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Article

Tunneling, the Equilibrium Constant, andEpicatalysis: A Second-Law Paradox?

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Abstract: Consider one particle (which could be an atom, molecule, Brownian particle, etc.) in thermodynamic equilibrium with a heat reservoir at temperature T. This particle can be in a low-potential-energy well L whose energy floor is E_L and whose degeneracy is G_L or in a higher (or at least equally high) potential-energy well H whose energy floor is E_H and whose degeneracy is G_H. L and H are separated by a barrier B, which the particle can traverse. The Second Law of Thermodynamics asserts that the ratio of the probability of this particle being in H to that of it being in L, i.e., the equilibrium constant K_{eq} corresponding to its dissemination between the two wells L and H, is in accordance with the Boltzmann (or canonical) distribution: $K_{\text{eq}} = (G_H/G_L)\exp[-(E_H - E_L)/kT]$. Given thermodynamic equilibrium this indeed *always* obtains if transits between L and H occur only via thermal excitation of our particle. But we show that *despite thermodynamic equilibrium* this does *not* obtain if transits between L and H occur both via thermal excitation and via tunneling. Implications concerning the Second Law of Thermodynamics are discussed. Next, we provide general remarks pertaining to catalysis versus epicatalysis. Then we spotlight that only *one* aspect of the Second Law can challenged: the aspect thereof that precludes a *net* decrease in entropy. Following concluding remarks, the minimum work that the Second Law requires to change K_{eq} is evaluated in the Appendix.

Keywords: equilibrium constant K_{eq}; thermal excitation; tunneling/anti-tunneling; entropy; Second Law of Thermodynamics; thermodynamic equilibrium; Boltzmann (canonical) distribution; catalysis/epicatalysis; Type-A systems; Type-B systems

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1. Introduction

Consider one particle (which could be an atom, molecule, Brownian particle, etc.) in thermodynamic equilibrium with a heat reservoir at absolute (Kelvin) temperature T. This particle can be in a low-potential-energy well L whose energy floor is E_L and whose degeneracy is G_L or in a higher (or at least equally high) potential-energy well H whose energy floor is E_H and whose degeneracy is G_H. L and H are separated by a barrier B, which the particle can traverse. The energy E_B required to surmount the barrier from the floor of L exceeds E_H.

The Second Law of Thermodynamics asserts that the ratio of the probability of this particle being in H to that of it being in L, i.e., the equilibrium constant $K_{\text{eq},L\rightleftarrows H}$ corresponding to its dissemination between the two wells L and H, is in accordance with the Boltzmann (or canonical) distribution as per

$$K_{\text{eq},L\rightleftarrows H} = \frac{P(\text{in } H)}{P(\text{in } L)} = \frac{G_H}{G_L} e^{-(E_H - E_L)/kT}, \tag{1}$$

where k is Boltzmann's constant. (Of course, the terms "Boltzmann distribution" and "canonical distribution" are synonymous [1–3]. Henceforth we will simply employ "Boltzmann distribution".) In Equation (1) we our construe our particle being in L as the reactant configuration and it being in H

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as the product configuration. If we instead construe it being in H as the reactant configuration and it being in L as the product configuration, then of course

$$K_{\text{eq},H\rightleftarrows L} = \frac{1}{K_{\text{eq},L\rightleftarrows H}} = \frac{P(\text{in }L)}{P(\text{in }H)} = \frac{G_L}{G_H}e^{-(E_L-E_H)/kT} = \frac{G_L}{G_H}e^{(E_H-E_L)/kT}. \quad (2)$$

Thus Equation (2) is redundant. Therefore henceforth we will employ only Equation (1) [except where also referring to Equation (2) adds emphasis].

In Section 2 we will show that, given thermodynamic equilibrium, Equation (1) [and, redundantly, also Equation (2)] is *always* obeyed in compliance with the Second Law if transits between L and H occur only via thermal excitation of our particle. But in Section 3 we provide the underpinning for showing that *despite thermodynamic equilibrium* this does *not* obtain, i.e., that Equation (1) [and, redundantly, also Equation (2)] is violated, if transits between L and H occur both via thermal excitation and via tunneling.

In Section 4 implications concerning the Second Law of Thermodynamics are discussed. Expanding on Section 2, we more thoroughly expound compliance with the Second Law if transits between L and H occur only via thermal excitation. But, expanding on Section 3, we more thoroughly expound that if transits between L and H also occur via tunneling there is at least a Second-Law paradox (what *prima facie* seems not compliant with the Second Law but with careful analysis is shown to be compliant), and perhaps even a challenge to the Second Law (what may *actually* be not compliant with the Second Law).

General remarks pertaining to catalysis versus epicatalysis are provided in Section 5. In Section 6, we spotlight (i) the *sole* aspect of the Second Law that can be challenged—the aspect thereof that precludes a *net* decrease in entropy—and (ii) that *all other aspects* of the Second Law, e.g., that entropy is a state function (and also Third-Law absolute entropies), remain inviolable. Following concluding remarks in Section 7, the minimum work that the Second Law requires to change K_{eq} is evaluated in the Appendix A.

2. The Equilibrium Constant K_{eq} Given Thermal Excitation Alone

In Section 2 we show that given thermodynamic equilibrium our system is compliant with the Second Law of Thermodynamics—specifically, with the Boltzmann distribution—as per Equation (1) [and, redundantly, also as per Equation (2)] if transits between L and H occur *only* via thermal excitation of our particle. This is an *approximation*: *some* tunneling *always* occurs, but in Section 2 we consider this *approximation*.

Consider again our one particle (which could be an atom, molecule, Brownian particle, etc.). Let it be of mass m in a uniform gravitational field g and be free to move between two gravitational-potential-energy wells, a lower well L of x-directional width X_L and floor at the datum elevation $z_L = 0$ and a higher (or at least equally high) well H of x-directional width X_H and floor at elevation $z_H \geq z_L = 0$ via traversal of a barrier B of x-directional width X_B and height z_B (see Figure 1 for a front view). In a top view (see Figure 2), the x-directional axis ($y = 0$) passes through the centers of the mutually adjacent L, B, and H, all three of which are of equal y-directional width $2Y$. The x-directional axis can be construed as negative-positive = west-east, the y-directional axis as negative-positive = south-north, and the z-directional axis as negative-positive = down-up. The west wall of L at $x = 0$, the east wall of H at $x = X_L + X_B + X_H$, and the south and north walls of the entire system at $y = -Y$ and $y = +Y$ are assumed to be arbitrarily tall in order to prevent the escape of our particle.

Our particle is in thermodynamic equilibrium via thermalization at its impacts with its heat reservoir at temperature T; this heat reservoir is comprised of the floors and walls of L and H, and the barrier B. Thus it can be construed as a one-particle isothermal atmosphere. Our results are easily generalizable to an $\mathcal{N}$-particle isothermal atmosphere sufficiently rarefied that the atmospheric particles collide essentially always with the floors and walls of L and H, and with B, but essentially

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never with each other: such an $\mathcal{N}$-particle isothermal atmosphere is essentially equivalent to $\mathcal{N}$ independent one-particle isothermal atmospheres.

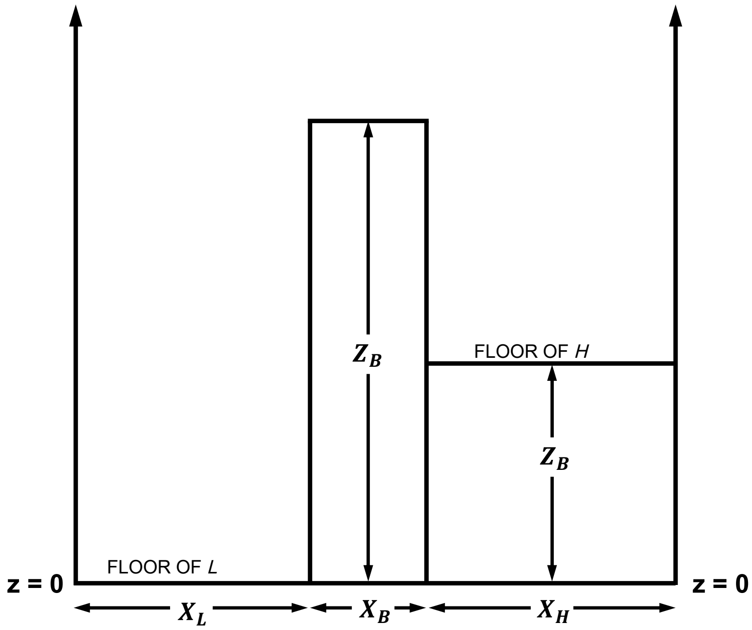

Figure 1. Front view of system.

