no net change of the macroscopic composition of the system without doing work on the system. Again, nothing in this statement precludes the possibility of there being a state of dynamic equilibrium in existence.

Statistical Treatment

In fact, not only does thermodynamics not preclude the existence of dynamic equilibrium or of reactions occurring in both directions at nonequilibrium points along the reaction coordinate, it actually suggests that such microscopic processes should be occurring. For example, consider the $2\text{NO}_2(\text{g}) \rightarrow \text{N}_2\text{O}_4(\text{g})$ system at point B in Figure 1, where the reaction coordinate is ξ_B , and the slope of the Helmholtz free energy curve is negative. The relevant thermodynamic potential energy in this case is the Helmholtz free energy, A . This potential can be represented by a Taylor series expansion in ξ about its value at point B, ξ_B . That is,

$$A(\xi) = \sum_{n=0}^{\infty} (n!)^{-1} \left(\frac{\partial^n A}{\partial \xi^n} \right)_{T,V} (\xi - \xi_B)^n \quad (4)$$

where the derivatives are evaluated at $\xi = \xi_B$. For extremely small changes in ξ that do not measurably alter the net composition of the system, only the $n = 0$ and $n = 1$ terms of eq 4 will be important. In this case, eq 4 becomes linear in $d\xi$:

$$A(\xi) = A(\xi_B) + \left(\frac{\partial A}{\partial \xi} \right)_{T,V} (\xi - \xi_B) = A(\xi_B) + \left(\frac{\partial A}{\partial \xi} \right)_{T,V} d\xi \quad (5)$$

where $d\xi = (\xi - \xi_B)$.

Consider the execution of such infinitesimal changes in the reaction coordinate in each direction starting at point B. Both changes are too small to produce any measurable alteration of the system composition. This situation is illustrated in Figure 2. The Helmholtz free energies at points $\xi_B + d\xi$ and $\xi_B - d\xi$ are

$$A(\xi_B + d\xi) = A(\xi_B) + \left(\frac{\partial A}{\partial \xi}\right)_{T,V} d\xi \quad \text{and} \quad (6)$$

$$A(\xi_B - d\xi) = A(\xi_B) - \left(\frac{\partial A}{\partial \xi}\right)_{T,V} d\xi \quad (7)$$

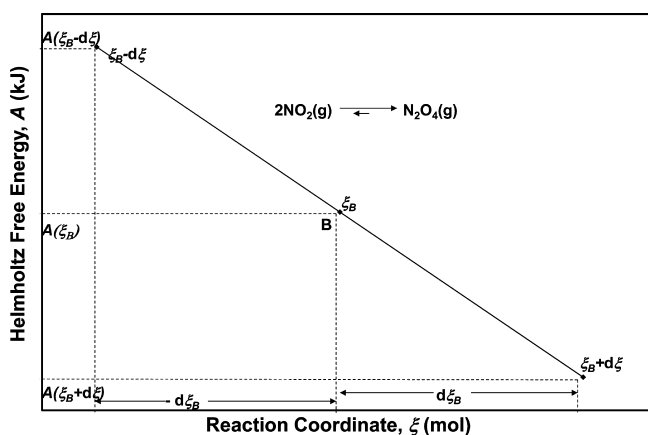


Figure 2. Variation of the Helmholtz free energy about Point B in Figure 1 for infinitesimally small changes in the reaction coordinate $\pm d\xi$ too small to produce any measurable change in the system composition. The size of the arrows in the chemical equation qualitatively reflects the value of $r(T)$ in eq 10.

The corresponding thermodynamic probabilities that the system will be found at these points can be obtained from eq 3 by recognizing that the relevant thermodynamic potential governing the progress of the $\text{NO}_2 - \text{N}_2\text{O}_4$ reaction at constant temperature and volume is the Helmholtz free energy. When Φ_α is replaced by the values of A in eqs 6 and 7, we obtain at each point

$$P(\xi_B + d\xi; T) = C \exp\left[-\frac{A(\xi_B) + (\partial A/\partial \xi)_{T,V} d\xi}{k_b T}\right] \quad \text{and} \quad (8)$$

$$P(\xi_B - d\xi; T) = C \exp\left[-\frac{A(\xi_B) - (\partial A/\partial \xi)_{T,V} d\xi}{k_b T}\right] \quad (9)$$

The ratio, $r(T)$, of the thermodynamic probabilities that a system originally at $\xi = \xi_B$ will move to point $\xi_B + d\xi$ rather than to point $\xi_B - d\xi$ is, therefore,

$$r(T) = \frac{P(\xi_B + d\xi; T)}{P(\xi_B - d\xi; T)} = \exp\left[-\frac{2(\partial A/\partial \xi)_{T,V} d\xi}{k_b T}\right] \quad (10)$$

In refs 4–6, the macroscopic chemical driving force, F , is discussed in detail. It is shown that this force is given by

$$F = -\left(\frac{\partial A}{\partial \xi}\right)_{T,V} \quad (11)$$

if T and V are constant. If the reaction is conducted under conditions of constant temperature and pressure, G replaces A in eqs 4–11. It is important to note that it is this driving force that controls the overall direction of the chemical reaction. This is apparent if the ratio of forward to reverse reaction probabilities is written in the form

$$r(T) = \frac{P(\xi_B + d\xi; T)}{P(\xi_B - d\xi; T)} = \exp\left[\frac{2Fd\xi}{k_b T}\right] \quad (12)$$

If F is positive, then the driving force acts to move the overall system in the direction of increasing ξ , that is, toward the products. If F is negative, the forward reaction will be nonspontaneous, and the system composition will shift toward the reactants.

