Partitioning Entropy with Action Mechanics: Predicting Chemical Reaction Rates and Gaseous Equilibria of Reactions of Hydrogen from Molecular Properties

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Abstract

Clausius' virial theorem set a basis for relating kinetic energy in a body of independent material particles to its potential energy, pointing to their complementary role with respect to the second law of maximum entropy. In action mechanics, expressing the entropy of ideal gases as a capacity factor for sensible heat or enthalpy *plus* the configurational work to sustain the relative translational, rotational and vibrational action yields algorithms for estimating chemical reaction rates and positions of equilibrium. All properties of state including entropy, work potential as Helmholtz and Gibbs energies and activated transition state reaction rates can be estimated, using easily accessible molecular properties, such as atomic weights, bond lengths, moments of inertia and vibrational frequencies. Understanding how Clausius' virial theorem balances the internal kinetic energy with field potential energy justifies partitioning between thermal and statistical properties of entropy, yielding a more complete view of the evolutionary nature of the second law of thermodynamics. The ease of performing these operations is illustrated by three important chemical gas phase reactions, the reversible dissociation of the hydrogen molecules, lysis of water to hydrogen and oxygen and the reversible formation of ammonia from nitrogen and hydrogen. Employing the *ergal* also introduced by Clausius to define the reversible internal work to overcome molecular interactions *plus* the configurational internal work of negative Gibbs energy as a function of volume or pressure may provide a practical guide for managing risk in industrial processes and climate change at the global scale.

Keywords: Entropy; enthalpy; equilibrium' ergal; free energy; Gibbs energy; Haber process; Helmholtz energy; hydrogen dissociation; transition state; water dissociation; virial theorem

1. Introduction

The concept of action space was introduced as a useful surrogate for the phase-space of statistical mechanics [1-4]. Its significance is that all matter exist in action space, including the primary particles or molecules, sustained in real-time Brownian motion by impetus from resonant radiant energy in the field. Following Einstein, who proposed [5] such a mobilising force field in his papers on Brownian motion, we can also assume that matter gains potential energy (V) from this field, formally equivalent to elevated quantum states. Given that kinetic energy T is $½mv^2$ for particles of velocity v, then we have total energy E equal to $mc^2 – ½mv^2$ as a conserved property [1] as the first law of thermodynamics [1].

$$V = mc^2 – mv^2 \tag{1}$$

Then the total energy E can be given.

$$E = mc^2 - \tfrac{1}{2}mv^2 \tag{2}$$

1.1. The Virial Theorem

Classically, prior to Einstein's theories of special and general relativity, the base level for potential energy (Equation 1) omitted the mc^2 term involving the invariant speed of light c, setting the base potential energy (V) as zero by convention. A need for clarity regarding energy and the first law of thermodynamics prompted Clausius [6] to define the virial theorem relating the mean kinetic energy ($T = \Sigma mv^2/2$) of a system of particles to the mean potential energy ($V=\Sigma(-mv^2)$). When considering particles as material points at common gravitational potential, Clausius defined an internal work function (W) he termed the *ergal* as the following expression in rectangular coordinates (x, y, z), where X, Y and Z were Cartesian components of central force fields exerted on the particles ($X=md^2x/dt^2$,$Y=md^2y/dt^2$, $Z=md^2z/dt^2$); he had sought to find a short alternative to Rankine's new definition of potential energy.

$$W = \Sigma(Xdx + Ydy + Zdz) \tag{3}$$

He distinguished internal work within the body from external work as subject to different conditions and also equated the variation in the *ergal* or internal work to variation in the internal kinetic energy.

$$d\Sigma mv^2/2 = \Sigma(Xdx/dt + Ydy/dt + Zdz/dt)\underline{dt} \tag{4}$$

We remark that this thermal variation in the *vis viva* or kinetic energy was thus equated to the variation of the power expressed by the *ergal*, integrated with time as separate and complementary forms of energy.

"The work done during any time by the forces acting upon a system is equal to the increase in the vis-viva of the system during the same time". Clausius [7] separated the *ergal* from kinetic energy as a function of the integrated forces acting in the system of material particles, indicated by the letter J. In the Mathematical Introduction of his text on *The Mechanical Theory of Heat* he related the force originating in both attractions and repulsions exerted on the moving points as depending on distance and therefore acting as central forces.

$$\Sigma(Xdx + Ydy + Zdz) = -dJ \tag{5}$$

Thus, the kinetic work done in any time could be regarded as equal to the decrease in the potential given by the ergal. He further defined that "The sum of the vis-viva and the ergal remains constant during the motion".

$$U = T + J \tag{6}$$

Here, U is regarded as the total internal energy of the system, understood as the principle of the conservation of energy.

1.2 Two Kinds of Virial Effects

We can distinguish two separate applications of the virial theorem since Clausius' definition.

(i) The virial theorem has been adopted by physicists for systems of particles such as the hydrogen atom responsible for the solar spectrum and the gravitational structure of stars, defining the kinetic and potential energy of particles for variations involve absorption or emission of quanta travelling at light speed. For verification in quantum theory, variations in kinetic energy are set equal to the energy of the quanta, with their absorption resulting in increased potential energy equal to the decrease in kinetic energy. So the change in potential energy is equal to the sum of the decrease in the kinetic energy plus the quantum absorbed into the local field. Considering a single particle subject to a quantum excitation (Σhv) in a central field, the variation in potential energy can be expressed.

$$\Sigma hv \ + -\delta T \ = \ \delta V \tag{7}$$

Variation in potential energy of collapsing stars can be expressed by the same equation in reverse. We have claimed elsewhere [8] that molecules in the Earth's atmosphere are subject to this form of the virial theorem, yielding a lapse rate with temperature from balancing thermal and gravitational energies of 6.9 K per km.

(ii) By contrast, in systems of molecules moving as material points providing a multiplicity of central forces, as in an ideal gas, the relationship between kinetic and potential energy differs as a function of temperature and pressure. This is illustrated in the case of water where the molecules can exist frozen at low temperature, aggregated as clusters in liquid able to flow under gravity and as separate molecules in the gas or vapor phase. All three forms exist on the Earth's surface, in contrast with all other gaseous constituents of the atmosphere existing as vapor. Heat transmitted as quanta does reversible work on all three phases of water, melting or vaporizing water while raising the temperature of the gas. The absorption of quanta no longer results in decreased temperature of orbiting particles, in contrast to matter bound by a dominant central force, such as electrons in atoms or matter by gravity. Clausius' Equation (8) describes the reversible effect of heat on the system [6]. This equates the effect of heat dQ on the variation in the quantity of sensible heat in the body dH plus the internal work or potential of the ergal dJ and the external work dW.

$$\mathrm{d}Q = \mathrm{d}H + \mathrm{d}J + \mathrm{d}W \tag{8}$$

For liquid water, dH predicts changes in the sensible heat content of molecules as shown by their temperature; dJ refers to heat needed to disaggregate water molecules from H-bonded clusters and that needed to expand them some 1630 times while doing work dW against atmospheric pressure. Alternatively, the work of expansion is against the much greater back pressure reversibly exerted by a heat engine as in the Carnot cycle [4]. To simplify the equation on the grounds that only the sum of H and J could then be measured, Clausius combined them as U, referring to this as the *Energy* of the body of particles. Here dQ clearly refers to the sum of changes in both kinetic and potential forms of energy.

$$\mathrm{d}Q = \mathrm{d}U + \mathrm{d}W \tag{9}$$

However, there is a possible flaw in combining the ergal in U as energy specific to a particular system of molecules, Their configuration may also include different potentials for internal work needed to sustain external work, in terms of Newton's law that for every action there is an equal and opposite reaction.

1.3 Some Lessons from Revising the Carnot Cycle

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In an action revision of the Carnot cycle [4], we have shown how the negative Gibbs energy of the working fluid could be equated to Carnot's caloric. As quanta, this field energy would sustain the configuration of the working fluid as material particles while expanding isothermally, supporting Carnot's opinion that the specific heat was also logarithmically variable with the change of volume of the working fluid (Fig. 1). By including this internal work supporting external work in the term specific heat Carnot perhaps extended this term too far. Furthermore, the extra heat required was a function of the increased ratio of the volumes of gas rather than their mass. The extra heat required in the isothermal system meant that the total energy of the system could be varied. Then the maximum work possible for a fully reversible cycle was equal in Carnot's terms to the difference between the caloric absorbed isothermally by the working fluid at a high temperature in stage 1 of the cycle the lesser caloric absorbed isothermally by the low temperature sink. These same amounts of heat were logarithmic functions of changes in volume of the working fluid at the higher temperature and for change of volume at the lower temperature. This difference could equally well be obtained from the inversed ratio of internal pressures in the cylinder at the hot and cold temperatures. We showed how these reversible work processes affected the Gibbs energy of the working fluid and so correspond to the second part of the ergal as defined by Clausius during the isothermal processes. When steam was generated from water, the heat of disaggregation of the water clusters would comprise the non-ideal part of the gas behaviour, but for the permanent gases argon and nitrogen in the Carnot cycle, this part of the ergal as significant aggregation is absent.

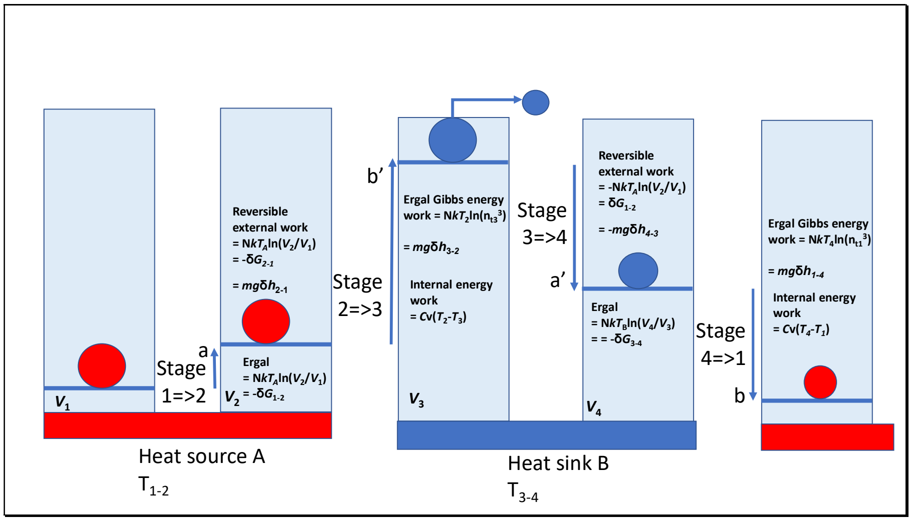

Figure 1. Variations in internal work (ergal) and external work (δ*mgh*) in a Carnot cycle with argon as the working substance [4]. Note the equality of internal and external work in a reversible process with an ideal gas. The isentropic processes are shown with translational quantum numbers n_{t3} and n_{t1} that do not vary in the adiabatic stages when heat neither enters nor leaves [4]. The Carnot cycle is neither a constant volume nor a constant pressure system therefore more heat is required than either the energy or the enthalpy.

In this paper, we reinterpret the role of the *ergal* in modern terms as including this requirement for thermal energy as virtual quanta in the field supporting the internal work of sustaining the configutaion of then molecules. That there is some equivalence between changes in kinetic energy and the configurational ergal does not mean that added heat is consumed in the kinetic energy; it is partly required as a form of energy sustaining the configuration of the system, thus supporting that kinetic heat of molecular motion. This is important as the pressure exerted by the material points is required for the system to perform external work. Although we distinguish between specific heat under constant volume systems or constant pressure systems, the Carnot cycle is neither so the formula for energy or enthalpy that applies to these systems needs modification, given by the logarithmic functions of volume or pressure used to calculate the Gibbs function. On page 28 of his book, Clausius [7] explained how the higher pressure in a working fluid at a higher temperature could do more work than one at a lower temperature and pressure; Carnot interpreted the same changes in relative volumes in the isothermal stages 1 and 3, but at different temperatures, as the source of net work because of the variable elasticity. These different approaches by Clausius and Carnot, completely unknown to one another, demonstrate how the product of pressure (p) and volume (a^3) in a fluid is constant at a given temperature, as a mean value for all material particles.

$$pa^3 = kT; \quad p = \mathrm{N}kT \tag{10}$$

The significance of the virial theorem for molecular systems is that kinetic energy obviously changes directly with temperature if volume changes, but the configurational energy or ergal of the field also varies logarithmically with temperature, proportional to $T\ln T$, also varying logarithmically with volume or internal pressure [$\ln(V)$ or $\ln(1/\mathrm{P})$]. Carnot was aware of this in defining his cycle for heat engines [4]. Boltzmann [9] would also perceive this to good purpose in his definition of entropy as a function of $k\ln(T^{3/2}V)$ as well as by statistical distributions as shown on his tombstone as $S = k\ln W$. This paper will show that these complementary results from the virial theorem also form the basis of the relation of action to entropy and conversion to entropic forms of energy denoted by the scaling factor, absolute temperature.

