

THERMODYNAMICS OF SELF-ORGANISING SYSTEMS

By

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THERMODYNAMICS OF SELF-ORGANISING SYSTEMS

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SCOPE AND CONTENT:

This dissertation is concerned with increasing the understanding of self-organising systems by a detailed investigation of several simple radiation absorbing models. We identify two important thermodynamic functions, the rate of entropy production and the free energy, which can be used to characterize the self-organising characteristics of the models. In addition to the minimal behaviour usually associated with the rate of entropy production we recognize a maximal behaviour. This mini-max principle for the entropy production rate, recognized in the models, is utilized as an evolutionary criterion for inanimate and animate systems. It is also demonstrated that the evolutionary character of the force dependent part of the entropy production rate for the models agrees with the earlier prescriptions of Prigogine and Li. Finally it is demonstrated that the multi-level models exhibit a kind of kinetic phase change which is accompanied by a population inversion in the models.

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CHAPTER 1

INTRODUCTION

Although there are still scientists who maintain that self-organisation, as exemplified by the life processes, cannot be described within the scope of present physical principles (e.g., Elsasser, 1958; and Polanyi, 1967 and 1968), there are others who have argued convincingly that current theory is adequate for an inclusive description and theory of self-organisation (e.g., Lotka, 1945; Schroedinger, 1944; Bertalanffy, 1950; and Prigogine and Wiame, 1946). It is with the aim of advancing our understanding in this area, and sharing the convictions of the latter authors, that we have undertaken a detailed investigation of the self-organising characteristics of a number of simple thermodynamic models.

The idea that the stable steady states of open thermodynamic systems, and in particular living systems, are characterised by a mini-max optimal state, rather than just a minimal state of the entropy production rate was first offered by Lotka (1945). Kirkaldy has attempted to locate the mini-max principle within the dissipation theorems of irreversible thermodynamics and has discussed application of the principle to both animate and inanimate systems (1964 IV; 1965 a, b; 1972).

It has long been recognised that constrained dissipative systems with appropriate initial conditions can spontaneously decrease their entropy and increase their store of available energy as a steady state

minimum in the dissipation rate is approached (Prigogine and Wiame, 1946; and Prigogine, 1955). This characteristic of self-organisation, as applied to living systems, has been designated by Prigogine and Wiame (1946) as "dynamic efficiency". The maximal part of the principle, emphasized in this contribution, adds a further essential dimension for it designates the tendency of self-organising (e.g., living) systems to spontaneously increase their intake of available energy as the system evolves towards stability with the environment (Kirkaldy, 1965 a and b). This characteristic was, long ago, recognized by Bertrand Russell and designated as "chemical imperialism" (Russell, 1927).

The failure of the principle of minimum entropy production to exactly predict the stable state has in the past been attributed to non-linear effects, and alternative potential functions (e.g., the local potential) (Glansdorff and Prigogine, 1964) and the thermo-kinetic potential (Li, 1962 a, b, c, d) have been sought which have a unique minimal behaviour. Such mathematical devices are unnecessary in the mini-max formalism, for the approach to a stable steady state along a given path must be a maximum or a minimum in the entropy production, whether the system is linear or not.

Following is a brief outline of this dissertation:

Chapter 2 is a critical review of certain important aspects of the thermodynamics of irreversible processes relevant to this study.

Chapter 3 discusses the concepts of "Organisation" and "Self-Organisation" from a thermodynamic viewpoint.

Chapter 4 presents the results of a detailed study of several radiation absorbing models. Although these models obey linear

differential equations they are highly non-linear thermodynamically.

Chapter 5 generalizes the results of Chapter 4 to include systems with non-linear differential equations.

Chapter 6 reviews several unusual applications of the thermodynamic procedures to inanimate and animate systems, and concludes by drawing a series of analogies between vital and non-vital systems.

CHAPTER 2

ELEMENTS OF THE THERMODYNAMICS OF IRREVERSIBLE PROCESSES

2.1 INTRODUCTION

Classical thermodynamics is restricted to the analysis of idealized reversible or quasi-reversible processes. Real processes such as the flow of heat, the transport of mass or electrical charge, and chemical reaction all lead to the irreversible production of entropy and form the subject matter for the Thermodynamics of Irreversible Processes*.

Onsager, in 1931, established the statistical basis of the T.I.P. Although there are critics of Onsager's formulation (esp. Truesdell, 1969), his well known reciprocal relations form the basis of most other formulations of the T.I.P. In 1940 Eckart derived a general method for calculating the rate of entropy production for various irreversible processes (e.g., heat flow, diffusion, etc.), thus unifying a previously unorganised set of equations. Tolman and Fine (1948) emphasized the importance of the irreversible production of entropy and modified the second law so that it could be written as an equality rather than an inequality. The monographs of De Groot (1952) and Prigogine (1955) have made important contributions to the synthesis of the subject. More

* henceforth called T.I.P.

recently, books by Katchalsky (1964) and Trincher (1965) have discussed important applications of the T.I.P. to biological problems. The recent monograph by Glansdorff and Prigogine (1971) on the "Thermodynamic Theory of Structure, Stability and Fluctuations" describes the most recent researches of Prigogine's group.

