

# A reassessment of the Carnot cycle and the concept of entropy

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## Abstract

It is argued that the Carnot cycle is a highly inaccurate representation of a steam engine, and that the net work obtained in its operation would be zero. This conclusion is also supported by an elementary mathematical approach, which reexamines the work done in the four individual steps of the cycle. An important consequence of this is that the concept of entropy, originally proposed on the basis of the Carnot theorem, may not be a fundamentally valid thermodynamic quantity. Also, the experimental approach generally adopted in the determination of entropy is questionable, and the importance of increasing randomness in natural processes not universally valid. In fact, a more viable basis, at least *vis-à-vis* chemical reactions, appears to be the ratio of mass to energy, which is apparently maximized in the case of a spontaneous process.

*Key words.* Adiabatic; Efficiency; Isothermal; Randomness; Steam engine; Work.

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## Introduction

The relationship between energy and work is a prime concern of thermodynamics, and one that has shaped, in a very fundamental way, the modern scientific view of nature and the universe. Our current ideas, however, apparently had very practical origins, more particularly in the mechanical era of steam engines and the thick of the industrial revolution. Steam engines essentially converted heat into mechanical work, and it was clearly of both theoretical and practical interest to understand this process, in particular defining and measuring its efficiency. Thus was born the well-known Carnot cycle.<sup>1-4a</sup>

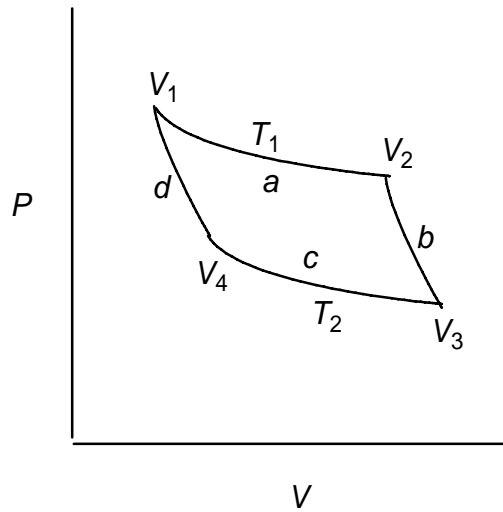
The Carnot cycle (1824) represents a highly idealized process that is engaged in the continuous conversion of heat into work, *via* a cyclic sequence of absorption of heat and its subsequent conversion to mechanical work. However, whereas a conventional steam engine employs steam as both the source of energy and the medium of its mechanical conversion, the Carnot cycle is based on a sealed container of ideal gas connected to a piston that captures the work performed. This may be either expansion or compression, depending on whether the container is placed in a hot or a cold reservoir, a cyclic sequence enabling the continuous nature of the conversion process.

## Discussion

*The Carnot cycle.* The Carnot cycle is essentially comprised of the following steps carried out reversibly (*cf.* Fig. 1).<sup>1-4a</sup> The sealed container of one mole of ideal gas at volume  $V_1$  is placed in a heat reservoir at a (higher) temperature  $T_1$  and the gas allowed to expand isothermally to volume  $V_2$ ; the container is removed from the reservoir, jacketed to prevent heat exchange, and the gas expanded adiabatically to temperature  $T_2$  and volume  $V_3$ . The jacket is removed, and the cylinder placed in a reservoir at a (lower)

temperature  $T_2$ , and the gas compressed isothermally to volume  $V_4$ ; the cylinder is again jacketed to prevent heat exchange, and the gas compressed adiabatically to the original volume  $V_1$  and temperature  $T_1$ .

Thus, apparently, the system has not only converted heat into work but also returned to the original state, ready to begin a new cycle (implicitly, *ad infinitum*). Note that in the two expansion steps heat is both absorbed and mechanically expended, into work performed upon the surroundings; conversely, in the compression steps work is performed upon the system which thus acquires heat. The splitting of the expansion and compression stages into isothermal and adiabatic steps is arbitrary, but apparently enables the calculation of the overall work performed as follows.



**Fig. 1.** The Carnot cycle represented as a pressure-volume ( $P$ - $V$ ) diagram. (All symbols have their usual meaning as explained in the text.)