The concept of *ergal* also has an important role in drawing attention to the reversible equivalence of heat and work. We can easily see its significance in the hydrological cycle on the Earth's surface and atmosphere. This comprises an internal ergal for work done by the evaporative power of sunlight, eventually replenished at the surface when rain falls having transported vast quantities of thermal energy into the atmosphere. Given that the negative Gibbs energy of the ergal has been neglected [4] in favour of the sensible heat content of a body of molecules (H) an important source of variation is being overlooked. It is unfortunate that Regnault's careful work showing that the heat capacity of gases is independent of density was widely misinterpreted as showing that the internal expansion and compression work for particles moving independently would invalidate Carnot's conclusion regarding logarithmic changes in volume or pressure. Even Clausius [7] failed to perceive that Carnot's principle required a varying 'specific heat' and total energy per molecule in the case of the isothermal stages of Carnot's heat engine, having no access to Carnot's original work of 1824 in his lifetime.

On the contrary, our analysis has shown [4] that the negative Gibbs energy does vary with the relative isothermal changes in volume affecting density. The source of this misinterpretation has been the fact that Regnault's measurements [10] from one to 10 atmospheres pressure were conducted at constant pressures, without internal work processes involving change of volume. The marginal change in temperature of one degree Celsius or Kelvin normally used in heat capacity measurements has a negligible effect on a logarithmic variation in pressure, within the error of the measurement as we have shown [4]. However, this ergal is easily measured in the case of the atmospheric working fluid at a pressure dictated by its weight and it can be estimated in the case of the working fluid of a reversible heat engine as performed by Carnot (Fig.1). Part of Clausius' ergal related to the work of the negative Gibbs energy must be considered as the internal structural work necessary to sustain the external work. For reversible systems, these should be equal as shown in Figure 1, though this is not true for irreversible systems where the external work performed with be less than the internal work necessary to provide the expansion.

1.4 Clausius' entropy and the ergal

Also defined by Clausius [7,11], entropy can be considered a property of state measuring the "self reservoir of heat required to raise the temperature of a system of ideal gas molecules to the temperature *T*". Clausius pointed out that the heat indicated by the entropy must include sensible or detectable heat affecting temperature or kinetic energy as well as 'work-heat', where this form of heat included in the entropy was actually "nowhere present" [11], effectively abolishing the caloric theory's axiom of the conservation of heat. Internal heat content and internal and external work were regarded as reversible in nature, subject in systems at equilibrium to conservation in the first law of thermodynamics. The virial theorem validates these changes of state. The theorem was applied in a mechanistic hypothesis of atmospheric warming [8], establishing a temperature lapse rate for dry air of 6.9 K per km as thermal energy is replaced by gravitational work. However, this entropic energy is positive, representing internal work as translational quantum numbers increase with height as energy is reassigned to gravity that can be considered as an extension of the molecules' ergal. The use of ergal could be a useful distinction as entropic energy (*ST*) is a term rarely used and it allows the corresponding decrease in Gibbs energy within the molecular system to be distinguished from internal or external work such as lifting a weight against gravity or activating a flywheel.

The potential energy of the action field referred to as the *ergal* could be considered as a complement to work in many chemical or biochemical processes, largely as a result of variations in the molecular bonding energy. The more firmly material particles are bound to each other, the greater the bonding energy that was released as quanta into the local field, increasing their kinetic energy thus lowering their remaining potential energy ($-mv^2$) as the virial theorem predicts. This is obvious in heat exchanges occurring chemically, but we also see binding energy made available in larger scale processes, such as the cyclical hydrological flows of water under gravity and in the multidimensional air flows of cyclones and anticyclones [4,8]. All such cycles involve periodic local absorptions of heat as work into the action field, followed by energy release in coupled processes achieving thermal work raising temperature, driven by the impetus of these energy flows as in turbulence.

These reflections on the different forms of energy providing a causal basis for action called for a simpler method for calculating entropy and free energy [3,4]. The total thermal energy required to sustain a molecular system, termed here the entropic energy (*ST*), can be expressed as the product of its entropy (*S*) and its absolute temperature (*T*). As defined by Clausius in 1875 [7], molecular entropy measures all the thermal energy needed to heat and sustain the evolving system, composed of kinetic heat affecting temperature as well as its work of configurational arrangement or conformation consuming heat, which does not. While Boltzmann's famous equation for entropy $S = k\ln W$, with W a statistic indicating diversity in configurations, is correct under isothermal conditions, it is less than the whole story [3,4] since temperature varies by location. This formula omits the enthalpic component of entropy, inherent in the virial theorem as kinetic heat, stating that the long-term average of the potential energy of a system of gravitationally bound particles is twice its average kinetic energy. Ultimately, this principle must explain the symmetry of variations in kinetic energy and radiant field energy as heat becomes work within each system, displayed in the higher electronic states of the hydrogen atom as increased entropy.

2. Action mechanics

An essential feature of action mechanics is the role of action, with dimensions similar to angular momentum (mrv), but a scalar including progressive angular motion ($mrv\delta\phi$). Relative action defines this property for the trajectories of particles per radian, allowing meaningful comparisons. The key component of mean radial separation (r) for N material particles is proportional to the cube root of volume V. Although the impulsive momentum δmv plays a critical role for conservation of momentum and force as the key feature of Hamiltonian theory, in action mechanics impulse is measured as variation in action δmvr and its rate as torque, defining temperature for molecules. The other variable component of action the mean velocity v is calculated from the root mean-square speed, shown in Table 2, as proportional to the square root of the temperature. Overall, the translational action $@_t$ varies as $(3kTI)^{1/2}/z_t^{1/3}$ (see Table 2). Relative rotational action $@_r$ for a diatomic system is determined (Table 2) with the formula $(2kTI/\sigma)$. I indicates the respective translational and rotational inertias ($I_t=mr_t^2$; $I_r=m_1m_2r^2/(m_1+m_2)$). These forms of relative action can be used to determine the configurational field of energy inferred by Clausius' virial. Compared to the reductionist factors of temperature, volume or pressure normally applied in statistical mechanics, molecular action is holistic, displaying the physical form of universal reality appealing to imagination.

For a mole of diatomic molecules in a canonical ensemble as defined by Gibbs [12], a concise relationship between the total or entropic energy, involving a thermal term ($RT\ln e^{7/2}$) and relative entropic energy for a diatomic molecule or air can be expressed in Equation (11). Note that this approach is only valid for calculations assuming mean values for action and energies for ensembles of molecules reflecting the Maxwell-Boltzmann distribution [13]. For estimating translational action a correction for the finite difference between the root-mean-square velocity and the actual mean speed of the molecules is also required (Table 2), the former being 1.085 times greater [13].

$$\begin{aligned} ST &= RT\ln[e^{7/2+\,f(\hbar\omega/kT)}(3kTI_t)^{3/2}(2kTI_r)Q_e/(\hbar^5 z_t\sigma)] = RT\ln[e^{7/2+\,f(x)}(@_t/\hbar)^3(@_r/\hbar)^2Q_e] \\ &= RT\ln[e^{7/2+f\,(x)}n_t^3 j_r^2 Q_e] \end{aligned} \tag{11}$$

In Equation (11) σ, z_t and Q_e refer to constants correcting for molecular symmetry (σ,z_t) and velocity (z_t) or electronic partition (Q_e). Rarely at ambient temperatures, some molecules such as oxygen (O_2) exhibit electronic partitioning, because of electrons in unpaired orbitals, giving three states with minimal differences in energy all of which are occupied. This asymmetry requires configurations of oxygen molecules to be considered as three separate species, increasing its translational entropy by $R\ln 3$ or 9.13 units (J/K). This requires 2.723 kJ mol^{-1} of extra heat to bring oxygen to 298.15 K from absolute zero [4].

The entropy of diatomic molecules can be functionally partitioned into several contrasting terms related to enthalpy ($kT\ln e^{7/2}$), rotational energy ($kT\ln(@_r/\hbar)$), vibrational energy ($kT\ln e^{f(\hbar\omega/kT)}$) – these three do not change unless the temperature changes – and a translational energy term ($kT\ln(@_t/\hbar)^3$) that changes with pressure or concentration as well as temperature. Thus, changes in temperature will cause changes in all four of these partitioned entropy terms. Conversely, if temperature remains constant, only translational entropy changes occur when pressure varies. Much of the confusion regarding entropy in its composite forms results from not understanding this complexity. Often, discussions of statistical variations in entropy are couched solely in terms of changes in physical configuration or conformation, but this is only true for constant temperature systems, existing rarely.

Ignoring the vibrational component of entropy as relatively small at ambient temperatures and pressures, we can partition the entropic energy ST of a mole (ca. 6×10^{23}) of diatomic molecules into its separate elements of internal energy ($E=2.5RT$), enthalpy ($H=E+RT=3.5RT$), Helmholtz (A) or Gibbs energy (G) [3,4].

$$ST = RT\ln[e^{7/2}(@_t/\hbar)^3(@_r/\hbar)^2] = RT\ln[e^{7/2}(n_t)^3(j_r)^2]$$

$$= 3.5RT + RT\ln[(n_t)^3(j_r)^2] = H - G \tag{12}$$

$$= 2.5RT + RT\ln[e(n_t)^3(j_r)^2] = E - A \tag{13}$$

In the above equations for entropic energy n_t and j_r are mean quantum numbers for translational and rotational action respectively. Their use is justified by Boltzmann's statistical definition of entropy S as $k\ln W$ where W is a statistical measure of diversity and statistical mechanics is given [4] n Supplement 1 at the MDPI website.

Gibbs and Helmholtz energies can also be written in their inverted or proper forms as follows. These formulae provide absolute values of these free energies, given that they are zero when the quantum states indicated by n_t or j_r are minimal near unity.

$$G = RT\ln[(@_t/\hbar)^{-3}(@_r/\hbar)^{-2}] = RT\ln[(1/n_t)^3(1/j_r)^2] = -RT\ln[(n_t)^3(j_r)^2] \qquad (14)$$

$$A = RT\ln[(@_t/\hbar)^{-3}(@_r/\hbar)^{-2}/e] = RT\ln[(1/n_t)^3(1/j_r)^2/e] = G - RT \qquad (15)$$

Gibbs and Helmholtz potentials or free energies commence at zero and decline as negative values as the entropy increases. They indicate the capacity of the molecular system to absorb more thermal energy, either by increases in temperature or volume. They are at their maximum in the most dense cold conditions, Often referred to as free energies, their character is more indicative of being free of field energy and the low state of action and quantum numbers. Every absorption of a quantum of energy involves a decrease in Gibbs or Helmholtz energies and an increase in entropy. This was a key statement of Planck [14] when he introduced the quantum of energy as required to avoid negative entropies. The Gibbs energy is the appropriate property to use in constant pressure systems where some of the work potential is needed for pressure-volume work mediated by translational kinetic energy. The Helmholtz potential indicates the work potential in a constant volume system. It is perhaps unfortunate that the Gibbs free energy or chemical potential involves a different sense than that of potential energy in the first law of thermodynamics, that is the result of a work process akin to the ergal. By contrast, the Gibbs free energy or thermodynamic potential indicates a capacity for work to be done on the system or for chemical reaction involving the uptake of thermal energy, leading to increased temperature and increased volume. These are also the conditions that have increased relative action as *mrv* and also of entropy. It may have been Clausius' intention in introducing the ergal to remove this source of confusion. Until this distinction of the meaning of potential is understood thermodynamics will be difficult to follow.

Equations (12) and (13) involving entropy (S) and entropic energy (ST) can be written in their more usual forms.

$$\begin{aligned} G &= H - ST \\ A &= E - ST \\ H &= E + RT \qquad (16) \end{aligned}$$

We will investigate later in this paper how vibrational and electronic energy states have a role in controlling reaction rates. For chemical reactions where internal energies designated by E may change, we also have to consider the resultant change in bonding energy between reactants and products. This energy change involving changes in enthalpy (H) is allocated to the Gibbs energy change for the reaction, used to heat or do work on molecules external to the system raising their entropy. As long as the temperature does not change the internal Gibbs energy, equal to the Helmholtz potential for individual molecules of reactants and products, will remain the same.

Also illustrated here, if the relative numbers of reactant and product molecules change with different bonding energies, radiant heat will be released changing the enthalpy while the Gibbs energy varies as the concentration of the reactant molecules changes. In rare cases of spontaneous reaction, the changes in conformational energy between reactants and products are such that the overall

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enthalpy change in the system is considered positive and heat is extracted from the environment, reducing external entropy. It should be noted that these releases or absorptions of field energy as heat or cold in chemical reactions will be reflected in changes of mass according to Einstein's $E = mc^2$, but these changes in mass are so small they can be ignored in chemical reactions.

In this paper, action mechanics will be applied to determine chemical reaction rates and conditions for equilibrium in a revision of Eyring's absolute transition state theory [15,16]. Despite its initial promise for the study of reaction rates from the mid-1930s, this theory has had little development in recent years. This paper aims to provide some novel clarifying tools that may help rejuvenate this area.

2.1 Methods

All thermodynamic calculations in this paper are based on satisfying the entropic energy of Equation (11). Table 1 shows primary data related to mass, bond lengths, moments of inertia for non-linear molecules such as water and vibrational frequencies needed to carry out these calculations. To aid this process a computer program (Supplement 1, Entropy6/cal), designed to calculate translational, rotational and vibrational entropies as well as heat capacities for gas molecules in one pass, was prepared. Its decision-making capability is indicated in Figure 2, facilitating thermodynamic calculations for all reactants and products needed in this paper. The only limit to the theoretical accuracy of the results is that of the inputs shown in Table 1a, although departure from ideality also affects results marginally. The results published for the entropy of atmospheric gases [3] agreed with third law experimental values to four or five significant figures.