In view of these comprehensive works and of the review articles by Davies (1956), Chester (1963), Ono (1961), and Caplan (1971), we will not attempt to review the entire field of the T.I.P. Rather, we chose to examine those specific areas of the discipline which are closely connected with our own study.

2.2 GENERAL FORMULATION

The argument begins with the definition of the extensive function, S , the entropy of a system. The variation of the entropy, dS , can be defined as the sum of two terms

$$dS = d_e S + d_i S \quad (2-1)$$

where $d_e S$ is the entropy supplied to the system by its surroundings and where $d_i S$ is the entropy produced inside the system by irreversible processes.

For a closed system which can only exchange heat with its surroundings, the Carnot-Celsius theorem gives

$$d_e S = \frac{dQ}{T} \quad (2-2)$$

where δQ is the heat supplied to the system by its surroundings at an absolute temperature of T degrees. In an open system which can exchange matter with the surroundings, in addition to heat $d_e S$ contains another term which represents the entropy change due to the exchange of matter. Depending on the type of interaction between the system and its surroundings the entropy flow term, $d_e S$, can be positive, negative or zero. The second law of thermodynamics guarantees that the term $d_i S$, due to the internal production of entropy, must always be non-negative. For reversible processes $d_i S$ is zero and

$$dS = d_e S = \frac{\delta Q}{T} \quad (2-3)$$

In the presence of irreversible processes $d_i S$ is positive and

$$dS > \frac{\delta Q}{T} \quad (2-4)$$

Classical thermodynamics is concerned mainly with relations (2-3) and (2-4) and hence provides no other information about irreversible processes than the direction of evolution. The T.I.P. requires the calculation of the entropy production within the form of (2-1). When it is possible to find such an expression many questions about the evolution of irreversible systems can be answered. For an alternate general viewpoint, consider a small system, A, which is enclosed in a much larger system, B. If we assume that the global system, A + B, is isolated then we can write

$$dS = dS^A + dS^B \geq 0 \quad (2-5)$$

The second law requires that

$$d_i S^A \geq 0 \quad \text{and} \quad d_i S^B \geq 0 \quad (2-6)$$

However, it is possible to have one of the terms in (2-5), say dS^A , negative if

$$dS^B \geq |dS^A| \quad (2-7)$$

This result is of relevance to biological systems which attempt to increase their structure (order) by surrendering entropy to the surroundings. Schroedinger in "What is Life" (1944) emphasized the importance of negentropy (negative entropy) to biological systems in this way.

2.3 THE LINEAR REGIME

2.3.1 Local Equilibrium

Let us assume that a given thermodynamic system is divided into small but macroscopic regions. At equilibrium all the thermodynamic quantities, and specifically the entropy, are functions of the energy of the subsystem E , the volume of the subsystem V and the mole number n_γ of each species in the local volume. That is, $S = S(E, V, n_\gamma)$. If we now consider a globally non-equilibrium system it can be conjectured that "local equilibrium" nonetheless prevails in each small section of

the system and that the local expression, $S = S(E, V, n_\gamma)$, remains true for non-equilibrium systems. This means that the non-equilibrium entropy depends only on the variables E, V and n_γ and not on new variables such as reaction rate or gradients.

Thus, we can write the total differential of the entropy, dS , according to the classical Gibb's formula

$$dS = \frac{dE}{T} + \frac{P}{T} dV - \sum_{\gamma} \left(\frac{\mu_{\gamma}}{T} \right) dn_{\gamma} \quad (2-8)$$

where T is the absolute temperature, P the pressure and μ_{γ} the chemical potential of species γ and E, V and n_{γ} are the local variables already defined.

The domain of validity of this conjecture of Local Thermodynamic Equilibrium (L.T.E.) is still not completely known from a microscopic viewpoint. However, Prigogine (1949) has shown that the assumption of L.T.E. is valid for gases which are characterized by a non-equilibrium molecular distribution function, f , which can be written

$$f \approx f_0 + f_1 \quad (2-9)$$

where f_0 is the equilibrium distribution function and f_1 is the first order correction. In addition, Prigogine (1949) also showed that L.T.E. was valid in systems involving sufficiently slow chemical reactions. As we shall see later, the results of most experiments agree with the consequences of L.T.E. The exceptions being in processes such as shock waves evolving far from equilibrium.

