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## Article

# Tunneling, the Equilibrium Constant, and Epicatalysis: 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:  $K_{eq} = (G_H/G_L) \exp[-(E_H - E_L)/kT]$ . 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. We then provide general remarks pertaining to catalysis versus epicatalysis, followed by concluding remarks.

**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

## 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  $K_{eq,L \rightleftharpoons H}$  corresponding to its dissemination between the two wells  $L$  and  $H$ , is in accordance with the Boltzmann (or canonical) distribution as per

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

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 construe our particle being in  $L$  as the reactant configuration and it being in  $H$  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

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

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 will show 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 epicalysis are provided in Section 5. Concluding remarks are provided in Section 6. In the Appendix, we evaluate the minimum work that the Second Law requires to change  $K_{eq}$ .

## 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 (and some anti-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 a higher (or at least equally high) well  $H$  of  $x$ -directional width  $X_H$ , via traversal of a barrier  $B$  of  $x$ -directional width  $X_B$ . In a top view, 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 floor, the walls, and the barrier  $B$ , and essentially never with each other: such an  $\mathcal{N}$ -particle isothermal atmosphere is essentially equivalent to  $\mathcal{N}$  independent one-particle isothermal atmospheres.

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 accomplished 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 (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,

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

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

and

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

where in accordance with standard notation

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

is the partition function, also called 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  $K_{\text{eq}, L \rightleftharpoons H}$  and hence on the dissemination of our particle between  $L$  and  $H$ ; therefore we need not consider the time it spends over (or tunneling through) 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

$$\langle t_L \rangle = \frac{2X_L}{\langle V_x \rangle} \quad (7)$$

and the average rate of these attempts is

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

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

$$\langle t_H \rangle = \frac{2X_H}{\langle V_x \rangle} \quad (9)$$

and the average rate of these attempts is

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

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

$$K_{\text{eq}, L \rightleftharpoons H}^{\text{thermal}} = \frac{P_{\text{thermal}}(\text{in } H)}{P_{\text{thermal}}(\text{in } L)} = \frac{\langle r_{\text{thermal}}(L \rightarrow H) \rangle}{\langle r_{\text{thermal}}(H \rightarrow L) \rangle} = \frac{\langle r_L \rangle e^{-N_H}}{\langle r_H \rangle} = \frac{\frac{\langle V_x \rangle}{2X_L} e^{-N_H}}{\frac{\langle V_x \rangle}{2X_H}} = \frac{X_H}{X_L} e^{-N_H}, \quad (11)$$

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 (and *some* anti-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  $mgz_B = N_B kT$  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  $H$ :

$$\begin{aligned} P(z_H \leq z < z_B \text{ in } H) &= P(\text{in } H)P(z_H \leq z < z_B | \text{in } H) \\ &= \frac{X_H e^{-N_H}}{Q} [1 - e^{-(N_B - N_H)}] \\ &= \frac{X_H (e^{-N_H} - e^{-N_B})}{Q}. \end{aligned} \quad (12)$$

The average rate of tunneling of our particle from  $H$  to  $L$  equals the fraction  $f_{\text{tun}}^{H \rightarrow L}$  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):

$$\begin{aligned} \langle r_{\text{tun}}(H \rightarrow L) \rangle &= f_{\text{tun}}^{H \rightarrow L} \frac{\langle V_x \rangle}{2X_H} \frac{X_H (e^{-N_H} - e^{-N_B})}{Q} \\ &= \frac{f_{\text{tun}}^{H \rightarrow L} \langle V_x \rangle (e^{-N_H} - e^{-N_B})}{2Q}. \end{aligned} \quad (13)$$

Tunneling can occur only to states of lower or equal energy, not to states of higher energy [6–8]. Therefore, tunneling from  $L$  to  $H$  *cannot* 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  $mgz_H = N_H kT$  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 *cannot* 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  $mgz_B = N_B kT$  relative to the datum elevation  $z_L = 0$



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,  $1 - (1 - e^{-N_H}) - e^{-N_B} = e^{-N_H} - e^{-N_B}$  as per the Boltzmann distribution, that it is in the altitude range  $z_H \leq z < z_B$  given that it is in  $L$ :