Table 1a: Molecular properties used in calculations

Gas	Mass Daltons	Bond length pm	Principal moments of inertia I_a, I_b, I_c x10^{40} gcm^2	Vibration frequencies cm^{-1}	Degeneracy	Multiplicity symmetry Q_e, rotational symmetry σ
H	1.008	-	-		-	-
H_2	2.016	74	-	4161	-	1, 2
N_2	28.014	110	-	2358	-	1, 2
O_2	16+16=32	121	-	1580	1	3, 2
NH_3	14+1+1+1=17	101 101 101	2.9638 2.9638 4.5176	3337 950 3447 1627	1 1 1 1	1, 3
CO_2	16+12+16=44	122+ 122= 244	Linear	1388 667 2349	1 2 1	1, 2
H_2O	16+1+1=18	74 74	1.024 1.920 2.947	3652 1595 3756	1 1 1	1, 2
N_2O	14+14+16=44	NN 112 NO 119	Linear	2224 1285 589	1 1 2	1, 1
CH_4	12+1+1+1+1=16	108 108	5.27 5.27	2914 1526	1 2	1, 12

		108 108	5.27	3020 1306	3 3	

Most of the data given is from Aylward and Findlay [17].

The average bond enthalpies [17] required for calculations in this paper are shown in Table 1b. Where the products contain less bond enthalpy in sum than the reactants, heat is released from the internal action field as a result of the reaction. This decrease in bond enthalpy is calculated as a spontaneous decrease in chemical potential when the reaction is conducted at constant pressure of 1 atmosphere and the heat evolved is transferred to the environment, increasing its entropy.

Table 1b: Average bond enthalpies

Bond	ΔH at 298 K kJ/mol	ΔH Ergs per molecule $\times 10^{12}$	Zero point vibrational energy cm^{-1}	Characteristic Temperature Rotation Θ_{rot} K	Characteristic Temperature Vibration Θ_{vib} K
H-H = H_2	436	7.19234576	2079.307	85.4	6210
C-H = CH_4	413	6.81293303			
N-H = NH_3	391	6.45001650	7214.5		
O-H = H_2O	463	7.01302636			
C=O = CO_2	745	11.2844953		0.561	
C-O-	358	5.42259921			
C-N=	305	4.61981217			
O-O-	146	2.21145108			
O=O = O_2	498	7.54316874	787.3797	2.07	2230
O-N=	201	3.04453196			
N=N-	418	6.33141472			
N_2	945	14.3138443	1175.778	2.86	3374
N=O	607	9.19418358			

The equations to be employed using this program are given in Table 2.

Table 2: Equations solved to obtain thermodynamic quantities

Property	Relevant equations
Entropic energy	$ST = RT\ln[Q_e e^{7/2}(3kTI/\hbar)^3(2kTI/\hbar)^2/(\sigma z_t)]$; H_2, O_2, N_2, CO_2 $ST = RT\ln[Q_e e^{7/2}(@_t/\hbar)^3(@_r/\hbar)^2]$
Translational action	$@_t = (3kTI)^{0.5}/z_t^{1/3}$; $z_t = 2^3.(1.085)^3 = 10.2297$
Rotational action	$@_r = (2kTI)^{0.5}/\sigma$
Q_e	Electron multiplicity partitioning translational entropy
σ, z_t	Rotational and translational symmetry constants
Vibrational action	$\Sigma k[x/(e^x - 1) - \ln(1 - e^{-x})]$ $x = h\nu/Kt$
Vibrational heat capacity	$\Sigma\{kTx^2/[2(\cosh x - 1)]$ $x = h\nu/Kt$

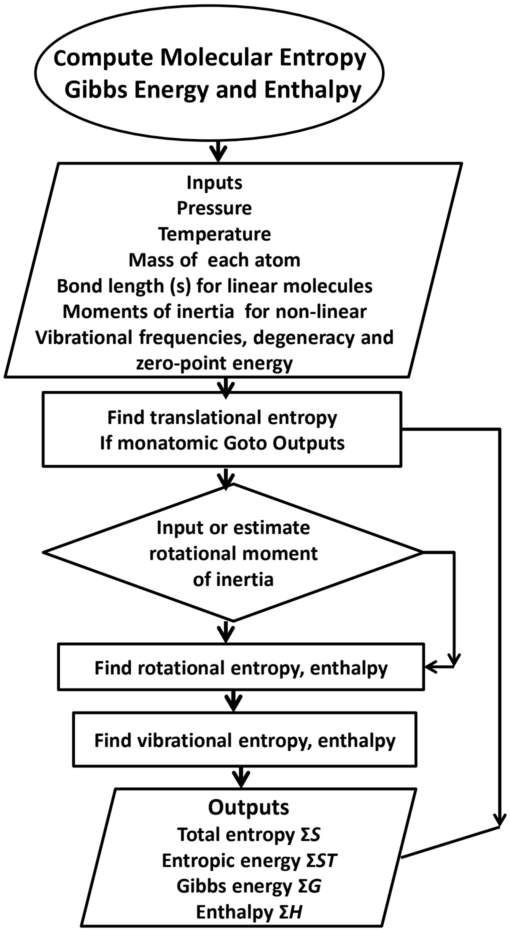

Figure 2: Flow diagram for computing absolute entropy and Gibbs energy (see Table 2 for relevant algorithms). A fully annotated description of the relevant algorithms and subroutines to compute entropy, Gibbs energy and enthalpy is available on request to the corresponding author.

3. Activated Transition States

3.1 Reaction kinetics

At the ambient temperatures of ecosystems, most chemical compounds are stable, atoms held together by bonding energy that was released to the universal field when the molecules were formed from their constituent primary particles (nucleons, electrons). As a result of an energy barrier substantially exceeding kT, their constituent elements such as C, N, P, S, Fe, Ca, Mg, etc. are unavailable for use by living organisms unless mobilised. To mobilise or release these elements in natural cycles, it is essential to provide the required activation energies to break bonds, allowing transition states to be achieved, from which desirable products may be synthesised. Such activated transition states are characterised by higher vibrational and translational action (and lower concentration) than the more stable ground states in which these compounds are normally found.

Higher action states can be generated in the following transitions:

(i) Absorption of energy quanta or photons, which activate the electrons in the absorbing molecules (N) to excited states (N*), present in concentration ratios given by the Boltzmann distribution, where ε is the difference in energy between the ground and excited levels.

$$N^*/N_0 = e^{-\varepsilon/kT} \qquad (17)$$

(ii) The larger the quantum of activation energy required for activation ($\varepsilon = hv$) the lower the concentration of the activated state N*. In general, the rate of the chemical reaction resulting from activation is dictated by the concentration or frequency of occurrence of the activated transition state, a state of lower free energy and higher entropic energy. According to Planck [14], any such activation as the result of the absorption of quanta increases the entropy, decreasing the Gibbs energy.

(iii) The absorption of photons in photosynthesis [1] raising electrons in the two photosystems of green plants (*PSII* and *PSI*) to higher action states of greater mobility is one important example of this process. The absorption of resonant infrared photons exciting vibrations in gaseous molecules like those shown in Table 1b, emitted from the earth's surface by polyatomic gas molecules such as H_2O, CO_2, CH_4 or N_2O, is another.

(iv) As indicated by Equation (17), raising the temperature provides another means of increasing the proportion of molecules in the activated state needed to allow a chemical transition to take place. This requirement explains why life only exists within an optimal temperature range. If conditions are too cold, below freezing, biological molecules will be too immobile for life. If too hot, the lifetime of biological bondings will be too short for stable organisms to occur.

(v) The most common means employed by living organisms to mobilise chemical species is by providing catalytic agents or coupling mechanisms lowering the activation energy for reaction or by providing a forceful mechanism to achieve it; thus, this raises the frequency or likelihood of activated transition state species and increasing the reaction rate as discussed below. This lowers the size of the quantum of energy *hv* needed to reach an activated state allowing transition.

(vi) This process of reducing the magnitude of the activation energy (actually reducing the negative Gibbs energy barrier) is known as catalysis and the biological catalysts involved are proteins called *enzymes*.

Evolving these specific coupling mechanisms or enzymes, able to direct metabolism by lowering activation energies, is one of the main tasks of the genes of living organisms [1]. Thus, enzymes as molecular products of specific and purposeful genetic information, destabilise all kinds of stable structures, mobilising their constituents and setting up molecular flows into alternative products. However, it is important to recognise that enzymes can also act to immobilise or fix simple compounds, such as atmospheric CO_2 and N_2 in the processes of photosynthesis and biological nitrogen fixation; these are major processes on Earth on which life utterly depends.

2.2 Action revision of Eyring's absolute transition state theory

In the molecular reaction with activated transition states of reactant and product (A^*, P^*), formed from standard states of reactant (A) and product (P),

$$A^{o} \quad \Leftrightarrow \quad A^{*} \Leftrightarrow P^{*} \quad \Leftrightarrow \quad P^{o} \tag{18}$$

the Eyring transition rate theory seeks to generate a rate constant for the forward reaction. The model here uses a single molecule of reactant and product in the standard state to simplify the description. However, A and P might be molecular isomers in different conformations, having changed bond lengths affecting moments of rotational inertia (I_r) and vibrational frequencies.

The rate constant k_f for the forward reaction was proposed to be a function involving a natural vibrational *frequency* of chemical bonding around 6.25 x 10^{12} at 300 K, from the energy-action quotient (kT/h) of Boltzmann's constant (k) and Planck's action constant (h), ignoring other possible factors such as the transmission rate, assumed here to be 1—that is all molecules reaching the transition state are on a trajectory of conversion to product. Then a quasi-equilibrium between the reactant A under standard conditions and the activated transition state A^* leads to Equation (19).

$$k_f = \frac{kT}{h} K_f{}^*, \text{ where } K_f{}^* = [A^*]/[A^o] \qquad (19)$$

By assuming that both A and A^* are at unit concentration [15,18], it is said to follow that $e^{-\Delta G^*{}_o/RT}$ is equal to K_f. Thus,

$$k_f = \frac{kT}{h} e^{-\Delta G^{*o}{}_f/RT} \qquad (20)$$

Since $e^{-\Delta G^*{}_{of}/RT} = K^*$

$$k_f[A^0] = \frac{kT}{h}[A^*] \qquad (21)$$

So the overall rate of the reaction producing P from A is proposed to depend simply on the concentration of a transition state $[A^*]$. This is not disputed.

Eyring's absolute transition state theory assumes that the transition intermediate A^* is in equilibrium with A in the ground state [15,16,18]. Then the standard free energy change for this equilibrium is assumed to be given as in the following equation.

$$\Delta G^{o*} = -RT \ln K^*$$

$$k_f = kT/h\, e^{-\Delta G_o^*/RT} = kT/h\, e^{\Delta S_o^*/R} e^{-\Delta H_o^*/RT} \qquad (22)$$

Then $$\ln k_f = \Delta S^{o*}/R - \Delta H^{o*}/RT + \ln kT/h \qquad (23)$$

This division into standard entropy (ΔS^{o*}) and enthalpy (ΔH^{o*}) of activation [19] has led to much discussion regarding differential effects of configuration and of energy on providing the activation energy. Frequently, the fact that the K_f^* is actually equal to $e^{-\Delta G_o^*/RT}$ for the standard free energy change is ignored and $e^{-\Delta G^*/RT}$ is assumed instead.

Also, the van't Hoff relationship is useful for analysis.

$$\begin{aligned} \mathrm{d}\ln k_f/\mathrm{d}T &= (\Delta H^{o*} - RT)/RT^2 \\ &= E_a/RT^2 \end{aligned} \qquad (24)$$

However, these equations imply that both A and A^* are in their standard states of unit concentration or pressure, that is, as A^o and A^{o*}. Logically, this absolute version of the Eyring theory requires that the equilibrium constant K^* is unity since it equals $[A^{o*}]/[A^o]$, when ΔG^{o*} must then be zero. It is legitimate to question this assumption in the Eyring theory, as being inconsistent with reality; realising unit concentration of the activated transition state as assumed seems impossible, given its extremely highly activated state. Then the status of Equation (23) and the relevance of the discussion often given seems uncertain. Many authors [19,20] avoid this flawed reasoning by ignoring the requirement for standard conditions, referring to ΔG^* only.