The work done in each adiabatic step is equal to the product of the heat capacity at constant volume ( $C_v$ ) and the temperature difference [ $\Delta T = (T_1 - T_2)$ ], i.e.  $C_v \Delta T$  (compression) and  $-C_v \Delta T$  (expansion); these clearly cancel each other out. The isothermal steps are believed to involve work of  $-RT_1 \ln(V_2/V_1)$  (expansion) and  $-RT_2 \ln(V_4/V_3)$  (compression). Thus, the overall work obtained in the Carnot cycle ( $W$ ) is considered to be given by eqn. 1.

$$W = -RT_1 \ln(V_2/V_1) - RT_2 \ln(V_4/V_3) \quad (1)$$

$$(V_1/V_4)^{\gamma-1} = (V_2/V_3)^{\gamma-1} = (T_2/T_1) \quad (2)$$

$$W = R \Delta T \ln(V_1/V_2) \quad (3)$$

Furthermore, for an adiabatic process the temperature and volume changes are believed to be related as in eqn. 2 ( $\gamma = C_p/C_v$ ,  $C_p$  being the specific heat at constant pressure). Thus, the overall work performed in the Carnot cycle upon the surroundings is considered to be given by eqn. 3 (from eqns. 1 and 2).

This is indeed a curious result, as the overall work in the Carnot cycle, which is reversibly performed at each stage and returns the system to its original state, must perforce be zero. Thus, the work obtained from the system in the expansion steps must be equal to the work done on the system in the compression steps. In fact, the only net effect of the Carnot cycle would be the transfer of the heat absorbed from the reservoir at  $T_1$  to the reservoir at  $T_2$ .

*The problems and their origins.* It would appear, therefore, that eqn. 3 is of dubious validity. Indeed, an analysis of the assumptions underlying the Carnot cycle provides interesting clues to the origin of the problem. In fact, a rather serious complication with the Carnot cycle is that all three properties defining the state of an

ideal gas, pressure ( $P$ ), volume ( $V$ ) and temperature ( $T$ ), are continuously varied during its operation (except in the isothermal stages, when  $T$  is constant). Thus, the cycle is represented by the familiar  $P$ - $V$  diagram shown in Fig. 1, which raises the following interesting questions.

$$(V_2 - V_1) = (V_3 - V_4) \quad (4)$$

$$(V_1/V_2) = (V_4/V_3) \quad (5)$$

$$(V_2 - V_1) = (V_3 - V_4)(V_2/V_3) \quad (6)$$

$$(V_4 - V_1) = (V_3 - V_2) \quad (7)$$

$$T_1 \ln(V_2/V_1) = T_2 \ln(V_3/V_4) \quad (8)$$

The  $P$ - $V$  diagram is normally displayed in a symmetrical manner, thus implying that the opposite sides of the ‘pseudo-parallelogram’ are equal, *i.e.*  $a = c$  and  $b = d$  (Fig. 1). This indicates that the volume changes are related as in eqn. 4. On this basis, the volume relationship in eqn. 5, as implied in eqn. 2, cannot be generally valid, as eqn. 5 implies eqn. 6. Thus, the net work in the isothermal steps will not be given by eqn. 3.

The calculation of the work performed in the adiabatic steps is also problematical. The assumption that this is equal to  $|C_v \Delta T|$  is questionable as  $C_v$  seems inappropriate in a process in which the volume is not constant. An average value of  $C_v$  is perhaps admissible, but only when the volume changes in the expansion and compression stages are equal, as given by eqn. 7. This, of course, follows from eqn. 4, and again implies a symmetrical  $P$ - $V$  diagram. (Even in the case of an unsymmetrical  $P$ - $V$  diagram, the net work will remain zero: this will correspond to the net energy expended, which would be independent of the path followed, hence zero in all analogs of the classical Carnot cycle.)

These arguments also imply that the work performed in the two isothermal steps must be equal (and opposite). Hence, the volumes would be related as in eqn. 8 (derived from eqn. 1, with  $W = 0$ , and regardless of the symmetry of the  $P$ - $V$  diagram).

Although it may seem remarkable that the Carnot cycle can be disproved by the above elementary mathematical approach, a direct ‘phenomenological’ approach apparently leads to the same conclusion. Thus, the claim that the Carnot cycle models a steam engine is dubious for the following reasons.

*The Carnot cycle and steam engines.*<sup>3,4a</sup> The Carnot cycle consists of two distinct stages (Fig. 1): expansion of volume from  $V_1$  to  $V_3$ , during which work is done upon the surroundings (by the system); and compression of volume from  $V_3$  to  $V_1$ , during which work is done upon the system (by the surroundings). A steam engine, however, only performs work upon the surroundings, *i.e.* the surroundings do not perform any work upon the system. The steam engine performs cyclically by virtue of a mechanical contrivance in the form of the action of a wheel, which returns the engine’s piston to its original position, but without any compression work being performed.