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

The average rate of tunneling of our particle from  $L$  to  $H$  equals the fraction  $f_{\text{tun}}^{L \rightarrow H}$  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):

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

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 its 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  $L$ :

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

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):

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

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  $H$ :

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

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 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  $f_{\text{tun}}$  should be the same with respect to tunneling in either direction, i.e., that  $f_{\text{tun}}^{L \rightarrow H} = f_{\text{tun}}^{H \rightarrow L} = f_{\text{tun}}$ , and likewise that  $f_{\text{antitun}}$  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  $K_{\text{eq}, L \rightleftharpoons H} = (G_H/G_L) \exp[-(E_H - E_L)/kT]$  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  $f_{\text{tun}}^{L \rightarrow H} = f_{\text{tun}}^{H \rightarrow L} = f_{\text{tun}}$  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):

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

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)  $\langle r_{\text{tun}}(L \rightarrow H) \rangle = \langle r_{\text{tun}}(H \rightarrow L) \rangle$ , 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  $K_{\text{eq}, L \rightleftharpoons H} = (G_H/G_L) \exp[-(E_H - E_L)/kT]$  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  $L$ :

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

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 presume *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  $f_{\text{tun}}$  and  $f_{\text{antitun}}$ , we can get off scot-free with this *approximation*.

#### 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:

$$\begin{aligned}
 K_{\text{eq},L\rightleftharpoons H}^{\text{total}} &= \frac{\langle r_{\text{total}}(L \rightarrow H) \rangle}{\langle r_{\text{total}}(H \rightarrow L) \rangle} = \frac{\langle r_{\text{thermal}}(L \rightarrow H) \rangle + \langle r_{\text{tun,net}}(L \rightarrow H) \rangle}{\langle r_{\text{thermal}}(H \rightarrow L) \rangle + \langle r_{\text{tun,net}}(H \rightarrow L) \rangle} \\
 &= \frac{\frac{\langle V_x \rangle}{2X_L} e^{-N_H} + \frac{\langle V_x \rangle [f_{\text{tun}}(e^{-N_H} - e^{-N_B}) - f_{\text{antitun}} e^{-N_B}]}{2Q}}{\frac{\langle V_x \rangle}{2X_H} + \frac{\langle V_x \rangle [f_{\text{tun}}(e^{-N_H} - e^{-N_B}) - f_{\text{antitun}} e^{-N_B}]}{2Q}} \\
 &= \frac{\frac{e^{-N_H}}{X_L} + \frac{f_{\text{tun}}(e^{-N_H} - e^{-N_B}) - f_{\text{antitun}} e^{-N_B}}{Q}}{\frac{1}{X_H} + \frac{f_{\text{tun}}(e^{-N_H} - e^{-N_B}) - f_{\text{antitun}} e^{-N_B}}{Q}} \\
 &= \frac{\frac{e^{-N_H}}{X_L} + \frac{f_{\text{tun}}(e^{-N_H} - e^{-N_B}) - f_{\text{antitun}} e^{-N_B}}{X_L + X_H e^{-N_H} + X_B e^{-N_B}}}{\frac{1}{X_H} + \frac{f_{\text{tun}}(e^{-N_H} - e^{-N_B}) - f_{\text{antitun}} e^{-N_B}}{X_L + X_H e^{-N_H} + X_B e^{-N_B}}} \\
 &= \frac{P_{\text{total}}(\text{in } H)}{P_{\text{total}}(\text{in } L)} \left\{ \begin{array}{l} \text{in general } \neq \frac{P_{\text{thermal}}(H)}{P_{\text{thermal}}(L)} = K_{\text{eq},L\rightleftharpoons H}^{\text{thermal}} = \frac{X_H}{X_L} e^{-N_H} \\ \text{iff } K_{\text{eq},L\rightleftharpoons H}^{\text{thermal}} = 1 \end{array} \right. \quad (23)
 \end{aligned}$$