By contrast, in action mechanics it is proposed that there is an equilibrium between A and A^* under all conditions, with zero Gibbs energy difference between both states as a result. Instead, the equality is actually between a Boltzmann distribution of internal vibrational and electronic states of the relevant bond in A determined by its bonding energy and the translational quantum state of the activated species, present with much longer radial separation, inertia and action. Thus, a decrease in internal Gibbs or chemical potential caused by activation directed to a bond-breaking transition state is equal to that between the ground translational state and the translational state of the activated species. Although ground and activated states have the same mean temperature and kinetic energy, the high moment of inertia of the activated state (i.e. its low concentration) requires much greater sustaining field energy. This implies that the number density N^* and pressure or concentration of the transition state A^* will depend on the internal vibrational or electronic bonding energy ΔE_v, or ΔH_v,.

$$AA_{\text{external}} \Leftrightarrow A^*A \Leftrightarrow AA_{\text{internal}}$$

$$N^*/N^o = K^* = e^{-\Delta E v/RT} \tag{25}$$

Thus the relative concentration of the transition state can be estimated by substituting the bonding energy ΔE in Equation (17) and (25). Using action mechanics, we can also calculate the change in entropic energy of the conversion of A to A^*. At ambient temperatures changes in vibrational entropy are relatively small and can be ignored. So, for a mole of diatomic molecules we will have the following difference between activated and ground state translational and rotational entropic energies.

$$\Delta ST = RT\ln[e^{7/2}({*@_t}/\hbar)^3({*@_r}/\hbar)^2] - RT\ln[e^{7/2}({^o@_t}/\hbar)^3({^o@_r}/\hbar)^2] \tag{26}$$

Given that the action varies in the same heat bath, both species have the same temperature and we can eliminate both kinetic enthalpy and rotational energy changes with concentration.

$$\begin{aligned} -\mathit{\Delta}G &= RT\ln[({*@_t}/\hbar)^3 - RT\ln[({^o@_t}/\hbar)^3] \\ &= RT\ln[({*@_t}/{^o@_t})^3] \\ &= -RT\ln[({^o@_t}/{^*@_t})^3] \\ &= -RT\ln[(N^*)/(N^o] \end{aligned} \tag{27}$$

Thus,

$$N^*/N^o = e^{-\Delta G_t/R} = e^{-\Delta E v/RT} = K_f^* = [A^*]/[A_o] \tag{28}$$

In action mechanics, we conclude there is equality between the change in vibrational and electronic energy - ΔEv on just breaking a bond and in the difference in translational statistical or Gibbs energy ΔG between the ground state molecules and the decrease in the transition intermediate. This result is consistent for an equilibrium reaction where ΔG for the conversion A to A^* is zero, given $\Delta G = \Delta H - T\Delta S$.

These results can be interpreted as indicating that the collisional work performed in raising the vibrational energy from the translational energy of a ground state molecule A to the transition state A^* is equivalent to the statistical entropic work between the translational states of A to that of the transition state A^*. Each molecule of A^* will have much lower concentration or greater separation and action than ground state molecules of *A, but moving with a greater moment of inertia, colliding with greater and more sustained force*. However, this effect will be more than offset by the lower frequency of occurrence of such activated species in uncatalyzed systems. However, these molecular processes can be considered to involve a specific increase in entropy of a molecule of A by absorption of thermal energy from the ground state.

For the reverse reaction of conversion of P to A, which is usually neglected in discussions on transition state theory, we must have an analogous set of relationships. Thus,

$$k_r = \frac{kT}{h} K_r{}^*, \text{ where } K_r{}^* = [P^*]/[P^o] \tag{29}$$

$$k_r = \frac{kT}{h} e^{-\Delta G^{*o}{}_r / RT} \tag{30}$$

This implies the concentration of the activated transition state P^* dictates the rate of the reverse reaction. Then according to the absolute transition state theory, if $\Delta G^{*o}{}_r$ is greater than $\Delta G^{*o}{}_f$, the rate of the forward reaction will be greater than the rate of the reverse reaction because the concentration of A^* will be greater than the concentration of P^*.

From this action analysis it is clear that the changes in standard free energy $-\Delta^* G^o$ usually suggested to be involved in Eyring's theory and equated to $\Delta^* H^o - T\Delta^* S^o$ is then consistent with Equation (26).

$$k_f = \frac{kT}{h} K_f{}^* \quad \text{where } K_f^* = [A^*]/[A_o] \text{ is equivalent to}$$

$$k_f = \frac{kT}{h} e^{-\Delta G^{*o}{}_f / RT} \tag{31}$$

Realistically, a standard unit concentration transition state cannot be in equilibrium or even in quasi-equilibrium with its ground state at the same unit concentration. In action mechanics, the effective $-\Delta G$ factor in the reaction must be the Gibbs energy difference for the transition $*A_f \Leftrightarrow *P_r$ from forward and reverse directions and not that for the transition ${}^*A^o \Leftrightarrow A$.

Then, taking both forward and reverse reactions,

$$\frac{k_f}{k_r} = e^{-(\Delta G^o{}_f{}^* - \Delta G^o{}_r{}^*)/RT} = e^{-\Delta G^o/RT} = K_{eq}$$

$$= K_f{}^*/K_r{}^* = [A^*][P^o]/[A^o][P^*] = [A^*]/[P^*] \tag{32}$$

since $$\Delta G^o = -RT\ln K_{\mathrm{eq}} = \Delta H^o - T\Delta S^o \tag{33}$$

Thus, with standard concentrations of reactants and products, it is clear from this action revision that the rate of the forward reaction is greater than the reverse reaction by a relative factor equal to the equilibrium constant for the reaction.

For the non-standard conditions that usually exist in ecosystems, most reactants and products will be present at concentrations in the mM range of less, rather than 1 molal or at 1 atmosphere; however reaction rates can then be predicted by simply multiplying the respective rate constant by the actual concentration or pressure. Thus, the forward reaction rate,

$$k_{\mathrm{f}}\,[A] = kT[A^*]/h$$

and the reverse reaction rate $$k_{\mathrm{r}}\,[P] = kT[P^*]/h$$

result in the equilibrium constant.

$$k_f/k_r \;=\; K_f^*/K_r^* \;=\; [A^*][P]/[A][P^*] = K_{eq} \qquad (34)$$

For non-standard concentrations of ground state molecules, the concentrations of reactant and product transition state molecules will differ simply in proportion to the relative concentrations. Where reactants and products are in standard states of unity, the ratio of the forward and reverse rates will be equal to the equilibrium constant. In the case where the ratio of $[P]$ and $[A]$ is equal to the equilibrium condition (K_{eq}), then the ratio of activated states $[A^*]$ and $[P^*]$ will be equal to 1.0 and no chemical work is possible. These conclusions are key to the consideration of equilibria in the case studies examined later in this paper such as the thermal dissociation of water into hydrogen and oxygen.

3.3 Radial action

The feature mentioned above for vibrational excitation was the quasi-equilibrium or equality between the probability of the excited quantum state to the translational action of the excited particle. Excited translational states operate with greater radial action than the ground state according to the Boltzmann series. The excited translational action corresponds to a reduction in Gibbs energy compared to that of the ground species. Furthermore, the inertial impetus of the excited species moving on a straighter trajectory experiencing greater Brownian mobility has a capability of exerting greater force in collisions and has greater potential to reach a transition state if the collision process favours orbital steering. In action mechanics, this is a defining feature of the quantum state.

Table 3. Activated vibrational energy (ε) states for N_2 and CO_2 indicating translational action of molecules excited up to $\varepsilon_{vib} = 5h\nu/2$

640 K N_2	N_0/N_n $=V_n/V_o$	δε ergs	$r_n/r_o=$ $@_{tn}/@_{t0}$	ε ex action $kT\ln(n_{tn}/n_{to})^3$	288 K N_2	N_0/N_n $=V_n/V_o$	$r_n/r_o=$ $@_{tn}/@_{t0}$	ε ex action $kT\ln(n_{tn}/n_{to})^3$
$e\text{-}^{\delta\varepsilon vib/kT}$		x10^{13}		x10^{13}	$e^{-\delta\varepsilon vib}$		x10^{13}	x10^{13}
$e^{-2h\nu/kT}$	102582	10.1954	46.812	10.1954	$5h\nu/2$	1.367e^{11}	5151.40	10.1954
$e^{-h\nu/kT}$	320.284	5.0977	6.842	5.0977	$3h\nu/2$	369605	77.771	5.0977
e^o	1.000	0	1.000	0	$h\nu/2$	0	1.000	0
640 K CO_2	N_o/N_n $=V_n/V_o$	δε ergs	$r_n/r_o=$ $@_{tn}/@_{t0}$	ε ex action $kT\ln(n_{tn}/n_{to})^3$	288 K CO_2	N_o/N_n $=V_n/V_o$	$r_n/r_o=$ $@_{tn}/@_{t0}$	ε ex action $kT\ln(n_{tn}/n_{to})^3$
$\delta\varepsilon_{vib}$					$\delta\varepsilon_{vib}$		x10^{13}	x10^{13}
$e^{-2h\nu/kT}$	20.065	2.6499	2.717	2.6499	$e^{-2h\nu/kT}$	783.99	9.221	2.6499
$e^{-h\nu/kT}$	4.479	1.3250	1.648	1.3250	$e^{-h\nu/kT}$	28.000	3.037	1.3250
e^o	1.000	0	1.000	0	e^o	1.000	1.000	0

Table 3 compares nitrogen and carbon dioxide in terms of this radial effect of increasing excitation for the first two vibrational levels. The much lower probability of the vibrationally excited nitrogen states magnifies the radius by more than 100 times. This means the translational Gibbs energy declines much faster for nitrogen than carbon dioxide. Offsetting this, the frequency of such activated species is much lower for nitrogen rather than carbon dioxide, given that a doubling of radius involves an 8-fold increase in the specific volume for molecules ($8r^3 = a^3$).

An uncatalyzed transition state depends entirely on thermal activation, being the key variable in the scaling factor $e^{-\varepsilon/kT}$. Radial action provides an explanation why reaction rates may be catalyzed by quasi-inert particles, for example in the Haber process reacting N_2 with H_2 to be studied later in this paper. Interaction or surface binding of a species such as N_2 is proposed to increase the frequency of activated species because of the great radial inertia of the catalyst particles. The velocity of the particle varies inversely with the root of the particle mass, so that the overall linear momentum of the catalyst increases proportional to the mass of the particle. Taken with a much smaller frequency of catalyst particles inversely proportional to its specific volume, it is obvious that collisions involving adsorbed species will have a much greater chance of achieving sufficiently reduced Gibbs energy to achieve a transition state. The negative Gibbs energy of the catalytic particle can be transferred into the internal bonding disrupting electronic bonding during the collision.

Previously the focus in catalysis has been on energy surfaces regarded as static over the reaction coordinate which the activating complex traces, without specifying the nature of this process. The idea that enthalpic and entropic forces control the process as discussed in the Eyring theory can be accommodated in the action model of catalysis, but only as increases in the kinetic energy of activated bonds but also with decreases in Gibbs energy contributing the entropic factor. Given that entropy includes components of both enthalpy and negative Gibbs/Helmholtz, referring to the idea of entropic force may be considered as too general a concept. Entropic variation refers to both the internal and external ergals of molecules, given that bond excitation includes as much increase in potential energy as in kinetic energy.

3.4 Chemical potential and work

A chemical reaction can be thought of as an expansion process, such as of a flow through a membrane from one compartment to another.

$$[A]_A \quad <=|[A]^*|=> \quad [A]_P \tag{35}$$

The potential work per molecule (w) expanded is given below and per mole.

$$w = kT\ln([A]_P/[A]_A) \tag{36}$$

$$\Delta G = RT\ln([A]_P/[A]_A) \tag{37}$$

If $[A]_A$ is much greater than $[A]_P$, then ΔG is negative and the work potential is spontaneous. Similarly, we can take a chemical reaction under standard conditions of 1 molal concentration (or 1 atm pressure for gases).

$$A^o \quad <===> A^*<=>P^*< ===> \quad P^o \tag{38}$$

Here we have a transition process or trajectory in which the substrate molecule A is equilibrated in an ensemble with activated A^* able to select the spontaneous trajectory as activated product molecule P^*, which can deactivate to P ($A=>A^*=P^*=>P$) with no further work required. From transition state theory, an analogous reverse trajectory from P to $P^*=A^*$ to A must also occur, although at a different rate unless the concentrations of A and P are at equilibrium when $[A^*]/[P^*]$ equals 1.0 and no reaction occurs. This transition between reactant and product may occur in a collision with other molecules, at a catalytic site (as on an enzyme) or at the wall of a containing vessel (Fig. 3).

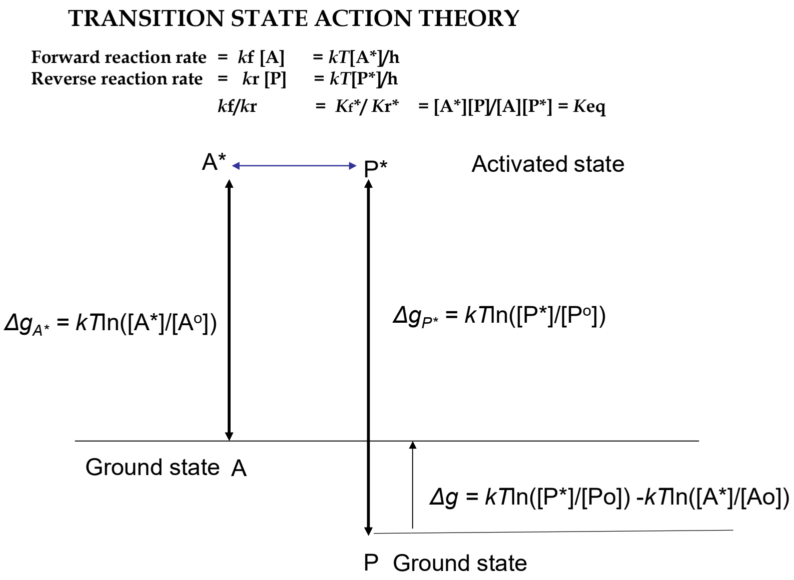

Figure 3. Action transition state diagram for conversion of $A \Leftrightarrow P$ showing excess work potential for conversion of $P^* \Rightarrow P$ compared to $A^* \Rightarrow A$. This model was first proposed in Kennedy [22].