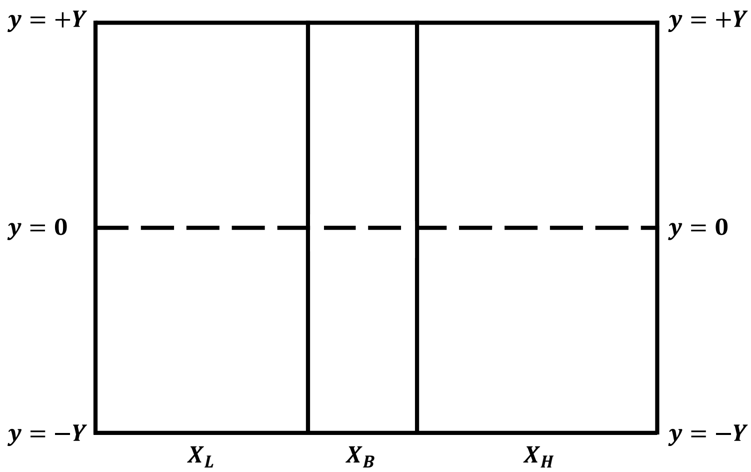

Figure 2. Top view of system

We set the datum elevation at the floor of the lower well L at the fixed value $z_L = 0$. Let the floor of the higher (or at least equally high) well H be at elevation z_H and the barrier be of height z_B: $z_B > z_H \geq z_L = 0$, i.e., we allow the choice $z_H = z_L = 0$ as well the choice $z_H > z_L = 0$, but require the *strict inequality* $z_B > z_H$. Thus the minimum possible gravitational potential energy of our particle relative to the datum elevation $z_L = 0$ is zero when it is in L, $E_H = mgz_H \equiv N_H kT \geq 0$ when it is in H, and $E_B = mgz_B \equiv N_B kT > E_H$ when it is over the barrier B. [$N_H \equiv E_H/kT = mgz_H/kT$, $N_B \equiv E_B/kT = mgz_B/kT$. We construe our particle to be in L (H) if it is within the *horizontal* areal extent of L (H) even if its altitude exceeds z_B.]

We will consider variations of the *vertical* coordinates z_H and z_B, as well as of the *horizontal* areal extents of L, H, and B. These horizontal variations can be most simply effected via those of B alone, by extending B into and/or retracting B from L and/or H—by increasing or decreasing the x-directional length of B in the direction of L and/or of H. Let G_L, G_H, and G_B be the degeneracies corresponding, respectively, to our particle occupying the lower well L, occupying the higher (or at least equally high) well H, or being over the barrier B. These degeneracies are proportional to area: they increase

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(decrease) monotonically—indeed, proportionately—with increasing (decreasing) horizontal areal extents of L, H, and B, respectively. Since the y-directional widths of L, H, and B are identical and fixed at $2Y$, G_L, G_H, and G_B are proportional to their respective x-directional lengths, X_L, X_H, and X_B. Thus henceforth we can substitute X_L, X_H, and X_B for G_L, G_H, and G_B, respectively.

At thermodynamic equilibrium, the Second Law of Thermodynamics—specifically, the Boltzmann distribution—asserts that the probabilities of our particle being in L, in H, or over the barrier B must be, respectively,

$$P(\text{in } L) = \frac{X_L}{X_L + X_H e^{-N_H} + X_B e^{-N_B}} \equiv \frac{X_L}{Q}, \tag{3}$$

$$P(\text{in } H) = \frac{X_H e^{-N_H}}{X_L + X_H e^{-N_H} + X_B e^{-N_B}} \equiv \frac{X_H e^{-N_H}}{Q}, \tag{4}$$

and

$$P(\text{over } B) = \frac{X_B e^{-N_B}}{X_L + X_H e^{-N_H} + X_B e^{-N_B}} \equiv \frac{X_B e^{-N_B}}{Q}, \tag{5}$$

where in accordance with standard notation

$$Q \equiv X_L + X_H e^{-N_H} + X_B e^{-N_B} \tag{6}$$

is the partition function (also known as the sum-over-states) of our system [4,5].

Let the x-directional component of our particle's average thermal scalar speed be $\langle V_x \rangle$. (Enclosure within angular brackets denotes averaging.) Because our particle is at thermodynamic equilibrium with a heat reservoir at temperature T, $\langle V_x \rangle$ is identical irrespective of our particle's altitude and of whether it is in L, in H, or over the barrier B (see, for example, Reif [2], Sections 6.1–6.4; especially, in Section 6.3, the subsections entitled "Molecule in an ideal gas" and "Molecule in an ideal gas in the presence of gravity"). We focus on $K_{\text{eq},L\rightleftarrows H}$ and hence on the dissemination of our particle between L and H; therefore we need not consider the time it spends traversing the barrier B.

When our particle is in L, it bounces through an x-directional distance of $2X_L$ between attempts to transit from L to H. Hence the average time that our particle spends in L between attempts to transit from L to H is

$$\langle t_L \rangle = \frac{2X_L}{\langle V_x \rangle} \tag{7}$$

and the average rate of these attempts is

$$\langle r_L \rangle = \frac{1}{\langle t_L \rangle} = \frac{\langle V_x \rangle}{2X_L}. \tag{8}$$

Similarly, when our particle is in H, it bounces through an x-directional distance of $2X_H$ between attempts to transit from H to L. Hence the average time that our particle spends in H between attempts to transit from H to L is

$$\langle t_H \rangle = \frac{2X_H}{\langle V_x \rangle} \tag{9}$$

and the average rate of these attempts is

$$\langle r_H \rangle = \frac{1}{\langle t_H \rangle} = \frac{\langle V_x \rangle}{2X_H}. \tag{10}$$

For every attempt to transit from H to L via thermal excitation that succeeds, in accordance with the Boltzmann distribution there is a probability e^{-N_H} that an attempt to transit from L to H via

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thermal excitation will succeed. Hence considering the dissemination of our particle between L and H via *thermal excitation alone*, the *thermal* equilibrium constant is

$$K^{\text{thermal}}_{\text{eq},L\rightleftarrows H} = \frac{P_{\text{thermal}}(\text{in } H)}{P_{\text{thermal}}(\text{in } L)} = \frac{\langle r_{\text{thermal}}(L \to H)\rangle}{\langle r_{\text{thermal}}(H \to L)\rangle}$$
$$= \frac{\langle r_L\rangle e^{-N_H}}{\langle r_H\rangle} = \frac{\frac{\langle V_x\rangle}{2X_L}e^{-N_H}}{\frac{\langle V_x\rangle}{2X_H}} = \frac{X_H}{X_L}e^{-N_H}, \tag{11}$$

where $P_{\text{thermal}}(\text{in } L)$ [$P_{\text{thermal}}(\text{in } H)$] is the probability that our particle is in L [H] if transits between L and H occur *only* via thermal excitation over the barrier B. This is in compliance with the Second Law—specifically, with the Boltzmann distribution.

We re-emphasize that *some* tunneling *always* occurs, but in Section 2 we considered *thermal excitation alone* as an *approximation*.

3. Thermal Excitation and Tunneling

Tunneling from L to H is unnecessary for traversal of the barrier B if our particle attains by thermal excitation altitude of at least z_B and hence gravitational potential energy of at least $mgz_B = N_BkT$ relative to the datum elevation $z_L = 0$ at the floor of L. Likewise, tunneling from H to L is unnecessary for traversal of the barrier B if our particle attains by thermal excitation altitude of at least $z_B - z_H$ and hence gravitational potential energy of at least $mg(z_B - z_H) = (N_B - N_H)kT$ relative to the elevation z_H at the floor of H. But tunneling from H to L can occur if our particle is in the altitude range $z_H \leq z < z_B$ in H. The probability of our particle being in this altitude range in H equals the probability that it is in H as per Equation (4) times the probability, $1 - e^{-mg(z_B - z_H)/kT} = 1 - e^{-(N_B - N_H)}$ as per the Boltzmann distribution, that it is in the altitude range $z_H \leq z < z_B$ given that it is in H:

$$P(z_H \leq z < z_B \text{ in } H) = P(\text{in } H)P(z_H \leq z < z_B|\text{in } H)$$
$$= \frac{X_H e^{-N_H}}{Q}\left[1 - e^{-(N_B - N_H)}\right]$$
$$= \frac{X_H\left(e^{-N_H} - e^{-N_B}\right)}{Q}. \tag{12}$$

The average rate of tunneling of our particle from H to L equals the fraction $f^{H\to L}_{\text{tun}}$ of tunneling attempts from H to L that succeed times the average rate of tunneling attempts from H to L as per Equation (10) times $P(z_H \leq z < z_B \text{ in } H)$ as per Equation (12). [In employing Equation (10), we assume that our particle is massive enough, the temperature is high enough, and X_H and $2Y$ are large enough that its translational motion in H can be treated classically.] Thus applying Equations (10) and (12):

$$\langle r_{\text{tun}}(H \to L)\rangle = f^{H\to L}_{\text{tun}}\frac{\langle V_x\rangle}{2X_H}\frac{X_H\left(e^{-N_H} - e^{-N_B}\right)}{Q}$$
$$= \frac{f^{H\to L}_{\text{tun}}\langle V_x\rangle\left(e^{-N_H} - e^{-N_B}\right)}{2Q}. \tag{13}$$