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 four lines of Equation (23). If these terms become negligible, owing either to Case (i): both  $f_{\text{tun}}$  and  $f_{\text{antitun}}$  being negligibly small (they cannot *individually* be *exactly* zero: the probability of neither tunneling nor anti-tunneling never *totally* vanishes) or Case (ii): the  $f_{\text{antitun}}$  term cancelling the  $f_{\text{tun}}$  term (*cancellation* to *exactly* zero is possible, at least in principle),  $K_{\text{eq},L\rightleftharpoons H}^{\text{total}} \rightarrow K_{\text{eq},L\rightleftharpoons H}^{\text{thermal}} = \frac{X_H}{X_L} e^{-N_H}$  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 four 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  $N_H = \ln \frac{X_H}{X_L} \implies K_{\text{eq},L\rightleftharpoons H}^{\text{total}} = K_{\text{eq},L\rightleftharpoons H}^{\text{thermal}} = 1$  is our system in compliance with the Second Law of Thermodynamics—specifically, in compliance with the Boltzmann distribution. If  $N_H > \ln \frac{X_H}{X_L}$ ,  $K_{\text{eq},L\rightleftharpoons H}^{\text{thermal}} < K_{\text{eq},L\rightleftharpoons H}^{\text{total}} < 1$  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. And if  $N_H < \ln \frac{X_H}{X_L}$ ,  $K_{\text{eq},L\rightleftharpoons H}^{\text{thermal}} > K_{\text{eq},L\rightleftharpoons H}^{\text{total}} > 1$  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. (Note that in both cases wherein  $K_{\text{eq},L\rightleftharpoons H}^{\text{total}} \neq K_{\text{eq},L\rightleftharpoons H}^{\text{thermal}}$ ,  $K_{\text{eq},L\rightleftharpoons H}^{\text{total}}$  is intermediate between  $K_{\text{eq},L\rightleftharpoons H}^{\text{thermal}}$  and unity. Of course, in all three cases the allowable range of values of  $\frac{X_H}{X_L}$  is restricted to that wherein  $N_H \geq 0$ .) At least *prima facie*, this seems to pose at least a Second-Law paradox, and perhaps even a challenge to the Second Law. We will show that this also obtains in the high-temperature and extreme-high-temperature/ $N_H \rightarrow 0$  limits of Equation (23), but not in the extreme-low-temperature limit thereof.

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  $K_{\text{eq},L\rightleftharpoons H}^{\text{total}}$ —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  $K_{eq,L\rightleftharpoons H}^{total}$ —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  $K_{eq,L\rightleftharpoons H}^{total}$  as per Equation (23) in particular, but *any* equilibrium constant  $K_{eq}$  in general. (See the Appendix.)

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

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

$$\lim_{T \rightarrow \infty} K_{eq,L\rightleftharpoons H}^{total} = \frac{\frac{1-N_H}{X_L} + \frac{f_{tun}(N_B-N_H)-f_{antitun}(1-N_B)}{X_L+X_H(1-N_H)+X_B(1-N_B)}}{\frac{1}{X_H} + \frac{f_{tun}(N_B-N_H)-f_{antitun}(1-N_B)}{X_L+X_H(1-N_H)+X_B(1-N_B)}}. \quad (24)$$

In the high-temperature limit, if and only if  $N_H = 1 - \frac{X_L}{X_H} \implies K_{eq,L\rightleftharpoons H}^{total} = K_{eq,L\rightleftharpoons H}^{thermal} = 1$  is our system in compliance with the Second Law of Thermodynamics—specifically, in compliance with the Boltzmann distribution. If  $N_H > 1 - \frac{X_L}{X_H}$ ,  $K_{eq,L\rightleftharpoons H}^{thermal} < K_{eq,L\rightleftharpoons H}^{total} < 1$  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. And if  $N_H < 1 - \frac{X_L}{X_H}$ ,  $K_{eq,L\rightleftharpoons H}^{thermal} > K_{eq,L\rightleftharpoons H}^{total} > 1$  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. (Note that in both cases wherein  $K_{eq,L\rightleftharpoons H}^{total} \neq K_{eq,L\rightleftharpoons H}^{thermal}$ ,  $K_{eq,L\rightleftharpoons H}^{total}$  is intermediate between  $K_{eq,L\rightleftharpoons H}^{thermal}$  and unity. Of course, in all three cases the allowable range of values of  $\frac{X_H}{X_L}$  is restricted to that wherein  $N_H \geq 0$ .) At least *prima facie*, this seems to pose at least a Second-Law paradox, and perhaps even a challenge to the Second Law.