Excess work potential per molecule reacted under standard conditions is given by the difference in chemical potential between the product transition state and the reactant transition state.

$$\Delta g = kT\ln([P^*]/[P^o]) - kT\ln([A^*]/[A^o]) \qquad (39)$$

$$= kT\ln([P^*]/[A^*]) + kT\ln([P^o]/[A^o])$$

$$= kT\ln([P^*]/[A^*]) = kT\ln 1/\mathrm{K} = -kT\ln\mathrm{K} \qquad (40)$$

Thus, work potential per mole (N) or standard Gibbs energy is given by

$\Delta G^o = -RT\ln\mathrm{K}$ (multiplying by N, Avogadro's No. for a mole)

Under non-standard conditions we find the work potential per molecule requires two additional expansion or action changing terms to be inserted for the transitions of A and P from standard (1 molal or 1 atm) to the actual non-standard conditions:

$$\delta g = kT\ln([P^*]/[P]) - kT\ln([A^*]/[A]) + kT\ln([P]/[P^o]) - kT\ln([A]/[A^o] \qquad (41)$$

$$= kT\ln([P^*][A]/[P][A^*]) + kT\ln([P]/[A])$$

$$= -kT\ln\mathrm{K} + kT\ln\mathrm{q}$$

where q is the quotient $[P]/[A]$).

Thus, work possible per mole (N) for non-standard conditions

$$\Delta G = -RT\ln\mathrm{K} + RT\ln\mathrm{q}$$

$$= RT\ln(\mathrm{q}/\mathrm{K})$$

$$= -RT\ln([A^*]/[P^*]),\ \text{just as under standard conditions.} \qquad (42)$$

But under this case, the effective concentrations of the transition states [A*] and [P*] will no longer have a ratio equal to the equilibrium constant. We can conclude that the capacity to do work is caused entirely by the inequality of the concentrations of the two transition states generated from A and P respectively. Obviously, if $RT\ln K = RT\ln q$ (i.e. ratio of product to reactant concentrations = K, then ΔG is zero and no work is possible, for we have equilibrium with equal concentrations of the transition state generated from each direction.

On the other hand, if q = 1 as in standard conditions, then $\Delta G^o = -RT\ln K$ as shown above. It is noteworthy that any case where the ratio of product to reactant concentrations is 1.0 yields the same result and standard conditions are not strictly required for ΔG to equal $-RT\ln K$. This means that the transition state concentrations [A*] and [P*] will always have the same ratio as K if the ratio is unity, although the actual concentrations of [A*] and [P*] and rates of reaction will dependent on the absolute concentrations of [A] and [P].

Thus, the rates of chemical reactions can be viewed as the result of a set of 'action processes' in which activated transition states are equilibrated with reactants but not equilibrated with products. Product formation can then occur as a spontaneous expansion of this non-equilibrated transition state product into the product action field. Furthermore, chemical work is possible by coupling such unbalanced action states of reactants and products to other reactions that can thus be driven up and energy gradient. For example, the phosphorylation of adenosine diphosphate (ADP) to adenosine triphosphate (ATP) can be driven by a coupled pH gradient [1].

The potential for chemical systems in the environment to initiate *action*, whether biological or not, depends on the existence of unbalanced thermodynamic potentials that offer sources of free energy or work potential. For biological systems, the exploitation of these chemical potentials involves primary coupling of oxidation/reduction reactions to processes of phosphorylation that enables the overall chemical systems to approach equilibrium.

3.4 Comparing Eyring's Theory and Action Mechanics Transitions

The action revision given here differs from the Eyring model in several respects:

(i) In action mechanics, the activated transition state A^* more realistically cannot be considered as actually in a standard state. The concentration is considered to be set as a Boltzmann exponential by the magnitude of the vibrational bonding energy of the reactant molecules.

(ii) While Eyring's theory usually analyses reaction rate in terms of Gibbs energy differences between the ground state reactant and the activated transition state molecules, in action mechanics there can be no difference in chemical potential of the two states. This follows because the increased enthalpy and potential energy of molecules in the activated transition state, corresponding to decreased chemical or Gibbs energy in each activated molecule, according to the quanta required to be absorbed; this decrease in potential is paid for by the increased potential of the ground state molecules. This is essential, given the Boltzmann equilibrium between ground and activated states for the ensemble of molecules.

(iii) Proponents of Eyring's transition state theory often fail to consider the reverse reaction as having a significant role in determining reaction rates. This may be valid in reactions proceeding far from equilibrium. However, action mechanics implies that in reactions closer to equilibrium the chemical potentials for both reaction directions must be considered, given that the net reaction rate depends on the ratio of the transitions states A* and P*. Furthermore, the relative rates of forward and reverse reactions must always comply with the overall thermodynamic properties of the reaction, as shown above.

In contrast to Eyring's absolute transition theory, the action transition state theory suggests that overall chemical potential changes for reactions can be estimated directly from the energies of the bonds broken and reformed and the changes in entropic energy of reactants and products. Indeed, using action mechanics it is possible to do direct calculations of all thermodynamic properties from molecular properties.

4. Catalytic Action

This analysis of the transition state has deemed the energy required to reach the activated transition state as equivalent to the bonding enthalpy of particular atoms or groups involved in reactions. If radiant energy or heat equivalent to the bonding energy can be injected into the bond, the bond may break. However, except for the weakest bonds, this may mean that, without catalysis, the likelihood of achieving a transition state is exceedingly low. The majority of reactions, except those that are diffusion limited not requiring activation above kT, may never occur at a significant rate without some form of catalysis. For sufficiently large bonding energies requiring activation, there may be no activated species in a given volume of reaction at a given time.

The essence of catalysis, still consistent with transition state theory, is that either the activation energy for transition to a product can be reduced or the temperature raised. Thus near 4000 K as discussed later, the hydrogen molecule is spontaneously about 50% dissociated into two hydrogen atoms. Many chemical reactions in industry are thus conducted at higher temperature to reduce the need for more activation energy from collisions.

More remarkable is the action of catalysts that can reduce activation energy without the need for increased temperature. For example, by rearranging electronic orbitals, the resonant frequency of a molecular bond key to the reaction can be reduced with bond lengthening, the activation energy to the transition state would be less and more readily provided in a collision. As a result, the concentration of the activated transition state would increase exponentially, in proportion to the reduction in the bond enthalpy. An increase by a catalyst in the frequency of occurrence of the activated transition state is effectively an increase in its translational chemical potential.

4.1 Are catalysts also inertial anvils?

Catalysts are invariably colloidal particles, whether chemical or biochemical in nature. The most sophisticated catalysts are the colloidal proteins coded by DNA known as enzymes, with highly specialised functions of great subtlety, such as intra-molecular group transfers. Some enzymes are capable of enhancing the rate of simple reactions such as hydrolysis or decarboxylation by factors as large as 10^{17} [21,23]. Given their ubiquitous effect, we can enquire as to whether binding to colloidal particles has a unique function in catalysis.

Being bound to the surface of an inert colloidal particle will have an influence on the inertia of a reactant, in effect the particle providing an inertial 'anvil' where the reactant molecule may be properly oriented for further reaction. The inertia of the colloidal particle present at relatively low concentrations must have the potential to exert greater force during collisions, given its high momentum, thus increasing the probability of bimolecular reactions and weakening of bonds. Colloidal particles possess relatively high translational entropic energy being more widely separated, with large rotational energy and larger vibrational energy, given the large number of degrees of vibrational freedom. These properties contribute to more substantial inertia (i.e. tendency to continue their current trajectory), subject always to the statistical or stochastic character of their Brownian motion. To some extent remaining to be determined, the bound substrate (Fig. 3) must share the greater inertia and negative Gibbs energy of the colloidal particle.

If the properties of the catalytic colloid also have attractive effects for a second reactant, while orienting the molecule (orbital steering, Fersht [21], the likelihood of reaction must be increased. The decrease in entropic energy of the reactant molecules on binding to a colloidal surface has been regarded as a contribution of increased Gibbs energy to the reactant molecules, providing a measure of this effect. In addition, catalysts such as enzymes may have specific binding interactions that increase the strength of binding, conferring specificity for binding and subsequent reaction.

4.2 Effect of binding energy on catalysis

Jencks [24] and his younger colleague, Fersht [20,21] provided extensive arguments regarding the effect of substrate binding energy to a catalyst on reaction rate. The binding of a substrate A to a colloid involves a significant loss of translational and rotational entropy, effectively increasing the chemical potential of the substrate, now more constrained. However, as indicated by the discussion around Equation (11), entropy is a complex function and loss of entropy in one molecular system may involve an increase in the entropy of another. It must also be understood that a larger Gibbs energy indicates a greater potential to absorb radiant energy to remobilise the system while work is being performed. The conversion of heat to work always involves a decrease in Gibbs energy and *vice versa*.

Binding energy is maximised when all binding groups on the substrate or reactant are complementary to binding sites on the enzyme. Haldane and Pauling had suggested it would be catalytically advantageous for the enzyme to be complementary to the activated transition state of the substrate ($E + S^* \Leftrightarrow ES^*$) rather than the original ground state molecule S before binding. In such cases, the initial binding of the substrate to the enzyme ($E + S \Leftrightarrow ES$) may be relatively loose, sufficient to immobilise the substrate and to effectively increase the concentration of other reactants where more than one is involved.

Figure 4 shows this activation scheme as a diagram indicating the action path from ground state reactant through transition state to ground state product. Incidentally, most authors including Jencks and Fersht have suggested that activation to the transition state must involve an increase in the Gibbs energy. This is true if we are following the substrate's translational pathway and the translational potential, considering an increased concentration of the transition state as in Figure 4. However, recall that a high Gibbs energy is synonymous with a low quantum state as shown in Equation (14). From the virial theorem [8], internally activated molecules with either increased electronic or vibrational energy must both have increased potential energy, entropy and diminished Gibbs energy [25]. Increased potential energy of electronic orbitals requires a quantum of radiant energy $h\nu$ absorbed simultaneously with diminishment of kinetic energy of the same magnitude as the quantum; so the electronic potential energy increases with twice the magnitude of the absorbed radiant energy. While a robust collision or compression of a substrate may be involved in the process of catalysis generating repulsive potential energy, the actual achievement of the transition state on rebound with a virial process of absorption of quanta must involve a decrease in internal Gibbs energy. Bound substrates are constrained on trajectories of greater translational action and entropy compared to the unbound state, contributing to the transition state.

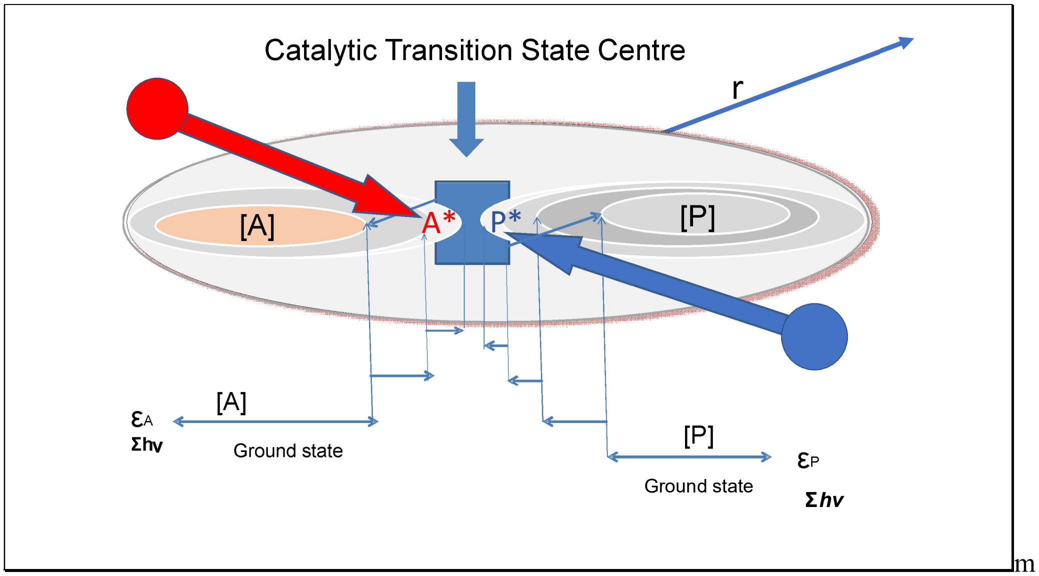

Figure 4: Radial action transition states on a Brownian catalyst, proposed to generate activation energy for reversible reactions $A \Leftrightarrow P$ by forceful (δmvr) inertial collisions. Concentrations of A^* and P^* of similar chemical potential to bulk reactants A and P stabilize in potential wells, binding loosely. At constant temperature, the difference in ground state energy $\varepsilon_{Po} - \varepsilon_{Ao}$ represents the enthalpy and chemical potential changes for the reaction.

The absorption of an infrared quantum of radiation hv increases both kinetic and potential energy of the vibration by $hv/2$. The Gibbs or Helmholtz energies of the activated molecules must decrease internally, becoming more negative as quanta are absorbed. The greater the activation, the lower the internal Gibbs energy. The translational entropy will become larger as the activation energy is reduced by the catalyst. Thus, the rate equation can be written in terms of translational Gibbs energy.

$$k_f = kT/h e^{-\Delta G_t/RT} \qquad (43)$$

In effect, ΔG_t becomes smaller as the internal activation energy to achieve transition is reduced by catalysis.

4.3. Effect of transition state complementarity

Fersht [21] explained that the full binding energy is realised only when the enzyme is complementary in structure to the transition state. Under these conditions, the initial binding of the substrate to the enzyme indicated by the raised Michaelis K_a value is less strong. An enzyme with a high K_m value is generally regarded as having a higher catalytic rate. For example, glutamate dehydrogenase (GDH) from lupin nodules with a K_m for ammonia of about 70 mM [26] has a turnover number (molecules of product per molecule of enzyme per sec) some 50 times higher than glutamine synthetase (K_m for ammonia 12.5 µM [27] from the same source – an enzyme regarded as having a scavenging role for ammonia that can be poisonous if its concentration is excessive.