Tunneling can occur only to states of lower or equal energy, not to states of higher energy [6–8]. Therefore, tunneling from L to H can*not* occur if our particle is in the altitude range $z_L = 0 \leq z < z_H$ in L [6–8]. If tunneling from L to H is to occur, our particle must first attain by thermal excitation altitude of at least z_H in L and hence gravitational potential energy of at least $mgz_H = N_HkT$ relative to the datum elevation $z_L = 0$ at the floor of L. The probability that it can do so at any one given attempt is $e^{-mgz_H/kT} = e^{-N_H}$, and hence the probability that it can*not* do so at any one given attempt is $1 - e^{-mgz_H/kT} = 1 - e^{-N_H}$. Moreover, as we have already mentioned, tunneling is unnecessary for traversal of the barrier B if our particle attains by thermal excitation altitude $z \geq z_B$ and hence gravitational potential energy of at least $mgz_B = N_BkT$ relative to the datum elevation $z_L = 0$

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at the floor of L: this occurs with probability $e^{-mgz_B/kT} = e^{-N_B}$ at any one given attempt. The probability of our particle being in the altitude range $z_H \leq z < z_B$ in L wherein tunneling from L to H can occur equals the probability as per Equation (3) that it is in L times the probability, $1 - \left(1 - e^{-N_H}\right) - e^{-N_B} = e^{-N_H} - e^{-N_B}$ as per the Boltzmann distribution, that it is in the altitude range $z_H \leq z < z_B$ given that it is in L:

$$\begin{aligned} P(z_H \leq z < z_B \text{ in } L) &= P(\text{in } L)P(z_H \leq z < z_B|\text{in } L) \\ &= \frac{X_L}{Q}\left(e^{-N_H} - e^{-N_B}\right). \end{aligned} \tag{14}$$

The average rate of tunneling of our particle from L to H equals the fraction $f_{\text{tun}}^{L\to H}$ of tunneling attempts from L to H that succeed times the average rate of tunneling attempts from L to H as per Equation (8) times $P(z_H \leq z < z_B \text{ in } L)$ as per Equation (14). [In employing Equation (8), we assume that our particle is massive enough, the temperature is high enough, and X_L and $2Y$ are large enough that its translational motion in L can be treated classically.] Thus applying Equations (8) and (14):

$$\langle r_{\text{tun}}(L \to H)\rangle = f_{\text{tun}}^{L\to H}\frac{\langle V_x\rangle}{2X_L}\frac{X_L}{Q}\left(e^{-N_H} - e^{-N_B}\right) = \frac{f_{\text{tun}}^{L\to H}\langle V_x\rangle\left(e^{-N_H} - e^{-N_B}\right)}{2Q}. \tag{15}$$

We must also consider anti-tunneling: our particle being reflected back to L even if it has acquired by thermal excitation altitude $z \geq z_B$ and hence gravitational potential energy of at least $mgz_B = N_B kT$ relative to the floor of L, and being reflected back to H even if it has acquired by thermal excitation altitude $z \geq z_B - z_H$ and hence gravitational potential energy of at least $mg(z_B - z_H) = (N_B - N_H)kT$ relative to the floor of H.

The probability that our particle is in the altitude range $z \geq z_B$ in L equals the probability as per Equation (3) that it is in L times the probability, e^{-N_B} as per the Boltzmann distribution, that it is in the altitude range $z \geq z_B$ given that it is in L:

$$\begin{aligned} P(z \geq z_B \text{ in } L) &= P(\text{in } L)P(z \geq z_B|\text{in } L) \\ &= \frac{X_L}{Q}e^{-N_B}. \end{aligned} \tag{16}$$

The average rate of anti-tunneling of our particle back to L equals the fraction $f_{\text{antitun}}^{\text{in } L}$ of anti-tunneling attempts in L that succeed times average rate of anti-tunneling attempts in L as per Equation (8) times $P(z \geq z_B \text{ in } L)$ as per Equation (16). [In employing Equation (8), we assume that our particle is massive enough, the temperature is high enough, and X_L and $2Y$ are large enough that its translational motion in L can be treated classically.] Thus applying Equations (8) and (16):

$$\langle r_{\text{antitun}}(\text{in } L)\rangle = f_{\text{antitun}}^{\text{in } L}\frac{\langle V_x\rangle}{2X_L}\frac{X_L}{Q}e^{-N_B} = \frac{f_{\text{antitun}}^{\text{in } L}\langle V_x\rangle e^{-N_B}}{2Q}. \tag{17}$$

The probability that our particle is in the altitude range $z \geq z_B$ in H equals the probability as per Equation (4) that it is in H times the probability, $e^{-(N_B - N_H)}$ as per the Boltzmann distribution, that it is in the altitude range $z \geq z_B$ given that it is in H:

$$\begin{aligned} P(z \geq z_B \text{ in } H) &= P(\text{in } H)P(z \geq z_B|\text{in } H) \\ &= \frac{X_H e^{-N_H}}{Q}e^{-(N_B - N_H)} = \frac{X_H}{Q}e^{-N_B}. \end{aligned} \tag{18}$$

The average rate of anti-tunneling of our particle back to H equals the fraction $f_{\text{antitun}}^{\text{in } H}$ of anti-tunneling attempts in H that succeed times average rate of anti-tunneling attempts in H as per Equation (10) times $P(z \geq z_B \text{ in } H)$ as per Equation (18). [In employing Equation (10), we assume that our particle is

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massive enough, the temperature is high enough, and X_H and $2Y$ are large enough that its translational motion in H can be treated classically.] Thus applying Equations (10) and (18):

$$\langle r_{\text{antitun}}(\text{in } H)\rangle = f_{\text{antitun}}^{\text{in } H}\frac{\langle V_x\rangle}{2X_H}\frac{X_H}{Q}e^{-N_B} = \frac{f_{\text{antitun}}^{\text{in } H}\langle V_x\rangle e^{-N_B}}{2Q}. \quad (19)$$

Our particle must be in the same altitude range, namely $z_H \leq z < z_B$, in both L and H in order for tunneling to occur in either direction, i.e., either from L to H or from H to L, respectively. And it must be in the same altitude range, namely $z \geq z_B$, in both L and H in order for anti-tunneling to occur back to L or back to H, respectively. Therefore the most plausible conjecture is that f_{tun} should be the same with respect to tunneling in either direction, i.e., that $f_{\text{tun}}^{L\to H} = f_{\text{tun}}^{H\to L} = f_{\text{tun}}$, and likewise that f_{antitun} should be the same with respect to anti-tunneling in both wells, i.e., that $f_{\text{antitun}}^{\text{in } L} = f_{\text{antitun}}^{\text{in } H} = f_{\text{antitun}}$. This conjecture is rendered even more plausible given that our system is at thermodynamic equilibrium—irrespective of whether or not $K_{\text{eq},L\rightleftarrows H} = (G_H/G_L)\exp[-(E_H - E_L)/kT]$ as the Second Law (specifically, the Boltzmann distribution) asserts: at equilibrium—irrespective of whether or not that equilibrium is that which Second Law (specifically, the Boltzmann distribution) asserts—we should expect the average rate of *any* process and its reverse to be equal. Moreover, the issue of the validity of our challenge to the Second Law, let alone of our Second-Law paradox, does *not* hinge on the equalities $f_{\text{tun}}^{L\to H} = f_{\text{tun}}^{H\to L} = f_{\text{tun}}$ and $f_{\text{antitun}}^{\text{in } L} = f_{\text{antitun}}^{\text{in } H} = f_{\text{antitun}}$. Therefore let us accept these equalities.

Hence in accordance with the immediately preceding paragraph, applying Equations (13) and (15):

$$\langle r_{\text{tun}}(L\to H)\rangle = \langle r_{\text{tun}}(H\to L)\rangle = \frac{f_{\text{tun}}\langle V_x\rangle\left(e^{-N_H} - e^{-N_B}\right)}{2Q}. \quad (20)$$

And likewise in accordance with the immediately preceding paragraph, applying Equations (17) and (19):

$$\langle r_{\text{antitun}}(\text{in } H)\rangle = \langle r_{\text{antitun}}(\text{in } L)\rangle = \frac{f_{\text{antitun}}\langle V_x\rangle e^{-N_B}}{2Q}. \quad (21)$$

Since by Equation (20) $\langle r_{\text{tun}}(L\to H)\rangle = \langle r_{\text{tun}}(H\to L)\rangle$, tunneling from L to H is on the average counterbalanced by tunneling from H to L. And since by Equation (21) $\langle r_{\text{antitun}}(\text{in } L)\rangle = \langle r_{\text{antitun}}(\text{in } H)\rangle$, likewise anti-tunneling back to L is on the average counterbalanced by anti-tunneling back to H. Hence as we should expect since our system is at thermodynamic equilibrium —irrespective of whether or not $K_{\text{eq},L\rightleftarrows H} = (G_H/G_L)\exp[-(E_H - E_L)/kT]$ as the Second Law (specifically, the Boltzmann distribution) asserts—tunneling, anti-tunneling, and most importantly *net* tunneling = tunneling minus anti-tunneling from L to H is on the average counterbalanced by that from H to L.