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

$$\lim_{T \rightarrow \infty} K_{eq,L\rightleftharpoons H}^{total} = \frac{\frac{1}{X_L} + \frac{f_{tun}(N_B-N_H)-f_{antitun}}{X_L+X_H+X_B}}{\frac{1}{X_H} + \frac{f_{tun}(N_B-N_H)-f_{antitun}}{X_L+X_H+X_B}}. \quad (25)$$

In the extreme-high-temperature/ $N_H \rightarrow 0$ , limit, if and only if  $X_H = X_L \implies K_{eq,L\rightleftharpoons H}^{total} = K_{eq,L\rightleftharpoons H}^{thermal} = 1$  is our system in compliance with the Second Law of Thermodynamics—specifically, in compliance with the Boltzmann distribution. If  $X_H > X_L$ ,  $K_{eq,L\rightleftharpoons H}^{thermal} > K_{eq,L\rightleftharpoons H}^{total} > 1$  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  $X_H < X_L$ ,  $K_{eq,L\rightleftharpoons H}^{thermal} < K_{eq,L\rightleftharpoons H}^{total} < 1$  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. At least *prima facie*, this seems to pose at least a Second-Law paradox, and perhaps even a challenge to the Second Law.

Hence in both the high-temperature and extreme-high-temperature/ $N_H \rightarrow 0$  limits as per Equations (24) and (25), as in the general case in accordance with Equation (23), if  $K_{eq,L\rightleftharpoons H}^{total} \neq K_{eq,L\rightleftharpoons H}^{thermal} \neq 1$  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/ $N_H \rightarrow 0$  limits (unless  $K_{eq,L\rightleftharpoons H}^{total} = K_{eq,L\rightleftharpoons H}^{thermal} = 1$ )  $K_{eq,L\rightleftharpoons H}^{total}$  is intermediate between  $K_{eq,L\rightleftharpoons H}^{thermal}$  and unity.] Moreover, as in the general case, in the high-temperature

and extreme-high-temperature/ $N_H \rightarrow 0$  limits at least *prima facie* it seems that, at least in principle,  $X_L$ ,  $X_H$ ,  $N_H$ , and/or  $N_B$ —and hence  $K_{\text{eq},L \rightleftharpoons H}^{\text{total}}$ —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, to the Second Law.

Furthermore, in both the high-temperature and extreme-high-temperature/ $N_H \rightarrow 0$  limits, as in the general case in accordance with Equation (23), both of these 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  $f_{\text{tun}}$  and  $f_{\text{antitun}}$  being negligibly small (they cannot *individually* be *exactly* zero: the probability of neither tunneling nor anti-tunneling never *totally* vanishes) or Case (ii): the  $f_{\text{antitun}}$  term cancelling the  $f_{\text{tun}}$  term (*cancellation to exactly zero is possible*, at least in principle),  $K_{\text{eq},L \rightleftharpoons H}^{\text{total}} \rightarrow K_{\text{eq},L \rightleftharpoons H}^{\text{thermal}} = \frac{X_H}{X_L}$  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  $T \rightarrow 0$  K, if  $N_H > 0$  the fourth line of Equation (23) simplifies as per:

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

(Since  $N_B > N_H$ ,  $e^{-N_B} \rightarrow 0$  faster than  $e^{-N_H} \rightarrow 0$ , and  $e^{-N_H} - e^{-N_B} \rightarrow 0$  faster yet, as  $T \rightarrow 0$  K.) In the extreme-low-temperature limit  $T \rightarrow 0$  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  $T \rightarrow 0$  K because in the limit  $T \rightarrow 0$  K *only* tunneling from  $H$  to  $L$  is possible (no tunneling from  $L$  to  $H$ , no thermal excitation, and no anti-tunneling in  $H$ ) and therefore if  $N_H > 0$  our particle becomes frozen in  $L$ .