The exact mechanism of the much lower turnover time of glutamate dehydrogenase compared to glutamine synthetase is not fully understood. But the loose primary binding of ammonia to GDH and high Michaelis K_m requiring a higher concentration to achieve maximum velocity may allow the process of conversion to the transition state to be more firmly bound with the binding energy contributing to easier activation and a high k_{cat}. It is suggested that these new viewpoints of action mechanics and radial inertia by large colloids offer opportunities for new theoretical developments, not being pursued here.

5. Equilibrium

Chemical equilibrium requires that both systems of molecules have the same Gibbs energy. That requires that the action or quantum fields are equal and the concentrations of activated transition states for forward and reverse reactions are also equal, as discussed in Section 3. Gibbs energy can be calculated directly based on Equations (12 and 14). We have prepared a single program capable of calculating all results given in this paper in one pass for each molecule and temperature, based on their molecular properties given in Table 1. This program is attached to this paper as Supplement 1.

5.1 *Statistical and action mechanics*

K_f* for the activation equilibrium aA + bB = [*AB] is given in statistical mechanics as the following Equation [44]. The Q factors represent canonical partition factors, often rendered as Z values [15].

$$K_f* = [(Q*/V)/(Q_{A/}V)^a(Q_B/V)^b]\ e^{-\Delta E o/RT} \qquad (44)$$

Here V is taken as the system volume occupied by the molecules; ΔEo represents the difference in bonding energy between reactants and product at absolute zero. These enthalpy values must be corrected at temperatures above zero Kelvin.

The Q values refer to the overall product of the electronic, translational, rotational and vibrational partition functions of the reactants. These have been shown [3,4] to be effectively action ratios, indicating quantum states of the reactants and are given in their classical form following: Translational partition function, $Q_t = (2\pi mkT/h^2)^{3/2}V$; rotational partition function (linear molecule), $Q_r = 8\pi IkT/h^2$; rotational partition function (non-linear molecule), $Q_r = \pi^2(8\pi^3 I_A I_B I_C)^{1/2}(kT/h^2)^{3/2}$, vibrational partition function (polyatomic molecules)$Q_{vi} = \Pi_i\,[1 - \exp^{-h\nu i/kT}]^{-1}$where Π_i indicates a product of i separate functions, one for each mode of vibration. At normal temperatures, the electronic function Q_e can be ignored with a small number of exceptions (e.g. paramagnetic O_2).

In action thermodynamics and mechanics [1,4] for the gaseous reaction $A \Leftrightarrow P$, assuming no role for excited vibrational states or electronic states (Q_e), we can express entropic energy for as follows.

$${}^{A}sT = kT\ln[e^{7/2}({}^{A}@_t/\hbar)^3({}^{A}@_r/\hbar)^2]$$

$${}^{A}sT = kT\ln[e^{7/2A}(n_t^{\,3})({}^{A}j_r^{\,2})] \qquad (45)$$

A similar equation can be written for the mean value of entropic energy for diatomic product molecules, where n_t and j_r are translational and rotational quantum numbers.

$${}^{P}sT = kT\ln[e^{7/2}({}^{P}@_t/\hbar)^3({}^{P}@_r/\hbar)^2]$$

$${}^{P}sT = kT\ln[e^{7/2P}n_t^{\,3P}j_r^{\,2}] \qquad (46)$$

These are easily adjusted for monatomic and polyatomic molecules, as is demonstrated later.

Apart from the exponential term ($e^{7/2}$), the translational and rotational quantum numbers relate to the work term that is associated with changing internal Gibbs energy. As explained in the Introduction, Clausius referred to the internal work done in the system as the *ergal*, effectively the negative of the internal Gibbs energy related to the configurational entropy term; initially, he used the term in the opposite sense but it is more convenient as he eventually decided to apply it positively to increasing field energy content as the Gibbs energy becomes more negative. Unfortunately, the term was apparently considered unnecessary when the kinetic work associated with enthalpy (h) took precedence. The enthalpic term ($k\ln e^{7/2} = 3.5k = h$) will vary if there is a change in the molecular bonding, the numbers of molecules or the degrees of freedom of motion possessed by the molecule.

If a single molecule of reactant A becomes product P, the system's enthalpy may change, even cooling the system; but if new bonds are formed involving electronic and vibrational rearrangements, a negative enthalpy change (δh) may occur where heat or work is exported to the exterior of the system. Under these conditions, where heat is exported to the exterior, an additional negative change in Gibbs energy occurs. Overall, this is expressed in the work equation for an average molecule following, for an isothermal system.

$$\delta g = \delta h - \delta sT \qquad (47)$$

We might write this work process entirely in potential terms, simply by specifying the location of the work (negative δg) in a subscript.

$$\delta g_{\text{total}} = \delta g_{\text{external}} + \delta g_{\text{internal}} \qquad (48)$$

Spontaneity is shown as a negative δg, either by export of heat from excess bonding energy to the exterior, or as an increase in entropy in the *ergal* (non-enthalpic δsT). Spontaneity can still exist, though rarely, when heat is consumed in internal bond rearrangements or elimination and δh is positive, cooling the exterior. In this case the magnitude of the decrease in the *ergal*, indicating less field energy is required to sustain the molecular configuration, is decisive.

The entropic energy of the product will be as given in Equation (49), with changes in translational and rotational action the only significant variables. For example, if P is more highly concentrated or at a higher pressure than A, then its translational entropy and energy will be less and there will need to be compensating increases in either the rotational action and entropy or the internal energy of bonding. That is, either the rotational moment of inertia has increased or the bonding energy could be less in P than A. Increases in either of these properties indicates that more heat is needed to do the internal work of sustaining the physical configuration of the molecule P than A As either rotation or vibration at the same temperature T.

Here, the bonding energy is given as $-H$, considered as a loss of entropy as the heat of bonding is lost from the molecular system to the environment. We use enthalpy H rather than energy E in a constant pressure system as we assume the system is free to expand doing work of lifting the atmosphere. Then we have the following difference in entropic energy between the reactant and product.

$$T^{P\text{-}A}\Delta S \;=\; RT\ln[({}^{P}@_{t}/{}^{A}@_{t})^{3}({}^{P}@_{r}/{}^{A}@_{r})^{2}/{}^{P\text{-}A}e^{\Delta H/RT}] \qquad (49)$$

Because both molecular systems are at the same temperature, the $e^{7/2}$ enthalpy term is eliminated, as well as the symmetry constants for rotation σ and translation z_t. Then we have the following relationship.

$$T\Delta S \;=\; RT\ln[({}^{P}@_{t}/{}^{A}@_{t})^{3}({}^{P}@_{r}/{}^{A}@_{r})^{2}] + \Delta H \;=\; -\Delta G + \Delta H \qquad (50)$$

When there is no change in the number of molecules, the variation in total kinetic energy is minimal and the enthalpy change is derived only from differences in bonding energy.

When we consider the familiar Gibbs equation for reaction (42) relating Gibbs energy change (ΔG) to enthalpy change (ΔH) and entropic energy change ($T\Delta S$) we need to be clear as to the meaning of these terms and where they apply. The $T\Delta S$ term refers strictly to the difference in entropy at T between the system's chemical products and reactants as depicted in equation (26). But the ΔG and

ΔH terms refer further afield to changes both within the reacting chemical system and external to the system, apparently under constant environmental conditions, as given in all standard texts on thermodynamics.

$$\Delta G = \Delta H - T\Delta S$$

However, this constancy is rarely true. By convention, if ΔH is negative, heat or work is transferred to the environment, both entropy-increasing processes externally. Because of its great thermal mass, the Earth's surface environment is considered to be constant in temperature, but in fact all heat-producing reactions will heat the environment -- though usually ever so slightly. Furthermore, if heat or pressure-volume work is transferred to the environment and gravitational or other shaft work is done, ΔG will be negative. So ΔG refers to entropy changes both within and without the molecular system. That means molecules other than those in the reacting system are heated or have work performed on then but they are not represented as such in the reaction. An important advantage of action mechanics is that its more realistic nature allows a clearer viewpoint regarding mechanisms of energy transfers as heat or work.

As stated in Methods (section 2.1), provided molecular properties such as atomic masses, bond lengths or moments of inertia, bonding energies, pressure and temperature are known, the entropy, the enthalpy and Gibbs energy changes can easily be calculated from first principles with no need to refer to standard tables of reaction. Where there are significant changes in vibrational energy between reactants and products this must also be taken into account and this will be illustrated with examples following. At equilibrium, ΔG is zero and $\Delta H = T\Delta S$; under standard conditions of 1 atm pressure or 1 molal concentration, ΔG^o is equal to $-RT\ln K_{eq}$ as discussed above. From the success of action thermodynamics at ambient temperatures where vibration is usually unimportant, we must conclude that there is a necessary relationship between the quantum number ratios of translational and rotational action only under adiabatic or isentropic conditions.

$$[({}^{P}@_t/{}^{A}@_t)^3({}^{P}@_r/{}^{A}@_r)^2] = 1 \text{ or } ({}^{P}@_t/{}^{A}@_t)^3 = ({}^{A}@_r/{}^{P}@_r)^2 \qquad (51)$$

Note that under isothermal conditions (constant temperature) the rotational quantum number for a reactant or product remains the same irrespective of concentration or pressure while the system behaves ideally. Only the translational quantum number is subject to change with concentration, thus affecting the chemical potential. The exact form of the equilibrium relationship will depend on particular molecular properties.

6. Illustrative case studies

Several important reactions of topical interest to industry are examined here in preliminary analyses using action mechanics. These include reactions that are effectively irreversible at ambient temperatures such as the thermal dissociation water and hydrogen gas and another that is more poised, the Haber-Bosch process for fixing atmospheric nitrogen (N_2). In the following reactions all involving hydrogen molecules as reactants, entropies and enthalpies are calculated at different temperatures using a program requiring only inputs given in Table 1, with Gibbs energy changes calculated by difference, to establish the temperatures where equilibrium is closest to achievement. This analysis allows choice of temperature ranges to discover the equilibrium point as well as to establish temperatures ensuring complete lysis of molecules such as hydrogen, water and ammonia.

6.1 Dissociation of H_2 to 2H

This reaction lysing molecules of hydrogen gas (H_2) to two hydrogen atoms at 1000 K under standard conditions is illustrated in Figure 5, showing entropic energies (ST), enthalpy (H) and standard Gibbs energy changes during the reaction, assuming each gas has one atmosphere pressure. Tables 4 gives the thermodynamic changes in *ST*, *H* and *G*, showing that under 1 atmosphere pressure of reactant and product, equilibrium is achieved at just under 4000 K. Thus at 6000 K, we can predict that the surface of the Sun consists of separated hydrogen atoms and not hydrogen molecules. The change in enthalpy is partly affected by the change in the kinetic energy of one molecule versus two, but mainly a result of the diminution in bonding energy in this conversion. The thermodynamics indicates that the reaction is strongly in favour of formation of the diatomic H_2 at the temperature of 1000 K, given that the changes in entropic energy and enthalpy are so far from balance; the action field contains far too little energy to sustain hydrogen atoms. According to conclusions made in the discussion on transition state theory (see section 2.2), the relative concentration of transition species to ground state species at 1000 K without catalysis ($N^*/N_o=e^{-\Delta H/RT}$) would be $1.67\text{x}10^{-23}$, about four molecules for each mole of hydrogen (H_2). By comparison at this temperature every atom of hydrogen would be activated for transition, yielding relative rates of reaction of $6\text{x}10^{22}$.

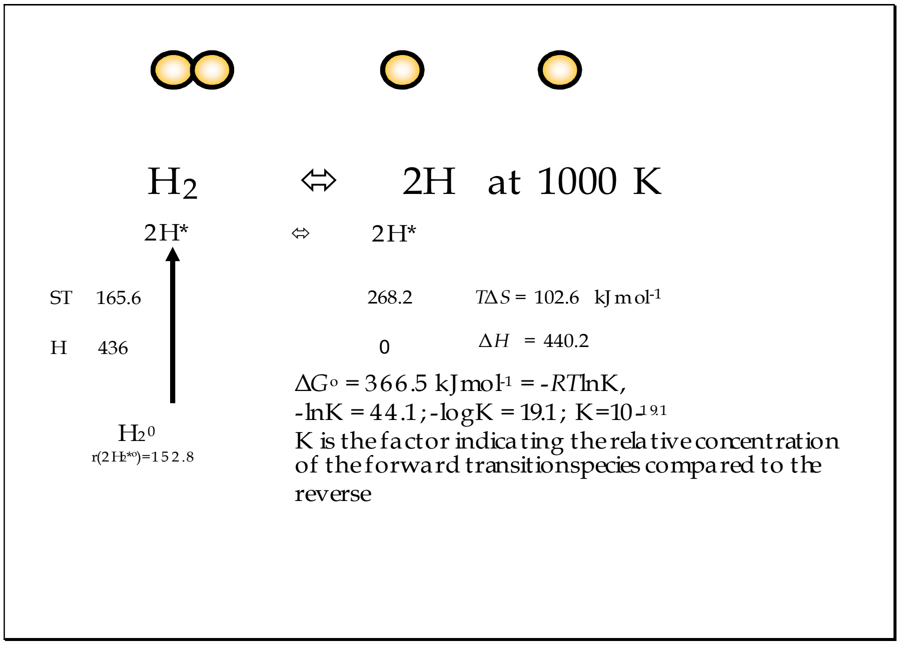

Figure 5. Gibbs energy change for the reaction dissociating diatomic H_2 to monatomic H. The change was estimated using the difference between cumulative bond energies and entropic energies. Bond energies at 298.15 K for HH is 436 kJ per mole.