Applying Equations (20) and (21), we have, for the average rate of *net* tunneling = tunneling minus anti-tunneling either from L to H or from H to L:

$$\begin{aligned}
&\langle r_{\text{tun,net}}(L\to H)\rangle = \langle r_{\text{tun}}(L\to H)\rangle - \langle r_{\text{antitun}}(\text{in } L)\rangle \\
&= \langle r_{\text{tun,net}}(H\to L)\rangle = \langle r_{\text{tun}}(H\to L)\rangle - \langle r_{\text{antitun}}(\text{in } H)\rangle \\
&= \frac{f_{\text{tun}}\langle V_x\rangle\left(e^{-N_H} - e^{-N_B}\right)}{2Q} - \frac{f_{\text{antitun}}\langle V_x\rangle e^{-N_B}}{2Q} \\
&= \frac{\langle V_x\rangle\left[f_{\text{tun}}\left(e^{-N_H} - e^{-N_B}\right) - f_{\text{antitun}}e^{-N_B}\right]}{2Q}.
\end{aligned} \quad (22)$$

As a brief aside, we mention that since no physically-realistic barrier or well can be *perfectly* square, the formulas for the probabilities of tunneling and anti-tunneling that assume *perfectly* square barriers and wells are *approximations* [9–14]. Thus construing our barrier B and wells L and H as *perfectly* square is an *approximation*. But since we do not require specific numerical values for f_{tun} and f_{antitun}, we can get off scot-free with this *approximation*.

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4. A Second-Law Paradox (and Perhaps Even Challenge)

Applying Equations (11) and (22), we have, for the *total* equilibrium constant, i.e., considering both thermal excitation and *net* tunneling = tunneling minus anti-tunneling:

$$\begin{aligned}
K^{\text{total}}_{\text{eq},L\rightleftarrows H} &= \frac{\langle r_{\text{total}}(L\to H)\rangle}{\langle r_{\text{total}}(H\to L)\rangle} = \frac{\langle r_{\text{thermal}}(L\to H)\rangle + \langle r_{\text{tun,net}}(L\to H)\rangle}{\langle r_{\text{thermal}}(H\to L)\rangle + \langle r_{\text{tun,net}}(H\to L)\rangle} \\
&= \frac{\frac{\langle V_x\rangle}{2X_L}e^{-N_H} + \frac{\langle V_x\rangle\left[f_{\text{tun}}\left(e^{-N_H}-e^{-N_B}\right)-f_{\text{antitun}}e^{-N_B}\right]}{2Q}}{\frac{\langle V_x\rangle}{2X_H} + \frac{\langle V_x\rangle\left[f_{\text{tun}}\left(e^{-N_H}-e^{-N_B}\right)-f_{\text{antitun}}e^{-N_B}\right]}{2Q}} \\
&= \frac{\frac{X_H e^{-N_H}}{X_L} + \frac{X_H\left[f_{\text{tun}}\left(e^{-N_H}-e^{-N_B}\right)-f_{\text{antitun}}e^{-N_B}\right]}{Q}}{1 + \frac{X_H\left[f_{\text{tun}}\left(e^{-N_H}-e^{-N_B}\right)-f_{\text{antitun}}e^{-N_B}\right]}{Q}} \\
&= \frac{\frac{X_H e^{-N_H}}{X_L} + \frac{X_H\left[f_{\text{tun}}\left(e^{-N_H}-e^{-N_B}\right)-f_{\text{antitun}}e^{-N_B}\right]}{X_L+X_He^{-N_H}+X_Be^{-N_B}}}{1 + \frac{X_H\left[f_{\text{tun}}\left(e^{-N_H}-e^{-N_B}\right)-f_{\text{antitun}}e^{-N_B}\right]}{X_L+X_He^{-N_H}+X_Be^{-N_B}}} \\
&= \frac{K^{\text{thermal}}_{\text{eq},L\rightleftarrows H} + \frac{X_H\left[f_{\text{tun}}\left(e^{-N_H}-e^{-N_B}\right)-f_{\text{antitun}}e^{-N_B}\right]}{X_L+X_He^{-N_H}+X_Be^{-N_B}}}{1 + \frac{X_H\left[f_{\text{tun}}\left(e^{-N_H}-e^{-N_B}\right)-f_{\text{antitun}}e^{-N_B}\right]}{X_L+X_He^{-N_H}+X_Be^{-N_B}}} \\
&= \frac{P_{\text{total}}(\text{in } H)}{P_{\text{total}}(\text{in } L)}\begin{cases} \text{in general} \neq \frac{P_{\text{thermal}}(H)}{P_{\text{thermal}}(L)} = K^{\text{thermal}}_{\text{eq},L\rightleftarrows H} = \frac{X_H}{X_L}e^{-N_H} \\ \qquad = K^{\text{thermal}}_{\text{eq},L\rightleftarrows H} \text{ iff } K^{\text{thermal}}_{\text{eq},L\rightleftarrows H} = 1 \end{cases}.
\end{aligned} \tag{23}$$

The inequality in the last line of Equation (23) poses, at least *prima facie*, a Second-Law paradox, and perhaps even a challenge to the Second Law. (iff means: if and only if.) This inequality obtains *solely* owing to the second (net-tunneling) terms in the numerators and denominators of the first five lines of Equation (23). If these terms become negligible, owing either to Case (i): both f_{tun} and f_{antitun} being negligibly small [they can*not individually* be *exactly* zero: the probability of neither tunneling nor (except at $T = 0\,\text{K}$) anti-tunneling never *totally* vanishes] or Case (ii): the f_{antitun} term cancelling the f_{tun} term (*cancellation* to *exactly* zero *is* possible, at least in principle), $K^{\text{total}}_{\text{eq},L\rightleftarrows H} \to K^{\text{thermal}}_{\text{eq},L\rightleftarrows H} = \frac{X_H}{X_L}e^{-N_H}$ and thus the consequent *prima facie* Second-Law paradox, let alone challenge to the Second Law, vanishes [for all practical purposes in Case (i) and up to exactly in Case (ii)].

Comparing Equations (11) and (23), if the second (net-tunneling) terms in the numerators and denominators of the first five lines of Equation (23) do *not* vanish, they imply at least *prima facie* Second-Law paradoxes, and perhaps even challenges to the Second Law with respect to the first (thermal) terms thereof.

For then, if and only if $N_H = \ln\frac{X_H}{X_L} \implies K^{\text{total}}_{\text{eq},L\rightleftarrows H} = K^{\text{thermal}}_{\text{eq},L\rightleftarrows H} = 1$ is our system in compliance with the Second Law of Thermodynamics—specifically, in compliance with the Boltzmann distribution. Since $N_H \geq 0$, this can obtain if and only if $\ln\frac{X_H}{X_L} \geq 0 \implies \frac{X_H}{X_L} \geq 1$. If $N_H > \ln\frac{X_H}{X_L}$, $K^{\text{thermal}}_{\text{eq},L\rightleftarrows H} < K^{\text{total}}_{\text{eq},L\rightleftarrows H} < 1$ and hence *in the face of thermodynamic equilibrium* our particle is more probably in H and less probably in L than the Second Law—specifically, the Boltzmann distribution—asserts. Since $N_H \geq 0$, this can obtain if and only if $N_H > \ln\frac{X_H}{X_L} \geq 0 \implies \ln\frac{X_H}{X_L} \geq 0 \implies \frac{X_H}{X_L} \geq 1$. And if $N_H < \ln\frac{X_H}{X_L}$, $K^{\text{thermal}}_{\text{eq},L\rightleftarrows H} > K^{\text{total}}_{\text{eq},L\rightleftarrows H} > 1$ and hence *in the face of thermodynamic equilibrium* our particle is more probably in L and less probably in H than the Second Law—specifically, the Boltzmann distribution—asserts. Since $N_H \geq 0$, this can obtain if and only if $0 \leq N_H < \ln\frac{X_H}{X_L} \implies \ln\frac{X_H}{X_L} > N_H \geq 0 \implies \frac{X_H}{X_L} > e^{N_H} \geq 1 \implies \frac{X_H}{X_L} \geq 1$.

Note that whether $K^{\text{total}}_{\text{eq},L\rightleftarrows H} > K^{\text{thermal}}_{\text{eq},L\rightleftarrows H}$ or $K^{\text{total}}_{\text{eq},L\rightleftarrows H} < K^{\text{thermal}}_{\text{eq},L\rightleftarrows H}$, $K^{\text{total}}_{\text{eq},L\rightleftarrows H}$ is intermediate between $K^{\text{thermal}}_{\text{eq},L\rightleftarrows H}$ and unity. Of course, whether $K^{\text{total}}_{\text{eq},L\rightleftarrows H} = K^{\text{thermal}}_{\text{eq},L\rightleftarrows H}$, $K^{\text{total}}_{\text{eq},L\rightleftarrows H} > K^{\text{thermal}}_{\text{eq},L\rightleftarrows H}$, or $K^{\text{total}}_{\text{eq},L\rightleftarrows H} < K^{\text{thermal}}_{\text{eq},L\rightleftarrows H}$, $K^{\text{total}}_{\text{eq},L\rightleftarrows H}$, the allowable range of values of $\frac{X_H}{X_L}$ is restricted to that wherein $N_H \geq 0$, i.e., to $\frac{X_H}{X_L} \geq 1$ in all three cases.