Thus, the work of the ‘return stroke’ would be marginal, and apparently originates in the wheel’s curtailing the ‘forward stroke’: the energy for the work of return must originate in the expansion stage. This is certainly true of a ‘single acting’ steam engine. In a ‘double acting’ steam engine, the return stroke of the piston is driven by a second burst of steam that is enabled by an ingenious system of valves. Even so, the engine performs work on the surroundings (*i.e.* the wheel) during both strokes, the distinction between the forward and return strokes being arbitrary.

Interestingly, however, it may be argued that the demarcation between system and surroundings is arbitrary in the case of a steam engine, as steam is introduced from the surroundings. Thus, in a ‘single acting’ steam engine the expansion stroke can be considered to perform work upon the surroundings, and the return stroke upon the system. However, in both single and double acting steam engines, the spent steam is vented out of the system during the return stroke, thereby avoiding compression. This is in contrast to the Carnot cycle, in which the system is returned to its original state by compression (with work performed on the system).

For the above reasons, the analogy between the steam engine and the Carnot cycle is apparently invalid.

*Consequences of the invalidity of the Carnot cycle.* On the basis that the overall work performed in the Carnot cycle is zero, not only is eqn. 3 invalidated, but also the notion that it leads to the efficiency of a steam engine. (The efficiency of the Carnot cycle would be zero as there is no net work.) The ‘efficiency’ of the Carnot cycle ( $E$ ) is derived from eqn. 3, defined in eqn. 9, and leads to the idea of entropy ( $S$ ) as defined in eqn. 10. [ $Q_1$  and  $Q_2$  are the heats absorbed at temperatures  $T_1$  and  $T_2$  respectively, and correspond to the work performed in the isothermal steps:  $Q_1 = RT_1 \ln(V_2/V_1)$  and  $Q_2 = RT_2 \ln(V_4/V_3)$ .]

$$E = W/Q_1 = (Q_1 + Q_2)/Q_1 = (T_1 - T_2)/T_1 \quad (9)$$

$$dS = dQ_{\text{rev}}/T \quad (10)$$

Thus, intriguingly, the invalidation of eqn. 3 leads to the collapse of the fundamental thermodynamic concept of entropy.

Also, eqn. 9 has led to the idea that the efficiency of a steam engine is limited by  $T_2$ , the temperature of the lower temperature ‘heat sink’, maximum efficiency being attained only at absolute zero. This appears unviable in the light of the above discussion, so the efficiency of a steam engine apparently remains an open question.

Interestingly, it may be argued that the work obtained by adiabatic expansion in the Carnot cycle ( $b$  in Fig. 1, *vide supra*), being equal to  $C_v \Delta T$ , would be greater at ever lower temperatures of the sink. Ostensibly, this corresponds to the temperature of the working environment in a steam engine. However, in an adiabatic expansion the system is thermally isolated from the environment, so the temperature of the sink is apparently of no significance. The efficiency would then be a function of largely the friction in the system (assuming constant external pressure).

These arguments further evidence the inappropriateness of the analogy between steam engines and the Carnot cycle.

*The entropy concept in general.* Originally, entropy was defined *vis-à-vis* steam engines (*vide supra*) as the heat inevitably wasted at the lower temperature sink. This was thus considered as unavailable heat, and led to the idea that there was a natural limit to the conversion of heat into work. However, as argued above, these ideas now appear unsustainable. (Even in the case of a steam engine, the efficiency appears to be limited by ‘non-thermal’ aspects, such as friction and external pressure.)

As the ideas of classical thermodynamics began to be generalized, an important conceptual development was the idea that entropy was related to randomness, as expressed in eqn. 11. ( $k_B$  is the Boltzmann constant and  $w$  the number of possible states, a measure of randomness).



$$S = k_B \ln w \quad (11)$$

$$G = H - TS \quad (12)$$

$$\Delta G = \Delta H - T\Delta S \quad (13)$$

$$\Delta G = -T\Delta S_{\text{total}} \quad (14)$$

$$\Delta G^0 = -RT \ln K \quad (15)$$

These ideas were enshrined in the classic Gibbs free energy function ( $G$ ), defined as in eqn. 12 and eqn. 13 (valid at constant  $T$ ), and apparently recaptured in the relation involving the changes in the Gibbs free energy in a process (eqn. 14). ( $H$  is the enthalpy;  $\Delta S_{\text{total}}$  is the total entropy change including both the system and surroundings, *i.e.*  $\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$ .)