From Table 4 we can observe that, under standard conditions of 1 atmosphere pressure, the reaction

$$H_2 \quad \Leftrightarrow \quad 2H \qquad (52)$$

is at equilibrium with K_p or the ratio of pressures $(H)^2/(H_2)$ equal to 1.0 at just over 4000 K, with a standard Gibbs energy change of -2 kJ per mole. At 298 K, the reaction spontaneously forms H_2 releasing energy from the field or chemical work as heat (ca. 436 kJ per mole), whereas at T greater than 4000 K, the reaction is increasingly displaced towards dissociation into H atoms, consuming heat from the field needed to sustain the translational entropic energy of the separated atoms. Thus, on stars such as the Sun, the spectrum observed from Earth is for translational or electronic states of H as a gas and no spectrum for H_2 is observed. Does this mean that in extremely cold conditions in space, we will expect to see hydrogen as the diatomic gas? Using the action methodology given here, we can easily calculate this by running the program at very low pressure and temperature, only changing these environmental parameters.

Table 4. Temperature variation of transition state Gibbs energies for dissociation of hydrogen molecules to hydrogen atoms

Temp K	Entropy (^{o}S) at 1 atm J/K	ST kJ/mole	Entropy (S) at 1 atm J/K	ST kJ/mole	$-T\Delta S$	$-\Delta H$ H_2=>2H = 436 kJ	Gibbs change ΔG
	H	2H	H_2	H_2			
1000	134.088	268.176	165.562	165.562	102.614	440.157	-366.543
2000	148.496	593.984	185.733	371.466	222.518	444.314	-216.796
3000	156.924	941.544	197.533	592.599	348.445	448.471	-99.526
4000	162.904	1303.232	205.904	823.616	479.616	481.628	-2.012
5000	167.542	1675.420	212.348	1061.990	613.010	456.785	+98.225
6000	171.332	2055.984	217.703	1306.221	749.763	460.942	+230.821
7000	174.536	2443.504	222.189	1555.323	888.181	465.099	+365.082
8000	177.312	2836.992	226.075	1808.600	1028.342	469.256	+501.086
9000	179.760	3235.680	229.503	2065.520	1170.160	473.413	+648.747

Table 4a. Partitioning of internal Gibbs energy (ergal) into translational and rotational virtual quanta

Temp	Translational *ergal* H	Trans lational virtual quanta	Mean energy H $h\omega$	Translational *ergal* H_2	Translational virtual quanta	Mean energy H_2 $h\omega$	Rotational *ergal*	Rotational virtual quanta	Mean energy H_2 $h\omega$
K	g_t x10^{12}	n_t	x10^{20}	g_t x10^{12}	n_t	x10^{14}	g_r x10^{13}	j_r	x10^{13}
1,000	1.8815	203.8	22.23	2.0250	288.3	0.702	4.8324	3.385	1.428
2,000	4.2414	363.2	8.853	4.5285	513.7	0.882	9.4958	4.788	1.983
3,000	6.7820	509.3	5.134	7.2127	720.2	1.001	11.7813	5.864	2.009
4,000	9.4399	647.2	1.459	10.0141	915.3	1.094	17.2972	6.771	2.555
5,000	12.1849	779.5	1.563	12.9028	1102.4	1.170	23.1626	7.570	3.060
6,000	14.9996	907.4	1.653	15.8608	1283.3	1.236	29.3055	8.292	3.534
7,000	17.8720	1031.8	1.732	18.8769	1459.2	1.293	35.6788	8.957	3.983
8,000	20.7938	1153.2	1.803	21.9422	1630.9	1.345	42.2504	9.575	4.413
9,000	23.7589	1272.2	1.868	25.0508	1799.1	1.392	48.9963	10.156	4.824

In Table 4, the *ergal* for hydrogen of $k\ln[(n_t)3(j_r)^2]$ is partitioned into translational and rotational work terms and also into mean values for virtual quanta, using the quantum numbers n_t and j_r derived in calculating the action and the entropy. It is noteworthy that as the temperature rises and the molecular number density declines maintaining constant pressure of 1 atmosphere, the size of the conjugate translational and rotational quanta decline. Even though the translational *ergal* for by hydrogen atoms and hydrogen molecules increases more than ten-fold between 1,000 and 9,000 K the mean size of the quanta sustaining the system only doubles. This reflects the relationship that the ergal varies proportional to $T\ln T$.

Surprisingly to the authors, the dissociation of hydrogen has received relatively little experimental interest, despite its current relevance for green energy. Langmuir and associates [28-29] made excellent studies on the lysis of various gases by exposure to tungsten filaments as heat sources, using heat conduction as a measure of dissociation of the molecules. The Nobel laureate Giauque [30] made a study of the thermodynamics of this dissociation, obtaining a very similar result for $\Delta G/T$ near 4000

K. Since the maximum temperature possible was just over 3000 K with 68% dissociation, tungsten filaments melted at higher temperature so Langmuir was unable to achieve the temperature of 4,000.

The theoretical pressure of hydrogen and the resultant reduction potential available in ecosystems has been made a special study by the senior author [1,22]. It was recommended by Manning Clark, inventor of the Clark electrode, early in the 20th century to use the negative logarithm to base 10 of the H_2 pressure instead of electrochemical reduction potential. He called this the rH value, by analogy with pH for acidity. It has the advantage of reporting the actual hydrogen pressure that a chemical system can sustain and is highly appropriate for environmental chemistry. In general terms, the more negative the rH value, the greater the potential for biological action and life systems. For the data in Table 4, the rH uncorrected for temperature is zero.

6.2 Association and dissociation of water

The dissociation of water into hydrogen and oxygen is also a reaction of much interest. The senior author in the 1960s once used electrochemical dissociation to prepare oxygen free of nitrogen gas for labelling experiments, given that the hospital oxygen then available contained significant nitrogen. But prospects of a convenient source of renewable energy using sunlight provides renewed interest in achieving significant breakdown of abundant water using catalysis.

Figure 6 shows reaction energy changes for standard concentrations for hydrogen, oxygen and water as reactants and product at 298.15 K, a reaction that is essentially irreversible under ambient conditions.

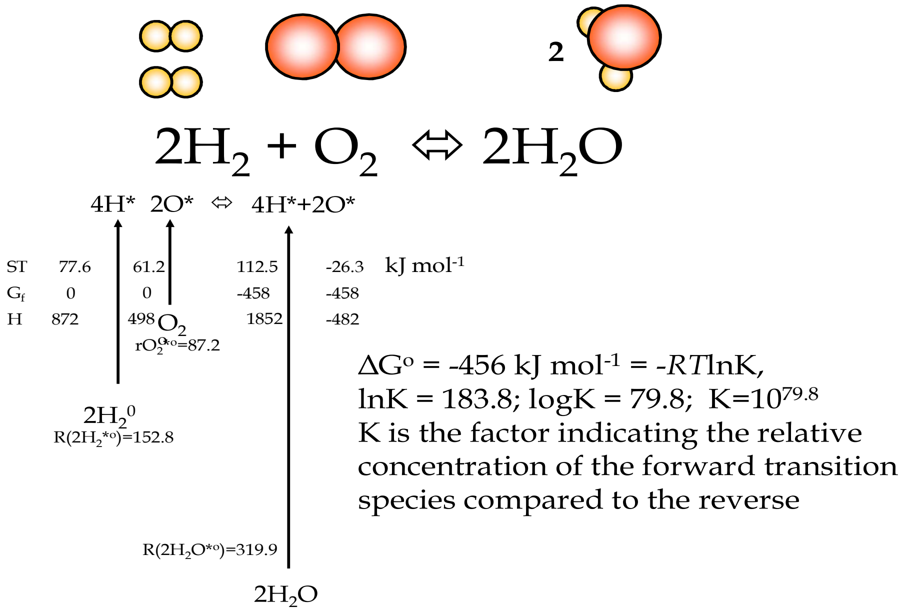

Figure 6. Standard Gibbs energy change for the irreversible reaction forming water from hydrogen and oxygen. Potential changes are usually estimated using standard tables or more simply from the differences between cumulative bond energies and entropic energies using action mechanics. Bond energies at 298.15 K for HH, OO and H_2O are 436, 498 and 926 kJ per mole respectively.

Table 5. Temperature variation for transition state Gibbs energies for dissociation of water into oxygen and hydrogen

K Temp	H_2O, *S*, *ST*	O_2, *S*, *ST*	H_2, *S*, *ST*	$T\Delta S$ $2H_2 + O_2$	$-\Delta H$ <> $2H_2O$	$\Delta G = \Delta H - T\Delta S$
	J/K, kJ/mole	J/K, kJ/mole	J/K, kJ/mole	kJ/mole	444 @ 0	
1000	232.397, 232.397	243.403, 243.403	165.671, 165.671	109.951	463.112	-353.161
2000	264.043, 528.086	267.976, 521.005	187.249, 374.498	213.829	474.273	-260.444
3000	285.241, 855.724	283.116, 849.348	201.024, 603.071	344.042	485.208	-141.166
4000	309.471, 1237.885	293.795, 1175.178	211.215, 844.858	389.124	496.715	-107.591
5000	313.582, 1567.910	302.104, 1510.519	219.280, 1096.402	567.503	508.680	+58.823
6000	323.942, 1943.651	308.904, 1853.422	225.943, 1335.658	637.436	520.770	+116.666
7000	332.760, 2329.319	314.658, 2202.607	231.613, 1621.291	786.551	532.904	+253.647
8000	340.431, 2723.448	319.646, 2557.165	236.545, 1892.359	894.987	545.178	+349.809
9000	347.217, 3124.451	324.047, 2914.642	240.907, 2168.167	1002.074	557.541	+444.533
10000	353.299,3533.00	327.985, 3279.850	244.818, 2448.176	1110.218	569.883	+540.335

Table 5 shows that significant dissociation is achieved only above 4000 K, showing how stable the water molecule is. It is even more stable than hydrogen gas, that requires a slightly lower temperature to dissociate (Table 4). In order to calculate the Gibbs energy change it is necessary to adjust the change in enthalpy change from that at absolute zero to the temperature of the reaction. The variation in enthalpy change with temperature is given in Table 5, taking into account the numbers of molecules of reactants and products, being three and two respectively. Table 5a gives the results obtained by the program for calculation of the reaction enthalpy, varying with temperature.

In Table 5 it was assumed that hydrogen and oxygen molecules remain undissociated, even at 10,000 K. However, this could only be momentarily true on rapid mixing as atomic oxygen and hydrogen will soon be present in the mixtures, increasingly as temperature is raised. The same approach can be applied to the mixture of water, hydrogen and oxygen molecules and hydrogen and oxygen atoms at any temperature. Solving this for equilibrium requires that all reactions compute to a Gibbs energy change of zero. However, this cannot be achieved for all gases to be at unit activity of 1 atm. Using action mechanics it is possible to estimate relative pressures of water, hydrogen, oxygen molecules and hydrogen and oxygen atoms at any given temperatures.

Table 5a. Change in enthalpies in water formation

Temperature	H_2O kJ/mol	O_2	H_2	ΔH
1000	37.141	34.598	29.398	-19.112
2000	83.468	73.149	62.030	-30.273
3000	130.953	111.084	96.015	-41.208
4000	177.954	148.719	129.952	-52.715
5000	224.562	186.366	163.719	-64.680
6000	270.918	223.898	197.354	-76.770
7000	317.144	261.396	230.898	-88.904
8000	363.201	298.824	264.378	-101.178
9000	409.213	336.339	297.814	-113.541
10000	455.171	373.793	331.216	-125.883

The data in Table 5 suggesting reaction Δ*G* is zero and that *K*= 1.0 with equal pressures of water vapor, hydrogen and oxygen near 4500 K is clearly incorrect. We have already shown hydrogen molecules are dissociated 50% into atoms at 4000 K (Table 4a) and Johnston and Walker [31] using thermodynamics showed oxygen molecules would be 50% dissociated into oxygen atoms at 3850 K. For that reason, these data should only be regarded of illustrative of the approach, which can easily be extended to include these secondary dissociations. The principle that all chemical potentials should be equal at equilibrium must be obeyed and can easily be employed in calculations. That can be considered as future work not required here.

The thermal dissociation of water studied here also has a biological analogy in the photosynthesis of water with carbon dioxide [1] at environmental temperatures. This also involves the splitting of water molecules into oxygen molecules and four reducing equivalents that are equivalent to hydrogen atoms, although these are effectively dissociated as protons and electrons. The extremely high temperatures needed to lyse water thermally contrasts with the absorption of sunlight at ambient temperatures. However, it is important to realize that solar energy is despatched in quantum packages resonant with atoms at a much higher surface temperature of 5900 K. It is the great virtue of the photosynthetic apparatus that it can provide capturing mechanism for these quanta that is completely inelastic and uses this thermal energy of the Sun’s ergal to do chemical work on Earth.