At least *prima facie*, this seems to pose at least a Second-Law paradox, and perhaps even a challenge to the Second Law.

Perhaps more importantly, at least *prima facie*, it seems that, at least in principle, X_L, X_H, N_H, and/or N_B—and hence $K^{\text{total}}_{\text{eq},L\rightleftarrows H}$—can, at least in principle, be *changed* (epicatalysis) with *zero* thermodynamic cost. Changes in X_L and/or X_H can be effected (most simply by extending B into and/or retracting B from L and/or H) at least in principle with *zero* net work input. Given that our particle constitutes a one-molecule gas, work is required to decrease X_L and/or X_H, because this renders our particle more constrained [15,16], i.e., more localized [15,16], in L and/or in H (see also Reif [2], Sections 3.1 and 3.2). But, at least in principle, all of this work can be recovered via a subsequent equal increase in X_L and/or X_H. Also, the work required to raise the floor of H (i.e., to increase N_H) and/or to raise the barrier B (i.e., to increase N_B) can, at least in principle, be recovered, e.g., via employment of a counterweight. (Of course, if instead N_H and/or N_B is decreased, a counterweight can be raised.) Thus X_L, X_H, N_H, and/or N_B—and hence $K^{\text{total}}_{\text{eq},L\rightleftarrows H}$—can, at least in principle, be *changed* (epicatalysis) with *zero* work input, i.e., with *zero* thermodynamic cost. At least *prima facie*, this seems to pose at least an even stronger Second-Law paradox, and perhaps an even stronger challenge to the Second Law. For, the Second Law of Thermodynamics requires a minimum work input as the cost of changing not only $K^{\text{total}}_{\text{eq},L\rightleftarrows H}$ as per Equation (23) in particular, but *any* equilibrium constant K_{eq} in general. (See the Appendix.)

We will show that both our non-Boltzmann-distribution and zero-cost-epicatalysis at least *prima facie* Second-Law paradoxes, and perhaps even challenges to the Second Law, also obtain in the high-temperature and extreme-high-temperature/$N_H \to 0$ limits of Equation (23), but not in the extreme-low-temperature limit thereof.

Let us now consider the high-temperature, extreme-high-temperature/$N_H \to 0$, and extreme-low-temperature limits of Equation (23), applying especially the fourth line thereof.

In the high-temperature limit, $e^{-N_H} \to 1 - N_H$, $e^{-N_B} \to 1 - N_B$, $e^{-N_H} - e^{-N_B} \to (1 - N_H) - (1 - N_B) = N_B - N_H$, and the fourth line of Equation (23) simplifies to

$$\lim_{T\to\infty} K^{\text{total}}_{\text{eq},L\rightleftarrows H} = \frac{\frac{X_H(1-N_H)}{X_L} + \frac{X_H[f_{\text{tun}}(N_B-N_H)-f_{\text{antitun}}(1-N_B)]}{X_L+X_H(1-N_H)+X_B(1-N_B)}}{1+\frac{X_H[f_{\text{tun}}(N_B-N_H)-f_{\text{antitun}}(1-N_B)]}{X_L+X_H(1-N_H)+X_B(1-N_B)}}. \tag{24}$$

In the high-temperature limit, if and only if $N_H = 1 - \frac{X_L}{X_H} \implies K^{\text{total}}_{\text{eq},L\rightleftarrows H} = K^{\text{thermal}}_{\text{eq},L\rightleftarrows H} = 1$ is our system in compliance with the Second Law of Thermodynamics—specifically, in compliance with the Boltzmann distribution. Since $N_H \geq 0$, this can obtain if and only if $1 - \frac{X_L}{X_H} \geq 0 \implies \frac{X_L}{X_H} \leq 1 \implies \frac{X_H}{X_L} \geq 1$. If $N_H > 1 - \frac{X_L}{X_H}$, $K^{\text{thermal}}_{\text{eq},L\rightleftarrows H} < K^{\text{total}}_{\text{eq},L\rightleftarrows H} < 1$ and hence *in the face of thermodynamic equilibrium* our particle is more probably in H and less probably in L than the Second Law—specifically, the Boltzmann distribution—asserts. Since $N_H \geq 0$, this can obtain if and only if $N_H > 1 - \frac{X_L}{X_H} \geq 0 \implies 1 - \frac{X_L}{X_H} \geq 0 \implies \frac{X_L}{X_H} \leq 1 \implies \frac{X_H}{X_L} \geq 1$. And if $N_H < 1 - \frac{X_L}{X_H}$, $K^{\text{thermal}}_{\text{eq},L\rightleftarrows H} > K^{\text{total}}_{\text{eq},L\rightleftarrows H} > 1$ and hence *in the face of thermodynamic equilibrium* our particle is more probably in L and less probably in H than the Second Law—specifically, the Boltzmann distribution—asserts. Since $N_H \geq 0$, this can obtain if and only if $0 \leq N_H < 1 - \frac{X_L}{X_H} \implies 1 - \frac{X_L}{X_H} \geq 0 \implies \frac{X_L}{X_H} \leq 1 \implies \frac{X_H}{X_L} \geq 1$.

Note that these results with respect to the high-temperature limit as per Equation (24) are consistent with those with respect to the general case as per Equation (23). Also note that, as with respect to the general case as per Equation (23), whether $K^{\text{total}}_{\text{eq},L\rightleftarrows H} = K^{\text{thermal}}_{\text{eq},L\rightleftarrows H}$, $K^{\text{total}}_{\text{eq},L\rightleftarrows H} > K^{\text{thermal}}_{\text{eq},L\rightleftarrows H}$, or $K^{\text{total}}_{\text{eq},L\rightleftarrows H} < K^{\text{thermal}}_{\text{eq},L\rightleftarrows H}$, $K^{\text{total}}_{\text{eq},L\rightleftarrows H}$, the allowable range of values of $\frac{X_H}{X_L}$ is restricted to that wherein $N_H \geq 0$, i.e., to $\frac{X_H}{X_L} \geq 1$ in all three cases.

In the extreme-high-temperature/$N_H \to 0$ limit, i.e., either in the limit $T \to \infty$ with any finite $N_H \geq 0$ or if $N_H = 0$ at any $T > 0\,\mathrm{K}$, $e^{-N_H} \to 1$, $e^{-N_B} \to 1$, $e^{-N_H} - e^{-N_B} \to (1 - N_H) - (1 - N_B) = N_B - N_H$, there is further simplification to

$$\lim_{T\to\infty} K^{\text{total}}_{\text{eq},L\rightleftarrows H} = \frac{\frac{X_H}{X_L} + \frac{X_H[f_{\text{tun}}(N_B - N_H) - f_{\text{antitun}}]}{X_L + X_H + X_B}}{1 + \frac{X_H[f_{\text{tun}}(N_B - N_H) - f_{\text{antitun}}]}{X_L + X_H + X_B}}. \tag{25}$$

In the extreme-high-temperature/$N_H \to 0$, limit, if and only if $X_H = X_L \implies K^{\text{total}}_{\text{eq},L\rightleftarrows H} = K^{\text{thermal}}_{\text{eq},L\rightleftarrows H} = 1$ is our system in compliance with the Second Law of Thermodynamics—specifically, in compliance with the Boltzmann distribution. If $X_H > X_L$, $K^{\text{thermal}}_{\text{eq},L\rightleftarrows H} > K^{\text{total}}_{\text{eq},L\rightleftarrows H} > 1$ and hence *in the face of thermodynamic equilibrium* our particle is more probably in L and less probably in H than the Second Law—specifically, the Boltzmann distribution—asserts. And if $X_H < X_L$, $K^{\text{thermal}}_{\text{eq},L\rightleftarrows H} < K^{\text{total}}_{\text{eq},L\rightleftarrows H} < 1$ and hence *in the face of thermodynamic equilibrium* our particle is more probably in H and less probably in L than the Second Law—specifically, the Boltzmann distribution—asserts.

Hence in both the high-temperature and extreme-high-temperature/$N_H \to 0$ limits as per Equations (24) and (25), as in the general case in accordance with Equation (23), if $K^{\text{total}}_{\text{eq},L\rightleftarrows H} \neq K^{\text{thermal}}_{\text{eq},L\rightleftarrows H} \neq 1$ our system is *not* in compliance with the Second Law of Thermodynamics—specifically, in *not* in compliance with the Boltzmann distribution. At least *prima facie*, this seems to pose at least a Second-Law paradox, and perhaps even a challenge to the Second Law. [Also, as in the general case, in the high-temperature and extreme-high-temperature/$N_H \to 0$ limits (unless $K^{\text{total}}_{\text{eq},L\rightleftarrows H} = K^{\text{thermal}}_{\text{eq},L\rightleftarrows H} = 1$) $K^{\text{total}}_{\text{eq},L\rightleftarrows H}$ is intermediate between $K^{\text{thermal}}_{\text{eq},L\rightleftarrows H}$ and unity.] Moreover, as in the general case, in the high-temperature and extreme-high-temperature/$N_H \to 0$ limits at least *prima facie* it seems that, at least in principle, X_L, X_H, N_H, and/or N_B—and hence $K^{\text{total}}_{\text{eq},L\rightleftarrows H}$—can be *changed* (epicatalysis) with *zero* work input, i.e., with *zero* thermodynamic cost. At least *prima facie*, this seems to pose an even stronger paradox, and perhaps even a stronger challenge, with respect to the Second Law.