Thus, although all terms in eqn. 13 referred to the system,  $\Delta H$  was the heat given off to the surroundings (so equal to  $-T\Delta S_{\text{surroundings}}$ ), which leads to eqn. 14. This led to the view that an increase in overall entropy (positive  $\Delta S_{\text{total}}$ ) was associated with a decrease in  $G$ , and that these signified spontaneity and applied to all processes occurring naturally (*i.e.* without human intervention).

These developments evidence the famous aphorism of Clausius: ‘Die energie der Welt ist constant; die Entropie der welt strebt einem Maximum zu.’ Thus, entropy was seen as the ‘arrow of time’, in the sense that the Universe evolved relentlessly towards increasing disorder. (For a note on the ‘Clausius inequality’, see Appendix.) However, perhaps the most important application of these ideas was in the area of chemistry, as discussed below.

*Entropy in chemistry.*<sup>1,2</sup> Extending the above ideas to chemical reactions led to the view that eqns. 13 and 14 predicted the direction of chemical change, as the equilibrium constant ( $K$ ) was related to the standard Gibbs free energy change ( $\Delta G^0$ , eqn. 15). This implied that chemical reactions occurred in the direction of decreasing Gibbs free energy.

However, an interesting problem with these views is that many natural processes increase rather than decrease order, *i.e.* decrease randomness. A particularly serious challenge to the ‘arrow of time’ concept is the evolution of life in the Universe, which generates an enormous level of order rather than disorder.

Many chemical processes, *e.g.* crystallization and polymerization, produce a high level of order, but can be explained by a decrease in enthalpy, *i.e.* increase in  $\Delta S_{\text{total}}$  (*cf.* eqn. 14). However, human civilization, in general, aims to produce order rather than disorder. As this activity is part of nature, it again questions the viability of the entropy concept in general. Thus, the persistence of ‘pockets of order’ in the Universe cannot be denied. (It is noteworthy that, at the level of the overall Universe, there is no meaningful distinction between ‘system’ and ‘surroundings’: thus, eqn. 14, rather than eqn. 13, would apply.)

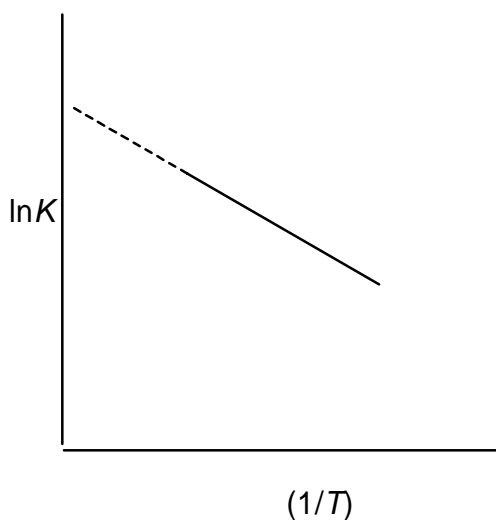
The experimental determination of entropy is also problematical, and underscores the limitations of entropy. A straightforward way to determine the standard entropy in a reaction is to expand eqn. 15 to eqn.16. Rearrangement of eqn. 16 leads to eqn. 17. It is seen that a plot of  $\ln K$  versus  $(1/T)$  should be linear with slope of  $(-\Delta H^0/R)$  and intercept of  $(\Delta S^0/R)$  (Fig. 2; ref. 2, p. 53). Thus, measuring the equilibrium constant ( $K$ ) as a function of temperature would lead to the standard enthalpy change ( $\Delta H^0$ ) and the standard entropy change ( $\Delta S^0$ ).

$$-RT \ln K = \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (16)$$

$$\ln K = -\Delta H^\circ/(RT) + \Delta S^\circ/R \quad (17)$$

However, it is noteworthy that the intercept (Fig. 2) leading to  $\Delta S^\circ$ , is obtained by extrapolating the above straight line to a value of  $(1/T) = 0$ , which implies  $T = \infty$ . Clearly such an exercise has no practical significance, and the value of  $\Delta S^\circ$  obtained thereby would not be meaningful.