6.3 The Haber-Bosch reaction

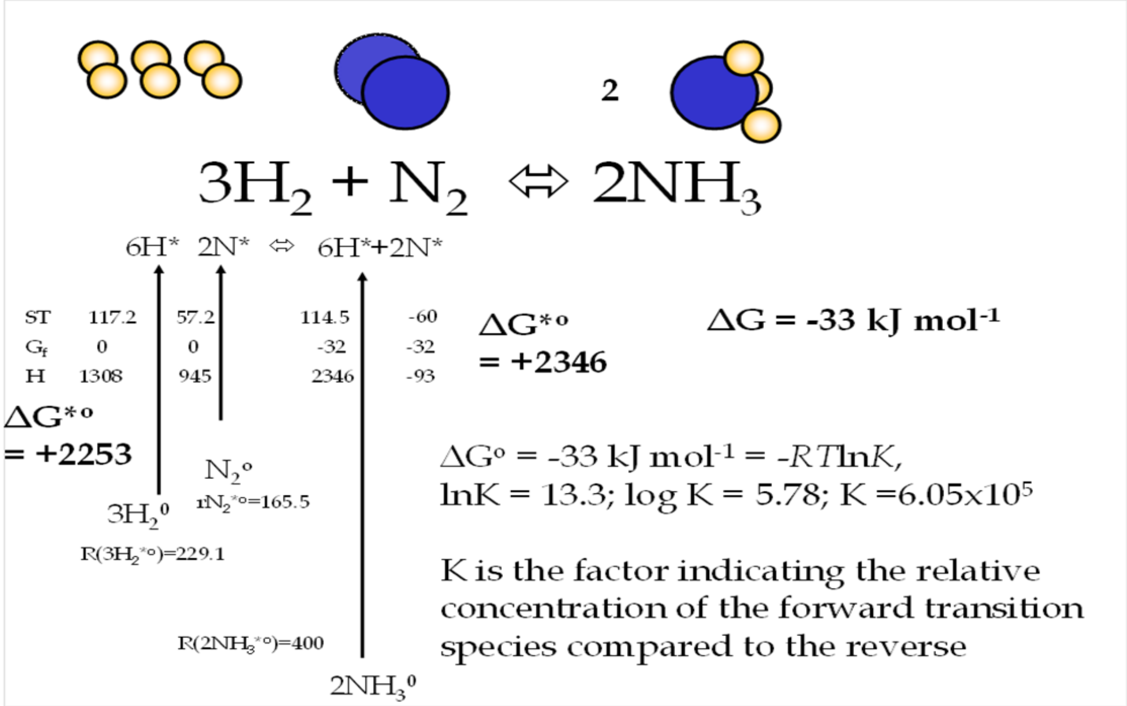

Figure 7. The Haber-Bosch fixation of dinitrogen. Bond energies at 298.15 K for HH, NN and NH_3 are 436, 945 and 1173 kJ per mole respectively.

A third chemical reaction, currently the most significant industrial synthesis on Earth, is the Haber-Bosch reaction of the fixation of atmospheric nitrogen (N_2) as ammonia (Fig. 7). Unlike the hydrolysis of water, the Haber process can be regarded as a reversible reaction given its low Δ*G* value. Indeed, at 450 K, its standard Gibbs energy is zero and K_p is equal to 1.0. At standard conditions 93 kJ of energy per mole of ammonia formed is evolved, a heat release that increases with increasing temperature, given that four molecules of hydrogen and nitrogen are reduced to two of ammonia. It has been proposed and demonstrated [33] that the Haber reaction could be used to provide renewable electrical power from sunlight with no need for battery storage. This is possible by using solar power to provide heat to decompose NH_3 into N_2 and H_2 in the daytime and to run the reverse reaction releasing heat at night. Steam generation continuously can produce electricity by traditional turbines. The process could be integrated with industrial chemistry, if augmented with renewable photosynthate in agroforestry [34] or with fossil fuels.

Table 6a. Variation with temperature of Gibbs energy for Haber-Bosch reaction

Temp. K	NH_3, S, ST	N_2, S, ST	H_2, S, ST	$T\Delta S$	$-\Delta H$ 93 at 0 K	$-\Delta G$
	J/K, kJ/mole	J/K, kJ/mole	J/K, kJ/mole	kJ/mole	kJ/mole	kJ/mole
400	203.727, 81.491	200.189, 80.076	138.898, 55.559	83.771	97.924	14.153
500	212.331, 106.166	206.683, 103.342	145.391, 72.696	109.098	96.996	-12.102
600	219.750, 131.850	211.989, 127.193	150.697, 90.418	134.747	95.300	-39.447
700	226.328, 158.430	216.475, 151.533	155.183, 108.628	160.557	93.000	-67.557
800	232.277, 185.822	220.361, 176.289	159.069, 127.255	186.410	90.094	-93.316
900	237.732, 213.959	223.788, 201.409	162.496, 146.246	212.229	86.630	-125.599
1000	242.789, 242.789	226.854, 226.854	165.562, 165.562	237.962	82.683	-155.279

Table 6b. Kinetic enthalpy for Haber process

	NH_3	N_2	H_2	ΔH
400	14.998	11.640	11.640	-4.924
500	19.842	14.550	14.550	-3.996
600	25.040	17.460	17.460	-2.300
700	30.555	20.370	20.370	0
800	36.373	23.280	23.280	2.906
900	42.470	26.190	26.190	6.370
1000	48.810	29.101	29.101	10.317

Table 6c uses data for entropy change including vibrational entropy for ammonia and also increased kinetic heat capacity, accepting mean vibrational energy is half kinetic and half potential energy. These results are significantly different at higher temperatures than those performed neglecting vibrational entropy and should be preferred in establishing the temperature of equilibrium for gases all at 1 atm pressure. Given the large bonding energies involved in these reactants and products, the concentrations of activated transition state molecules are extremely low. Indeed, it is highly improbable that any are present in a reaction vessel at any instant in time. These reactions almost certainly require catalysis on particulate matter or other catalytic surfaces that act to reduce the activation energy with a corresponding increase in the concentration of the transition state A^* (and equally of P^*) [20,21]. A catalytic surface reducing the activation energy will increase the concentration of the transition state from both directions equally. Once the reaction is ignited, the local generation of heat and temperature rise may further catalyse the reaction to an explosive extent. Although catalysts may speed up the achievement of equilibrium and are essential for the process, it must be remembered that they do not change the position of equilibrium.

Table 6c. Entropy and entropic energy changes, including vibrational heat capacity

Temp K	NH_3, S, ST	N_2, S, ST	H_2, S, ST	$T\Delta S + \Delta Cv$
	J/K, kJ/mole	J/K, kJ/mole	J/K, kJ/mole	kJ/mole
400	207.964, 83.186	200.189, 80.076	138.898, 55.559	-80.381
500	218.758, 109.379	206.683, 103.342	145.391, 72.696	-102.672
600	228.224, 136.934	211.989, 127.193	150.697, 90.418	-124.979
700	236.721, 165.705	216.475, 151.533	155.183, 108.628	-146.007
800	244.485, 195.588	220.361, 176.289	159.069, 127.255	-166.878
900	251.663, 226.497	223.788, 201.409	162.496, 146.246	-196.153
1000	258.342, 258.342	226.854, 226.854	165.562, 165.562	-206.856

*Ammonia triple point is near 400 K, condensing at 237 K at 1 atm, presenting an interesting problem

The actual molecular mechanisms of catalysis cannot be considered in any detail in this paper. Suffice it to say that a reactant bound to the surface of a colloidal particle will experience much greater inertial forces during collisions, given the large translational moments of inertia of colloidal particles as a result of their greater mass and greater inertial radius, given their lower concentration. This inertial effect is sustained by the field energy associated with the higher configurational entropic energy of such particles, but the reactant A itself is effectively frozen in position on the surface of such colloids, effectively increasing its translational Gibbs energy.

To establish the transition state in either direction it is assumed that, without catalysis, a total activation energy of 2253 kJ per mole (equal to the bonding energy of the atoms) of nitrogen for both reactants is required. For the reverse reaction, 2346 kJ per mole (the bonding energy of the hydrogen atoms in ammonia) is required, so that the concentration of the transition state in the forward reaction is equivalent to 93 kJ per mole more favourable. This determines that ammonia will be formed at a much greater rate than it decomposes. The entropic energy for reactants and product is easily determined, and ΔG determined by difference, as shown in Table 6a. In future work, we will apply action mechanics to the catalytic process.

7. Conclusion

Action mechanics provides a convenient means to employ thermodynamics more effectively. As s realistic model of chemical reactivity as an amalgam of statistical mechanics and quantum theory, it has the potential to rejuvenate the application of thermodynamics to general sciences. This would be consistent with relative action and the quantum theory defining the shapes of molecules, with any changes in action state and morphology accompanied by the absorption or the emission of energy as quanta or photons. In action mechanics theory this principle of sustainability by the impetus of field energy applies to all scales and magnitudes – from nuclear reactions, the binding of electrons in atoms and bonding in molecules and to all tertiary and quaternary interactions including the very long range interactions of gravitation [1]. All these scales are operative in ecosystems although their relative effects and frequencies vary enormously. The frequencies of quanta associated with transitions of state must vary in the frequency range of 10^{16} to 10^{-16} sec^{-1} – from gamma rays to long range gravitational energy exchanges.

The ease of calculation of the number and frequency of virtual field quanta from translational and rotational action (Table 4a), at least as mean values, is surprising. The magnitude of the energy as virtual quanta in the action fields is effectively the *ergal*. In principle the values calculated indicate the field energy sustaining the action states of reactants and products in chemical reactions. It should be possible to obtain direct evidence of the frequency and the intensity of these quantum fields by using resonant detectors, since they lie in the range of infra-red, microwave and radiowaves. There may be significant scope for controlling rates of reactions or even positions of equilibrium with sufficiently intense action fields. These possibilities can be investigated without delay. Catalysis by enzymes remains mysterious. Some enzymologists have considered that many enzymes are “too big” for their binding functions alone [34], although evolution of regulatory functions can also logically contribute to added size. However, if their inertial impetus in collisions is significant in forceful encounters with substrates the size can be explained.

Recognising the magnitude of the field energy as the *ergal* may have profound importance for quantitative accounting of energy in many scenarios. This energy field is rarely considered in areas as diverse as climate science, such as the potential or work energy stored in coherent cells of air such as anticyclones and cyclones, or in ‘calorie counting’ for human weight loss and nutrition. This fundamental principle of energy conservation was Clausius enunciated almost two centuries ago in the equivalence of heat and work, but it is largely neglected. To what extent are the increasing obstructions to smooth air flow of modern cities and the ubiquitous wind farms of Europe and further afield causing local warming? The ability of the magnitude of changes in the *ergal* to release equivalent amounts of temperature-raising heat seems to have no role in the global circulation models on which the International Panel of Climate Change.

Lambert and Leff [35] have pointed out how in solids standard entropy and enthalpy up to 298.15 K are very strongly correlated, with a slope of 0.0066 K^{-1}representing just the exponential terms in Equation (44), given that the mass of the solid is neither translating nor rotating and the scale of action is absent.

$$\Delta H^{o} = {}^{T}\!\int_{o} C_{p}(T)\,dT \tag{44}$$

Absorption of heat at constant atmospheric pressure to reach temperature T reflects not only the thermal energy stored in the solid ($RT\ln[e^{7/2}]$) but also how that energy ($RT\ln[e^{\Sigma xf(x)}]$) is stored, given the configurational work of expansion against the atmosphere. For most vibrations in solids below 298.15 K, the vibrational entropy given by each degree of freedom $R[x/(e^{x} – 1) – \ln(1 – e^{-x})]$ – effectively a work term – is negligible and contributes only slightly to the heat capacity. General chemistry texts usually emphasise “configurational entropy and the probability of locations”, but this is a minor feature in solids [35]. Nevertheless, all solid chemicals or their solutions maintain a vapour pressure characteristic of the absolute temperature and mole fraction. For unsaturated solutions the vapour pressure and corresponding fugacity (i.e. the ideal gas pressure) reflect the mole fraction of the substance. At equilibrium, the chemical potential, reflecting the change in Gibbs energy with concentration of a chemical substance, is equal in all phases.

This analysis suggests it should be possible to use fugacity as the effective pressure in each phase and to consider chemical reactivity on this basis, particularly at low pressures or concentrations where departures from the ideal gas law are minor. Even where they are larger, experimentally determined correction factors can be applied. The great advantage of fugacity is that it allows thermodynamic calculations yielding ΔG^{o} as performed here, providing fugacity-based K_{f} values from the equality of -ΔG^{o} and $RT\ln K_{f}$ to estimate the activity constant $K\gamma$ from graphs of activity coefficients and then to calculate the actual partial pressures from $K_{p} = K_{f}/K_{\gamma}$.

The illustrations given here are all for gaseous reactions acting ideally. However, there is no reason that action mechanics should not be extended to the liquid or even the solid states. Fugacity theory [36] has shown that equilibrium between phases depends on equality of vapour pressures of substances in equilibrium, whether in solid, liquid or gaseous states. This suggests it should be possible to use fugacity as the effective pressure in each phase and to consider chemical reactivity on this basis.

In the case of biological molecules such as proteins and nucleic acids, it should also be possible to deal with these using action mechanics, at least for aqueous systems. For such large molecules, moments of inertia will be correspondingly greater and there will be more internal motions such as bendings and rotations, all significantly contributing to the action and the corresponding *ergal*.

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