Furthermore, in both the high-temperature and extreme-high-temperature/$N_H \to 0$ limits, as in the general case in accordance with Equation (23), both our non-Boltzmann-distribution and zero-cost-epicatalysis at least *prima facie* Second-Law paradoxes, and perhaps even challenges to the Second Law, obtain *solely* owing to the second (net-tunneling) terms in the numerators and denominators of Equations (24) and (25), implying at least *prima facie* Second-Law paradoxes, and perhaps even challenges to the Second Law with respect to the first (thermal) terms thereof. If these net-tunneling terms become negligible, owing either to Case (i): both f_{tun} and f_{antitun} being negligibly small [they can*not individually* be *exactly* zero: the probability of neither tunneling nor (except at $T = 0\,\mathrm{K}$) anti-tunneling never *totally* vanishes] or Case (ii): the f_{antitun} term cancelling the f_{tun} term (*cancellation* to *exactly* zero *is* possible, at least in principle), $K^{\text{total}}_{\text{eq},L\rightleftarrows H} \to K^{\text{thermal}}_{\text{eq},L\rightleftarrows H} = \frac{X_H(1-N_H)}{X_L}$ in the high-temperature limit and $K^{\text{total}}_{\text{eq},L\rightleftarrows H} \to K^{\text{thermal}}_{\text{eq},L\rightleftarrows H} = \frac{X_H}{X_L}$ in the extreme-high-temperature/$N_H \to 0$ limit; and hence both of our at least *prima facie* Second-Law paradoxes, let alone challenges, to the Second Law, vanish [for all practical purposes in Case (i) and up to exactly in Case (ii)].

In the extreme-low-temperature limit $T \to 0\,\mathrm{K}$, if $N_H > 0$ the fourth line of Equation (23) simplifies as per:

$$\begin{aligned}
\lim_{T\to 0\,\mathrm{K}, N_H>0} K^{\text{total}}_{\text{eq},L\rightleftarrows H} &= \lim_{T\to 0\,\mathrm{K}, N_H>0} \frac{\frac{X_H e^{-N_H}}{X_L} + \frac{X_H\left[f_{\text{tun}}\left(e^{-N_H} - e^{-N_B}\right) - f_{\text{antitun}} e^{-N_B}\right]}{X_L + X_H e^{-N_H} + X_B e^{-N_B}}}{1 + \frac{X_H\left[f_{\text{tun}}\left(e^{-N_H} - e^{-N_B}\right) - f_{\text{antitun}} e^{-N_B}\right]}{X_L + X_H e^{-N_H} + X_B e^{-N_B}}} \\
&= \lim_{T\to 0\,\mathrm{K}, N_H>0} \frac{X_H}{X_L}\left[e^{-N_H} + f_{\text{tun}}\left(e^{-N_H} - e^{-N_B}\right) - f_{\text{antitun}} e^{-N_B}\right] \\
&= \frac{X_H}{X_L} \times 0 \\
&= 0.
\end{aligned} \tag{26}$$

(Since $N_B > N_H$, $e^{-N_B} \to 0$ faster than $e^{-N_H} \to 0$, and $e^{-N_H} - e^{-N_B} \to 0$ faster yet, as $T \to 0\,\text{K}$.) In the extreme-low-temperature limit $T \to 0\,\text{K}$, if $N_H > 0$ both of our at least *prima facie* Second-Law paradoxes, let alone challenges, to the Second Law, vanish: our particle becomes frozen in L. Emphasizing: Notwithstanding that both of our proposed at least *prima facie* Second-Law paradoxes, and perhaps even challenges to the Second Law, hinge *entirely* upon net tunneling, they vanish in the limit $T \to 0\,\text{K}$ because in the limit $T \to 0\,\text{K}$ *only* tunneling from H to L is possible (no tunneling from L to H, no thermal excitation, and no anti-tunneling) and therefore if $N_H > 0$ our particle becomes frozen in L.

In the extreme-low-temperature limit $T \to 0\,\text{K}$, $N_H = 0$ designates that N_H is *strictly equal* to 0; by contrast, $T \to 0\,\text{K}$ implies that T *approaches* arbitrarily closely to $0\,\text{K}$. Hence we are justified in setting $N_H = 0 \implies e^{-N_H} = 1$. Given the *strict inequality* $N_B > N_H$, we are also justified in setting $e^{-N_B} = 0$. Hence in the limit $T \to 0\,\text{K}$ if $N_H = 0 \implies e^{-N_H} = 1$ the fourth line of Equation (23) simplifies as per:

$$\begin{aligned}
\lim_{T\to 0\,\text{K}, N_H=0} K^{\text{total}}_{\text{eq},L\rightleftarrows H} &= \lim_{T\to 0\,\text{K}, N_H=0} \frac{\frac{X_H e^{-N_H}}{X_L} + \frac{X_H\left[f_{\text{tun}}\left(e^{-N_H}-e^{-N_B}\right)-f_{\text{antitun}}e^{-N_B}\right]}{X_L + X_H e^{-N_H} + X_B e^{-N_B}}}{1 + \frac{X_H\left[f_{\text{tun}}\left(e^{-N_H}-e^{-N_B}\right)-f_{\text{antitun}}e^{-N_B}\right]}{X_L + X_H e^{-N_H} + X_B e^{-N_B}}} \\
&= \frac{\frac{X_H}{X_L} + \frac{X_H f_{\text{tun}}}{X_L}}{1 + \frac{X_H f_{\text{tun}}}{X_L}} \\
&= \frac{\frac{X_H(1+f_{\text{tun}})}{X_L}}{\frac{X_L + f_{\text{tun}} X_H}{X_L}} \\
&= \frac{X_H(1+f_{\text{tun}})}{X_L + f_{\text{tun}} X_H}.
\end{aligned} \tag{27}$$

In the extreme-low-temperature limit $T \to 0\,\text{K}$, if $N_H = 0$ Equation (27) yields, quantitatively in accordance with quantum-mechanical evaluations: (i) $\lim_{T\to 0\,\text{K}, N_H=0} K^{\text{total}}_{\text{eq},L\rightleftarrows H} = \frac{X_H}{X_L}$ if the barrier B is tall enough and wide enough that $f_{\text{tun}} \to 0$, and (ii) $\lim_{T\to 0\,\text{K}, N_H=0} K^{\text{total}}_{\text{eq},L\rightleftarrows H} = 1$ if $X_H = X_L$ irrespective of the value of f_{tun}. If neither condition (i) or (ii) immediately above is met, Equation (27) yields, in accordance with what quantum mechanics predicts: (iii) $\frac{X_H}{X_L} > \lim_{T\to 0\,\text{K}, N_H=0} K^{\text{total}}_{\text{eq},L\rightleftarrows H} > 1$ if $X_H > X_L$ and (iv) $\frac{X_H}{X_L} < \lim_{T\to 0\,\text{K}, N_H=0} K^{\text{total}}_{\text{eq},L\rightleftarrows H} < 1$ if $X_H < X_L$. If neither condition (i) or (ii) immediately above is met, Equation (27) may be limited to qualitative accuracy as per (iii) and (iv) immediately above. This is an artifact of the derivation of Equation (23), of which Equation (27) is the extreme-low-temperature limiting case if $N_H = 0$, relying on (a) Equations (7)–(10), which assume a temperature high enough that the translational motion of our particle in L and H can be treated classically, and (b) the assumption that the barrier B is traversable both via thermal excitation and via tunneling. Of course, both of these assumptions break down in the limit $T \to 0\,\text{K}$, in which limit if $N_H = 0$ our particle becomes frozen in a quantum-mechanical ground state that occupies both L and H with traversals of the barrier B *solely* via tunneling in both directions between L and H (as opposed to it becoming frozen solely in L in the limit $T \to 0\,\text{K}$ if $N_H > 0$). The pertinent point is that, if $N_H = 0$ as if $N_H > 0$, in the limit $T \to 0\,\text{K}$ our particle becomes frozen in the ground state, and hence both of our proposed at least *prima facie* Second-Law paradoxes, let alone challenges to the Second Law, vanish.