In the extreme-low-temperature limit  $T \rightarrow 0$  K,  $N_H = 0$  designates that  $N_H$  is *strictly equal* to 0; by contrast,  $T \rightarrow 0$  K implies that  $T$  *approaches* arbitrarily closely to 0 K. Hence we are justified in setting

$E_H/kT = mgz_H/kT = 0 \implies e^{-E_H/kT} = e^{-mgz_H/kT} = 1$ . Hence in the limit  $T \rightarrow 0$  K if  $N_H = 0$  the fourth line of Equation (23) simplifies as per:

$$\begin{aligned} \lim_{T \rightarrow 0 \text{ K}, N_H=0} K_{\text{eq}, L \rightleftharpoons H}^{\text{total}} &= \lim_{T \rightarrow 0 \text{ K}, N_H=0} \frac{\frac{e^{-N_H}}{X_L} + \frac{f_{\text{tun}}(e^{-N_H} - e^{-N_B}) - f_{\text{antitun}}e^{-N_B}}{X_L + X_H e^{-N_H} + X_B e^{-N_B}}}{\frac{1}{X_H} + \frac{f_{\text{tun}}(e^{-N_H} - e^{-N_B}) - f_{\text{antitun}}e^{-N_B}}{X_L + X_H e^{-N_H} + X_B e^{-N_B}}} \\ &= \frac{\frac{1}{X_L} + \frac{f_{\text{tun}}}{X_L}}{\frac{1}{X_H} + \frac{f_{\text{tun}}}{X_L}} \\ &= \frac{\frac{1+f_{\text{tun}}}{X_L}}{\frac{X_L + f_{\text{tun}}X_H}{X_L X_H}} \\ &= \frac{X_H(1+f_{\text{tun}})}{X_L + f_{\text{tun}}X_H}. \end{aligned} \quad (27)$$

In the extreme-low-temperature limit  $T \rightarrow 0$  K, if  $N_H = 0$  Equation (27) yields, quantitatively in accordance with quantum-mechanical evaluations: (i)  $\lim_{T \rightarrow 0 \text{ K}, N_H=0} K_{\text{eq}, L \rightleftharpoons H}^{\text{total}} = \frac{X_H}{X_L}$  if the barrier  $B$  is tall enough and wide enough that  $f_{\text{tun}} \rightarrow 0$ , and (ii)  $\lim_{T \rightarrow 0 \text{ K}, N_H=0} K_{\text{eq}, L \rightleftharpoons H}^{\text{total}} = 1$  if  $X_H = X_L$  irrespective of the value of  $f_{\text{tun}}$ . If neither condition (i) or (ii) immediately above is met, Equation (27) yields, in accordance with what quantum mechanics predicts: (iii)  $\frac{X_H}{X_L} > \lim_{T \rightarrow 0 \text{ K}, N_H=0} K_{\text{eq}, L \rightleftharpoons H}^{\text{total}} > 1$  if  $X_H > X_L$  and (iv)  $\frac{X_H}{X_L} < \lim_{T \rightarrow 0 \text{ K}, N_H=0} K_{\text{eq}, L \rightleftharpoons H}^{\text{total}} < 1$  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  $T \rightarrow 0$  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  $B$  via tunneling in both directions between  $L$  and  $H$  (as opposed to it becoming frozen solely in  $L$  in the limit  $T \rightarrow 0$  K if  $N_H > 0$ ). The pertinent point is that, if  $N_H = 0$  as if  $N_H > 0$ , in the limit  $T \rightarrow 0$  K our particle becomes frozen in the ground state, and hence both of our proposed at least *prima facie* Second-Law paradoxes, and perhaps even challenges to the Second Law, vanish.

Thus the limit  $T \rightarrow 0$  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 can, at least *prima facie* and at least in principle, the inequality  $K_{\text{eq}, L \rightleftharpoons H}^{\text{total}} \neq K_{\text{eq}, L \rightleftharpoons H}^{\text{thermal}}$  obtain *spontaneously*: only then does there obtain our spontaneous non-Boltzmann-dissemination Second-Law paradox, and perhaps even challenge to the Second Law. And, furthermore, only then can  $K_{\text{eq}, L \rightleftharpoons H}^{\text{total}}$  be *changed* (epicatalysis) without 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 perhaps even Second-Law challenges, depend on traversal of the barrier  $B$  via tunneling, they fail in the limit  $T \rightarrow 0$  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 temperature increases: the first term in the numerator on the right-hand sides of the second, third, and fourth lines of Equation (23) eventually maximizes at  $1/X_L$  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  $T \rightarrow 0$  K if  $N_H > 0$  and if our particle is initially in  $H$ . In the limit  $T \rightarrow 0$  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  $T \rightarrow 0$  K:

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

by contrast,

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

Note that: (i) owing to zero-point energy—ultimately, owing to the uncertainty principle— $\lim_{T \rightarrow 0 \text{ K}} \langle V_x \rangle > 0$  and hence tunneling from  $H$  to  $L$  can occur in the limit  $T \rightarrow 0$  K in accordance with Equation (28), and (ii) not only traversal of the barrier  $B$  via thermal excitation in either direction but also, because our particle becomes frozen in  $L$ , tunneling from  $L$  to  $H$  and anti-tunneling in  $H$  becomes nonexistent in the limit  $T \rightarrow 0$  K. (Obviously, in the limit  $T = 0$  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  $K_{\text{eq}}$  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  $K_{\text{eq}}$  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 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  $K_{\text{eq}}$  and the rate of approach to equilibrium can be to within adequate accuracy reckoned as occurring via thermal excitation alone. But in the limit  $T \rightarrow 0$  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  $T \rightarrow 0$  K—can occur *only* via tunneling. The room-temperature-or-higher *approximations* of considering both  $K_{\text{eq}}$  and the rate of approach of chemical reactions to equilibrium 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 with 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  $K_{\text{eq}}$  being spontaneously alterable from Second-Law prognostications even at room temperature or higher. We also note that at very low temperatures quantization of energy modifies the rate of approach to equilibrium from

either direction, and if not equally from both directions hence also  $K_{eq}$  itself (epicatalysis), from the classical Arrhenius values [24,25]. (In these works [24,25] this is not explicitly implicated in regard to challenging the Second Law or even Second-Law paradoxes, 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  $a \rightleftharpoons b$  by *equal* ratios and hence *not* changing  $K_{eq,a \rightleftharpoons b}$  [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  $K_{eq,a \rightleftharpoons b}$  itself. By contrast, *epicatalysis* entails changing the forward and reverse rates of a process  $a \rightleftharpoons b$  by *unequal* ratios and hence *changing*  $K_{eq,a \rightleftharpoons b}$  [27–50], whether or not the rate of approach to equilibrium 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 not, to the best knowledge of the author, 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]. Type-B systems and processes include, but are not limited to, those that employ epicatalysis [19–23,51].

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. Conclusion: Brief Review of our System; Aspects of the Second Law

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-potential-energy well  $L$  and a higher- (or at least equally high) potential-energy well  $H$  via traversing a barrier  $B$ . (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 floor, the walls, and the barrier  $B$ , and 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. But in Sections 3 and 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 only via tunneling alone*, which obtains in the limit  $T \rightarrow 0$  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  $N_H = 0$ .)

In Section 5 we briefly 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 Second Law requires (see the Appendix). But if the required work per particle *is* less than 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.



We note that systems and processes that challenge the Second Law—Type-B systems and processes [19–23,51]—contravene *only* the aspect of the Second Law that forbids 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]. But other aspects of the Second Law, e.g., that entropy  $S = -k \ln \sum p_j \ln p_j$  statistically-mechanically and change in entropy  $dS = dq_{\text{reversible}}/T \iff \Delta S = \int dq_{\text{reversible}}/T$  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], retain absolute validity even for Type-B systems (see also Čápek and Sheehan [30], Chapter 1). And, of course, 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 forbids 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).

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

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  $K_{\text{eq},a \rightleftharpoons b}$ . 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. 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 [52,53]

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

and in general, whether at thermodynamic equilibrium or not,

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

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

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  $Q \neq K_{eq}$ , keeping  $K_{eq}$  itself fixed, is [52–55]

$$W_{\min} = kT \left| \ln \frac{Q}{K_{eq}} \right|. \quad (A3)$$

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 process is discussed (with respect to chemical systems) by Mahan and Myers [54] in Section 4.4, and by Wark [55] in Sections 14-1 and 14-2.] 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  $Q = K_{eq} + \Delta K_{eq}$ , as per

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

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  $\Delta K_{eq}$  is positive or negative.

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