For multiple-reaction systems, the thermodynamically most favored reaction pathway will always be in the direction of maximum chemical force, which eq 11 shows to be in the direction of the negative gradient of the Helmholtz free energy if T and V are constant or along the negative gradient of the Gibbs free energy if T and p are constant. The derivation and explanation of this result are given in ref 5.

Now consider a $\text{NO}_2(\text{g}) - \text{N}_2\text{O}_4(\text{g})$ system at Point B of Figure 1. At this point, it is clear that $(\partial A/\partial \xi)_{T,V} < 0$ so that the chemical force obtained from eq 11 is positive. Therefore, eqs 1a and 12 predict that the reaction will be spontaneous in the forward direction. That is, the composition of the system can measurably change to increase the amount of $\text{N}_2\text{O}_4(\text{g})$ present without the necessity to do work on the system. However, it should be noted that while eq 12 yields $r(T) > 0$, r is still finite. Consequently, $P(\xi_B - d\xi; T)$ is not zero. There is still a nonzero probability that some reactions will occur in the nonspontaneous direction. Thermodynamics requires only that the number of reactions occurring in the forward direction exceed the number moving toward the reactants so that the net composition change favors the products.

If a similar analysis is performed at point C, the results will be $(\partial A/\partial \xi)_{T,V} > 0$ and $r(T) < 0$. In this case, the forward reaction will be thermodynamically nonspontaneous, and the reverse reaction will be thermodynamically spontaneous. Nevertheless, $P(\xi_C + d\xi; T)$ is nonzero so that some reactions can occur in that direction, although the majority of reactions will be proceeding toward the reactants, causing the $\text{NO}_2(\text{g})$ concentration to increase.

At the $\text{NO}_2(\text{g}) - \text{N}_2\text{O}_4(\text{g})$ equilibrium Point D in Figure 1, the Helmholtz free energy reaches its minimum value so that $(\partial A/\partial \xi)_{T,V} = F = 0$. With no chemical force present, reactions in either direction are nonspontaneous, that is, the composition of the system cannot change in any measurable way without doing work on the system. However, since $P(\xi_D + d\xi; T) = P(\xi_D - d\xi; T)$ and $r(T) = 1$ at this point, reactions can be occurring with equal probability in either the forward or reverse directions. Thus, thermodynamics not only does not preclude the existence of a dynamic equilibrium, it actually predicts that it should exist.

■ PEDAGOGICAL RECOMMENDATIONS

For students in physical chemistry or any others who are thoroughly versed in thermodynamics, the foregoing analysis can be easily employed to demonstrate that the principles of equilibrium and spontaneity are compatible with the concept of competing reactions at all points along the reaction coordinate and with the idea of equal opposing rates at equilibrium.

In introductory chemistry courses or in courses where thermodynamics and equilibria are being treated in more a qualitative fashion, the compatibility of the spontaneity–equilibrium requirements of thermodynamics and the concept of dynamic equilibrium is best demonstrated by a careful phrasing of the definitions of spontaneity and nonspontaneity. Specifically, the definition of a “spontaneous” reaction should include not only the usual statement that a spontaneous reaction can proceed without the necessity to do work on the system, but also an explicit statement that the process must produce a measurable change in the composition of the system in the direction of the reaction. A clear delineation between what is occurring at the microscopic level and what is observable at the macroscopic level will help students clearly understand both spontaneity and dynamic equilibrium.

A suitable definition for a spontaneous reaction might be, “A thermodynamically spontaneous reaction at a given temperature is one that can move in a specified direction to produce a measurable change in the composition of the system without the necessity to do work on the system. At the microscopic level, reactions are taking place in both directions, but the reaction taking place in the spontaneous direction occurs at a greater rate because it is the more probable reaction.”

An appropriate definition for a nonspontaneous reaction would be similar,

“A thermodynamically nonspontaneous reaction at a given temperature is one that cannot move in a specified direction to produce a measurable change in the composition of the system unless work is done on the system. At the microscopic level, reactions are taking place in both directions, but the reaction taking place in the nonspontaneous direction occurs at a lesser rate because a reaction in that direction is less probable.”

A qualitative definition of equilibrium that is compatible with the concept of dynamic equilibrium might be,

“Thermodynamic equilibrium at a given temperature is a macroscopic state of the system in which chemical reactions that produce any measurable change in the system composition cannot occur without work being done on the system. At the microscopic level, reactions may nonetheless be taking place in both directions at the same rate because they have equal probabilities.”

When the above definitions are employed, students will understand that at nonequilibrium points, reactions can be occurring in both the forward and reverse directions so long as the net result is the composition of the system changes in the spontaneous direction. Likewise, at equilibrium, it will be realized by the students that reactions can be taking place in both directions so long as they occur with equal probability so as not to alter the system composition.

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Notes

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