Thus the limit $T \to 0\,\text{K}$ must *not* be imposed, in order that transits from L to H and from H to L can occur *both* via thermal excitation *and* via tunneling: only then, at least *prima facie* and at least in principle, can the inequality $K^{\text{total}}_{\text{eq},L\rightleftarrows H} \neq K^{\text{thermal}}_{\text{eq},L\rightleftarrows H}$ obtain *spontaneously*: only then does there obtain our spontaneous non-Boltzmann-distribution Second-Law paradox, and perhaps even challenge to the Second Law. And, furthermore, only then can $K^{\text{total}}_{\text{eq},L\rightleftarrows H}$ be *changed* (epicatalysis), at least in principle, with*out* any *net* expenditure of work: at least *prima facie*, even more strongly posing a Second-Law paradox, and perhaps even a challenge to the Second Law. Hence, while both of these Second-Law paradoxes and Second-Law challenges depend on traversal of the barrier B via tunneling, they fail in the limit $T \to 0\,\text{K}$, wherein barrier traversal is possible *only* via tunneling. The temperature must be high enough so that there is also *some* barrier traversal via thermal excitation.

With respect to *altering the equilibrium constant* $K_{\text{eq}}^{\text{total}}$—irrespective of whether or not any Second-Law challenge or even paradox obtains—thermal excitation becomes more important relative to net tunneling *only up to a limit* as the temperature increases: the first term in the numerator on the right-hand sides of the first five lines of Equation (23) eventually maximizes at X_H/X_L as per Equations (24) and (25).

With respect to the *rate of attainment of equilibrium*, tunneling necessarily becomes more important *without limit* relative to thermal excitation with decreasing temperature. Let us consider the attainment of equilibrium in the limit $T \to 0\,\text{K}$ if $N_H > 0$ and if our particle is initially in H. In the limit $T \to 0\,\text{K}$ attainment of equilibrium that requires traversal of a barrier is possible *only* via tunneling. Our particle, initially in H, can traverse the barrier B to its equilibrium state of being frozen in L *only* via tunneling: traversal of the barrier B from H to L via thermal excitation becomes nonexistent in the limit $T \to 0\,\text{K}$:

$$
\begin{aligned}
\lim_{T\to 0\,\text{K}} \langle r_{\text{tun,net}}(H \to L)|\text{in } H\rangle &= f_{\text{tun}} \frac{\langle V_x \rangle}{2X_H}\left[1 - e^{-(N_B - N_H)}\right] - f_{\text{antitun}} \frac{\langle V_x \rangle}{2X_H} e^{-(N_B - N_H)} \\
&= \frac{\langle V_x \rangle}{2X_H}\left\{ f_{\text{tun}}\left[1 - e^{-(N_B - N_H)}\right] - f_{\text{antitun}} e^{-(N_B - N_H)} \right\} \\
&= \frac{\langle V_x \rangle}{2X_H} f_{\text{tun}} \\
&> 0;
\end{aligned}
\tag{28}
$$

by contrast,

$$
\lim_{T\to 0\,\text{K}} \langle r_{\text{thermal}}(H \to L)|\text{in } H\rangle = \frac{\langle V_x \rangle}{2X_H} e^{-(N_B - N_H)} = 0. \tag{29}
$$

Note that: (i) owing to zero-point energy—ultimately, owing to the uncertainty principle—$\lim_{T\to 0\,\text{K}} \langle V_x \rangle > 0$ and hence tunneling from H to L can occur in the limit $T \to 0\,\text{K}$ in accordance with Equation (28), and (ii) not only thermal excitation and anti-tunneling but also, because if $N_H > 0$ our particle becomes frozen in L, tunneling from L to H becomes nonexistent in the limit $T \to 0\,\text{K}$. (Obviously, in the limit $T \to 0\,\text{K}$, $\langle V_x \rangle$ must be construed as a quantum-mechanical average speed, not as a thermal average speed.)

Of course, *attainment of equilibrium* is *always* within the strictures of the Second Law—this or any other example of *attainment of equilibrium* is in compliance with the Second Law—no Second-Law challenge or even paradox.

As an aside, we note that: (i) The equilibrium constant K_{eq} for chemical reactions is typically (e.g., in textbooks) given by Equation (11), i.e., based on the assumption that transitions between reactants and products occur via *thermal excitation alone*, and (ii) the rate of approach of chemical reactions to equilibrium is typically (e.g., in textbooks) discussed considering *only thermal excitation* over potential-energy barriers. But these are *approximations*: the correct, or at least a more correct, expression for K_{eq} is, in actuality, as per Equations (23)–(29); also, the rate of approach to equilibrium is always governed at least to some extent by net tunneling. Yet even though thermal excitation becomes more important relative to net tunneling *only up to a limit* as the temperature increases, this limit is sufficient for most—even if perhaps not all—chemical reactions that at room temperature or higher both the equilibrium constant K_{eq} and the rate of approach to equilibrium can be to within adequate accuracy construed as occurring via thermal excitation alone. But in the limit $T \to 0\,\text{K}$ thermal excitation over barriers becomes impossible, and the transition of any chemical system to its ground state—the equilibrium state into which any chemical system (indeed, any system whatsoever, chemical or otherwise) freezes in the limit $T \to 0\,\text{K}$—can occur *only* via tunneling. The room-temperature-or-higher *approximations* of construing both K_{eq} and the rate of approach of chemical reactions to equilibrium obtaining via thermal excitation alone typically results in errors small enough to neglect only because chemical reactions are typically *not* investigated at sufficiently low temperatures for tunneling to contribute appreciably, in comparison with thermal excitation, to barrier traversal. Perhaps we should consider at least the *possibility* that low-temperature chemical reactions [17] for which tunneling [17] contributes appreciably, in comparison to thermal excitation, to barrier traversal might be employed by Second-Law-abiding free-energy life [17,18] and, if it exists, also by Second-Law-challenging thermosynthetic life [18–23] in cold environments, e.g., on moons of the gas-giant planets in our solar system. Moreover, because thermal excitation becomes more important relative to net tunneling *only up to a limit* as temperature increases, perhaps for some chemical reactions—perchance including those employed by Second-Law-challenging thermosynthetic life [18–23]—net tunneling may contribute to K_{eq} being spontaneously alterable from Second-Law prognostications even at room temperature or higher.

We also briefly note that at very low temperatures quantization of energy modifies both the rate of approach to equilibrium from either direction and K_{eq} from the classical Arrhenius values [24,25]. If the rates of approach to equilibrium from both directions are modified by *un*equal ratios, K_{eq} is *further* modified—epicatalysis. [In these works [24,25] this is not explicitly implicated in regard to challenging the Second Law or even Second-Law paradoxes (via epicatalysis or otherwise), but perhaps such an implication cannot *prima facie* be ruled out].

5. Catalysis Versus Epicatalysis; Type-A Versus Type-B Systems and Processes

Catalysis entails changing the forward and reverse rates of a process $a \rightleftarrows b$ by *equal* ratios and hence *not* changing $K_{eq,a\rightleftarrows b}$ [26]. (The ratios can be either greater or less than unity: if less than unity it is often dubbed anticatalysis.) Hence catalysis changes the rate of approach to equilibrium but not $K_{eq,a\rightleftarrows b}$ itself. By contrast, *epicatalysis* entails changing the forward and reverse rates of a process $a \rightleftarrows b$ by *un*equal ratios and hence *changing* $K_{eq,a\rightleftarrows b}$ [27–50], whether or not the rate of approach to equilibrium in either direction or averaged over both directions is also changed. Catalysis of course does *not* in *any* case pose a Second-Law paradox, much less challenge the Second Law [26]. Epicatalysis poses at least a Second-Law paradox, and perhaps even challenges the Second Law, *if and only if* it can be accomplished with less work input per particle than the minimum that the Second Law requires (see the Appendix). This is *not* the case with respect to certain instances of epicatalysis [27–29]. (Epicatalysis is discussed, but without being dubbed "epicatalysis", in References [27,28].) But at least *prima facie*, it *does* seem to be the case that the required work input is *zero* in principle in the instance of epicatalysis investigated in this present paper. Furthermore, both theoretical and experimental evidence indicates that the required work input is *zero* not merely in principle but also *in practice* in the instances of epicatalysis discussed in References [30–50] (though, to the best knowledge of the author, not dubbed "epicatalysis" until 2018). And *in practice* implies a Second-Law *challenge*, not merely paradox.

Type-A systems and processes, which comply with both the First and Second Laws of Thermodynamics, have been distinguished from Type-B systems and processes, which comply with the First Law but contravene the Second Law [19–23,51,52].

It should be emphasized that Type-B systems and processes include, but are not limited to, those that employ epicatalysis [30–50]. Reference [52] provides a representative overview of and cites representative references pertaining to some of the many types of possible Type-B systems and processes.

The main question that we pose in this paper is whether or not our *prima facie* result—that the system considered herein is, even if only in principle, a Type-B system—is in fact correct.