Also, although standard entropy changes are more often determined *via* the variation of  $C_p$  with temperature, the above argument is one of definition. Thus,  $\Delta S^\circ$  as defined by eqn. 17 appears bereft of meaning or significance. (In fact, entropies of activation are determined *via* an extension of eqn. 17.<sup>5</sup>)



**Fig. 2.** The determination of the standard reaction entropy. A plot of  $\ln K$  vs.  $(1/T)$  yields a straight line of slope  $(-\Delta H^\circ/R)$ . Extrapolation of the line as shown by the dashed line yields the intercept  $(\Delta S^\circ/R)$ . (Symbols have the usual meaning as explained in the text.)

*Alternatives to entropy.* As seen above, although the entropy idea is apparently useful in practice, it is fundamentally dubious. (It is noteworthy that the criterion of randomness is based on the classical idea of entropy, as derived from the Carnot theorem.) These arguments apparently indicate that there might be a more fundamental concept that secretes the ‘illusion’ of entropy and randomness.

An interesting empirical observation apparently indicates that chemical reactions tend to minimize the ratio of energy to mass. In other words, reactions occur spontaneously to produce compounds with a lower overall energy to mass ratio than the reactants. This is generally true of associating reactions with equilibrium favoring products, *e.g.* the Diels-Alder reaction of cyclopentadiene (**1**) with maleic anhydride (**2**) (Fig. 3a).<sup>5</sup> The tricyclic adduct (**3**) is not only of higher mass than **1** or **2**, but also of lower energy content (reaction is exergonic).

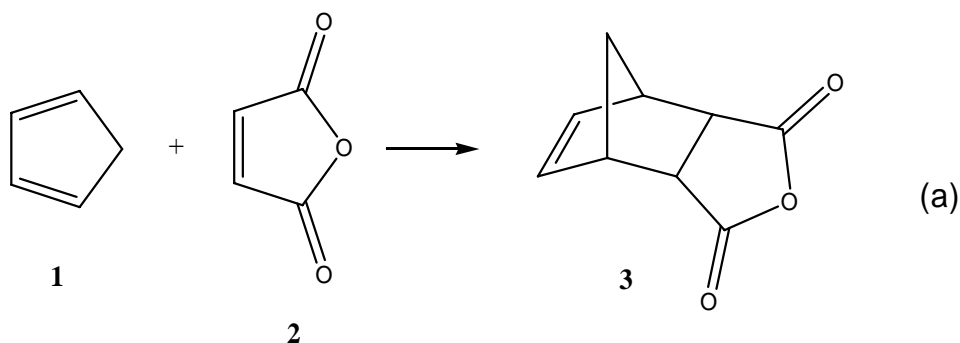
For the general dissociation process shown in Fig. 3(b), it can be shown that the sum of the energy to mass ratios of the products is generally minimized (*cf.* Appendix). Many such organic reactions are known, such as eliminations and extrusions, and are generally exergonic. They are considered to be entropy-driven, although they may also be enthalpy-driven.

*An intriguing possibility.* These arguments indicate that there exists a universal tendency towards a uniform distribution of energy in matter. This is the general implication of the above observation that chemical reactions apparently lead to products of high mass:energy ratio. Furthermore, it is noteworthy that mass and energy are interconvertible *via* the Einsteinian relationship (eqn. 18),  $c$  being the speed of light.<sup>4b</sup> An elementary (and perhaps oversimplified) interpretation of this is as follows.

$$E = mc^2 \quad (18)$$

$$(m_r/E_r) = c^{-2} \quad (19)$$

The energy ( $E$ ) in eqn. 18 refers to the energy associated with the rest mass along with other forms of energy possessed by the mass. The mass ( $m$ ) corresponds to the sum total of these forms of energy. In the case of chemical reactions, however, the mass of the atoms and molecules (normally) corresponds to the rest mass ( $m_r$ ), and its associated energy ( $E_r$ ) may be derived from eqn. 19.



**Fig. 3.** (a) The Diels-Alder cycloaddition of cyclopentadiene (1) with maleic anhydride (2) produces the tricyclic adduct 3 (stereochemistry is ignored). (b) The dissociation of reactant 'A' results in two products 'B' and 'C'.

Also, by the above arguments, a spontaneous chemical reaction may be seen as a process driven by the tendency of mass to possess the least amount of energy. This implies, in the limit, that the mass approaches the rest mass and its associated energy. In other words, the  $m/E$  ratio would tend towards the constant value of  $c^{-2}$  (eqn. 19). Importantly, note that  $m/E < c^{-2}$  in the reactants, as  $m$  is the rest mass, but  $E$  includes both the energy associated with  $m$  and other forms, *e.g.* chemical binding energy, part of which is lost upon reaction. (Although chemical binding energies are relatively small, eqn. 19 is useful in indicating that the  $m/E$  ratio cannot exceed the limiting value of  $c^{-2}$ .)

### **Conclusions**

The Carnot cycle, one of the cornerstones of thermodynamics, not only appears invalid *per se*, but also inappropriate as an analogy of a steam engine. The concept of entropy, derived on the basis of the Carnot cycle, is thus also questionable. Empirical observation suggests that natural phenomena tend to occur in the direction of maximum mass to energy ratio, which may well be a viable alternative to entropic randomness. This appears to be compatible with the emergence of life in the Universe, much better than does entropy.

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## Appendix

*The Clausius inequality.*<sup>1</sup> This is a direct consequence of eqn. 9 describing the efficiency of a Carnot cycle. It essentially states that, in a given process, the entropy changes of the system ( $dS$ ) and its environment ( $dS'$ ) are related as in eqn. A1.

$$\Delta S_{\text{total}} = (dS + dS') \geq 0 \quad (\text{A1})$$

Thus, the total entropy change ( $\Delta S_{\text{total}}$ ) is either zero (reversible process), or greater than zero (irreversible process). This requires that, whereas for a reversible process  $dS = -dS'$ , for an irreversible process  $dS > -dS'$ . This implies, however, that a quantity of heat ( $dQ$ ) may be transferred reversibly from the environment but absorbed irreversibly by the system. This is implausible, and also implies a breakdown of the definition of entropy for the irreversible case (eqns. A2 and A3).

$$dS = dQ/T \quad (\text{A2})$$

$$dS' > dQ/T \quad (\text{A3})$$

These inconsistencies are apparently a direct consequence of the energetic imbalance inherent in the Carnot cycle, as embodied in eqn. 9, and discussed at length above. (Eqns. A2 and A3 seemingly imply that less heat is absorbed by the system than is released by the environment, contradicting the first law of thermodynamics.)

*Mass-energy relationships in a dissociation process.* The object of this exercise is to show that the direction of chemical change is determined by the sum of the mass to energy ratios of the products (which should be greater than in the reactants). Thus, entropic disorder is not the driving force even for a dissociation reaction. (The associating case has been briefly discussed above.)

Consider the dissociating chemical reaction shown in Fig. 3(b). Let the masses of A, B and C be  $m$ ,  $m_1$  and  $m_2$  respectively, and their corresponding energies  $e$ ,  $e_1$  and  $e_2$ . Note that these energies correspond to the conventional enthalpies, and that these dissociation processes are generally considered to be strongly exergonic. (Conventionally, this would be due to increase in entropy.)

The sum of the mass to energy ratios of the two products,  $\sum(m_n/e_n)$ , would then be given by eqn. A4; eqn. A5 follows as there can be no loss of mass.

$$\sum(m_n/e_n) = (m_1/e_1) + (m_2/e_2) \quad (\text{A4})$$

$$m/e = (m_1 + m_2)/e \quad (\text{A5})$$

Expanding eqn. A4 and comparing it with eqn. A5 leads to the inequality in eqn. A6. This is seen to be valid by cross-multiplying to obtain eqns. A7 and A8. These are



seen to be valid for  $e > e_1$  and  $e > e_2$ , regardless of whether  $e > (e_1 + e_2)$  or  $e < (e_1 + e_2)$ . The latter case corresponds to the conventional entropy-driven process which occurs even if there is an overall increase in enthalpy. These prove the above proposal that  $\sum(m_n/e_n) > m/e$ .

$$(m_1e_2 + m_2e_1)/e_1e_2 > (m_1 + m_2)/e \quad (\text{A6})$$

$$(m_1ee_2 + m_2e_1e) > (m_1e_1e_2 + m_2e_1e_2) \quad (\text{A7})$$

$$m_1(e/e_1) + m_2(e/e_2) > (m_1 + m_2) \quad (\text{A8})$$

Eqn. A8 is not generally valid if  $e < e_1$  and  $e < e_2$ . These cases, of course, represent very highly endothermic reactions (in terms of enthalpy), *e.g.* the reverse of the reaction in Fig. 3a. They are thermodynamically disfavored despite the increase in entropy, and are usually driven by removal of products, *e.g.* vacuum pyrolyses.