6. Only *One* Aspect of the Second Law Can Be Challenged

Systems and processes that challenge the Second Law of Thermodynamics—Type-B systems and processes [19–23,51,52]—contravene *only* the aspect of the Second Law that precludes a *net* decrease in entropy and hence perpetual motion of the second kind [30]. It takes only *one* proven example of a Type-B system or process to set the contravention of *this aspect* of the Second Law in stone [30]. We emphasize that *only this aspect* of the Second Law is being questioned. *All other aspects* of the Second Law, e.g., that entropy $S = -k \ln \sum p_j \ln p_j$ statistical-mechanically and change in entropy

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$dS = dq_{\text{reversible}}/T \iff \Delta S = \int dq_{\text{reversible}}/T$ classically, that entropy is a state function depending only on the state of a system and not on the history of how the state was arrived at [1–5,15,16], and the many indispensable thermodynamic relations whose derivations are at least partially based thereon [1–5,15,16] preserve absolute inviolability for both Type-A and Type-B systems and processes. [See also Čápek and Sheehan [30], Chapter 1; Mahan and Myers [53], Chapter 8 (especially Sections 8.5–8.14); and Wark and Richards [54], Chapters 6–17 (especially Chapter 6, Section 7.2, and Chapter 12).]

For example, *both* a Type-A system *and* a Type-B system can undergo a decrease in entropy. The only difference is that in the case of a Type-A system, this decrease in entropy must be compensated for by a greater (in the limit of perfection or reversibility equal) increase in entropy elsewhere; by contrast, in the case of a Type-B system, no compensating increase in entropy is required. But for *both* the Type-A system *and* the Type-B system, the statistical-mechanical entropy in the initial (final) state is $S_{\text{initial}} = -k \ln \sum p_{j,\text{initial}} \ln p_{j,\text{initial}}$ ($S_{\text{final}} = -k \ln \sum p_{j,\text{final}} \ln p_{j,\text{final}}$), the change (in this particular example, the decrease) in entropy is $\Delta S = \int dq_{\text{reversible}}/T$ classically, and entropy is a state function depending only on the state of the system and not on the history of how the state was arrived at [1–5,15,16]. [See also Čápek and Sheehan [30], Chapter 1; Mahan and Myers [53], Chapter 8 (especially Sections 8.5–8.14); and Wark and Richards [54], Chapters 6–17 (especially Chapter 6, Section 7.2, and Chapter 12).]

Moreover, Third-Law absolute entropies also preserve absolute inviolability for both Type-A and Type-B systems and processes: (i) the statistical-mechanical entropy $S = -k \ln \sum p_j \ln p_j$ is the Third-Law absolute statistical-mechanical entropy [1–5,15,16], and (ii) $S = \int_{0\,\text{K}}^{T} dq_{\text{reversible}}/T' = \int_{0\,\text{K}}^{T} C_x(T')dT'/T'$, the Third-Law absolute classical entropy, is a special case of $\Delta S = \int dq_{\text{reversible}}/T$. [$C_x(T')$ is the heat capacity of the system under consideration maintained at condition x (e.g., isochoric, isobaric, etc.) expressed as a function of temperature.] (See also Mahan and Myers [53], Section 8.8, and Wark and Richards [54], pp. 711–716.)

We note that the existence of Type-B systems does not encroach on the ubiquity of Type-A systems: as has been noted, if the aspect of the Second Law that precludes a *net* decrease in entropy and hence perpetual motion of the second kind "is shown to be violable, it would nonetheless remain valid for the vast majority of natural and technological processes" (see Čápek and Sheehan [30], p. 13).

7. Conclusions

We investigated the thermodynamics of a system comprised of one particle (atom, molecule, Brownian particle, etc.) in thermodynamic equilibrium with its heat reservoir at temperature T. This particle can move between a low gravitational-potential-energy well L and a higher (or at least equally high) gravitational-potential-energy well H via traversing a barrier B; the floors and walls of the wells L and H, and the barrier B, comprising its heat reservoir. (The results for our one-particle isothermal atmosphere are easily generalizable to an $\mathcal{N}$-particle isothermal atmosphere sufficiently rarefied that the atmospheric particles collide essentially always with the floors and walls of L and H, and with B, but essentially never with each other: such an $\mathcal{N}$-particle isothermal atmosphere is essentially equivalent to $\mathcal{N}$ independent one-particle isothermal atmospheres.)

In Section 2 we showed that, in the *approximation* of considering the barrier to be traversable via *thermal excitation alone*, our system is compliant with the Second Law of Thermodynamics. By contrast, after providing underpinning in Section 3, in Section 4 we showed that if the barrier is traversable *also via tunneling*, at least on the face of it there seems to be at least a Second-Law paradox, and perhaps even a challenge to the Second Law. *But not if solely via tunneling*, which obtains in the limit $T \to 0\,\text{K}$ and our particle becomes frozen in L if $N_H > 0$, or in a quantum-mechanical ground state occupying both L and H if $N_H = 0$: *some* thermal excitation is necessary.

In Section 5 we compared and contrasted catalysis, which does not alter the equilibrium constant K_{eq}, versus epicatalysis, which does. We emphasized that catalysis *always* is compliant with the Second Law—and that epicatalysis is also compliant with the Second Law if the work input per particle required to change K_{eq} is not less than the minimum that the Second Law requires (see the Appendix).

But if the required work per particle *is* less than the minimum that the Second Law requires, epicatalysis presents at least a Second-Law paradox, and perhaps even a challenge to the Second Law—a Type-B process.

In Section 6 we emphasized that only *one* aspect of the Second Law can be challenged: that systems and processes that challenge the Second Law—Type-B systems and processes [19–23,51,52]—contravene *only* the aspect of the Second Law that precludes a *net* decrease in entropy and hence perpetual motion of the second kind [30]. And by the same token that *all other aspects* of the Second Law, e.g., that entropy is a state function (and also Third-Law absolute entropies), preserve absolute inviolability for *both* Type-A *and* Type-B systems and processes [1–5,15,16,53,54].

In the Appendix, we will evaluate the minimum work that the Second Law requires to change K_{eq}.

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Appendix A. Minimum Work that the Second Law Requires to Change K_{eq}

If a system capable of transitions between two configurations a and b is at thermodynamic equilibrium with a heat reservoir at temperature T, it is characterized by its equilibrium constant $K_{\text{eq},a\rightleftharpoons b}$ [55]. By contrast, the reaction quotient $\mathbb{Q}$ (not to be confused with the partition function or sum-over-states Q) characterizes the *actual* state of this system, whether at thermodynamic equilibrium or not [56]. (See also Mahan and Myers [53], Chapter 4, pp. 372–373, and Sections 8.9–8.11.) Consider a system whose constituent particles (atoms, molecules, Brownian particles, etc.) can be in either one of two configurations, a or b (possibly separated by a potential-energy barrier), construing a to be the reactant configuration and b to be the product configuration. Let $P_{\text{eq}}(a)$ and $P_{\text{eq}}(b)$ be the probability of finding any one given particle in configuration a or configuration b, respectively, given thermodynamic equilibrium. Let $P_{\mathbb{Q}}(a)$ and $P_{\mathbb{Q}}(b)$ be the probability of finding any one given particle in configuration a or configuration b, respectively, with the system in its *actual* state, whether at thermodynamic equilibrium or not. Thus at thermodynamic equilibrium

$$K_{\text{eq}} = \frac{P_{\text{eq}}(b)}{P_{\text{eq}}(a)}, \tag{A1}$$

and in general, whether at thermodynamic equilibrium or not,

$$\mathbb{Q} = \frac{P_{\mathbb{Q}}(b)}{P_{\mathbb{Q}}(a)}. \tag{A2}$$

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At thermodynamic equilibrium $P_{\mathbb{Q}}(a) = P_{eq}(a)$, $P_{\mathbb{Q}}(b) = P_{eq}(b)$, and hence $\mathbb{Q} = \mathbb{Q}_{eq} = K_{eq}$.

The Second Law of Thermodynamics asserts that the minimum work input per particle (atom, molecule, Brownian particle, etc.) required to force the system away from thermodynamic equilibrium, i.e., from K_{eq} to $\mathbb{Q} \neq K_{eq}$, *keeping* K_{eq} *itself fixed*, is [53–56]

$$W_{min} = kT\left|\ln \frac{\mathbb{Q}}{K_{eq}}\right|. \tag{A3}$$

Note the absolute value sign: equal work is required to force the system away from thermodynamic equilibrium by the same ratio in either direction, *keeping* K_{eq} *itself fixed*. [This is discussed (with respect to chemical systems) by Mahan and Myers [53] in Sections 8.9–8.11 and by Wark and Richards [54] in Chapter 14 (especially Sections 14-1 through 14-6 and 14-11).] But W_{min} is *also* the minimum work input per particle (atom, molecule, Brownian particle, etc.) that the Second Law requires to *change* K_{eq} *itself* to $\mathbb{Q} = K_{eq} + \Delta K_{eq}$, as per

$$W_{min} = kT\left|\ln \frac{K_{eq} + \Delta K_{eq}}{K_{eq}}\right| = kT\left|\ln\left(1 + \frac{\Delta K_{eq}}{K_{eq}}\right)\right|. \tag{A4}$$

As with respect to Equation (A3), note the absolute value signs: equal work is required to change K_{eq} by the same ratio in either direction, i.e., irrespective of whether ΔK_{eq} is positive or negative.

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