2.3.2 Forces and Fluxes

In the thermodynamics of irreversible processes it is assumed that certain "forces" and their conjugate "fluxes" exist. These forces are, for example, temperature and chemical potential gradients with conjugate flows of conservative quantities like energy and mass. Empirically, the fluxes and forces are not independent, combining in expressions such as Fourier's law relating heat flow and temperature gradient

$$\vec{J}_q = -\lambda \nabla \vec{T} \quad (2-10)$$

where λ is the thermal conductivity, the Hartley-Fick law relating the flow of matter to the chemical potential gradient

$$\vec{J}_m = -D \nabla \vec{\mu} \quad (2-11)$$

where D is the diffusion coefficient and Ohm's law relating the electrical current and the potential gradient

$$\vec{J}_e = -\gamma \nabla \vec{V} \quad (2-12)$$

where γ is the electrical conductivity. These relations are accurate when the gradients are small and when only a single independent flux is identifiable.

When two or more of these flows occur simultaneously in the same region of space they interfere with each other and give rise to cross effects. For example, when heat conduction and electrical

conduction are occurring simultaneously, thermoelectric cross effects such as the Peltier effect in which heat is evolved at an isothermal metal-metal junction due to the flow of electrical current across the junction occur (see Callen, 1948).

In the linear regime it is assumed that the forces and fluxes are related by

$$J_i = \sum_k L_{ik} X_k \quad (2-13)$$

where X_k is the k^{th} force, and J_k is the conjugate flux. If the off-diagonal terms in (2-13) are non-zero, there exists a coupling between two irreversible processes.

The identification of an appropriate set of fluxes and forces is achieved by combining (2-8) with the differential form of the conservation relations (mass, energy, momentum, etc.) which yields a bilinear expression for the rate of internal entropy production (De Groot and Mazur, 1962)

$$\frac{d_i S}{dt} = \sum_k J'_k X'_k \quad (2-14)$$

While this expression does not uniquely define the appropriate forces and fluxes, it suggests at least one identification to the effect that the forces are the gradients of intensive parameters in the entropy representation and that the fluxes are proportional to the time rate of change of the extensive parameters (Callen, 1960).

For example, in the case of heat flow the intensive parameter

is $1/T$, and thus the force can be defined as

$$\vec{X}_q = \nabla \left(\frac{1}{T} \right) = - \frac{1}{T^2} \nabla (T) \quad (2-15)$$

If energy alone is being transported, we can write the flux J_q (i.e., $\frac{dE}{dt}$) as

$$\vec{J}_q = L_{qq} \vec{X}_q = - \frac{L_{qq}}{T^2} \nabla (T) \quad (2-16)$$

and by comparison with Fourier's law (2-10), identify the kinetic coefficient L_{qq} as

$$L_{qq} = T^2 \lambda \quad (2-17)$$

Since this representation is not unique, the problem of the identification of forces and fluxes will be referred to again in the next section.

2.3.3 Onsager's Theory: The Reciprocal Relations

The reciprocal relations and an equivalent variational principle form the essence of Onsager's 1931 papers. We include here a brief outline of the proof.

Consider an adiabatically insulated system which is defined by a set of (local) extensive parameters A_i (r parameters such as volume, mass, etc.) and assume that the variables take the values A_i^0 in equilibrium. Then we can define a new set of local extensive variables α_i such that

$$\alpha_i = A_i - A_i^{\circ} \quad (i = 1 \dots r) \quad (2-18)$$

At equilibrium, the local entropy is a function of the A_i° and if we assume L.T.E. then we can write the local entropy as a function of the α 's, namely

$$S = S(\alpha_1 \dots \alpha_r) \quad (2-19)$$

The maximum value of S as defined by (2-19) occurs at equilibrium, that is

$$\begin{aligned} S_{\max} &= S(0, 0, \dots, 0) \\ &\equiv S_0 \end{aligned} \quad (2-20)$$

For systems not too far from equilibrium, we write a Taylor expansion of the entropy about the equilibrium state. If we retain the lowest non-zero terms in the expansion, then for a deviation from equilibrium

$$\Delta S \equiv S - S_0 = -\frac{1}{2} \sum_i \sum_k g_{ik} \alpha_i \alpha_k \quad (2-21)$$

where terms linear in α_i necessarily vanish, and where the

$$g_{ij} = \left(\frac{\partial^2 S}{\partial \alpha_i \partial \alpha_j} \right)_0$$

Differentiating (2-19) and (2-21) with respect to time, we obtain the parallel result that

$$\frac{dS}{dt} = \sum_k \frac{\partial S}{\partial \alpha_k} \frac{\partial \alpha_k}{\partial t} \equiv \sum_k X_k J_k \quad (2-22)$$

and

$$\frac{d(\Delta S)}{dt} = \frac{dS}{dt} = \sum_i \sum_k g_{ij} \alpha_i \dot{\alpha}_k \quad (2-23)$$

Hence by comparison of (2-23) and (2-22) we can make the correspondence that the X_k are given by

$$X_k = \sum_i g_{ik} \alpha_i \quad (2-24)$$

and the fluxes J_k are given by

$$J_k = \dot{\alpha}_k \quad (2-25)$$

These identifications, which are essential to Onsager's theorem, are consistent with the results of the previous section where the forces X_k were identified with the gradients of entropy representation intensive parameters, and the fluxes were identified with the time rate of change of the conjugate extensive quantities. Onsager's Theorem states that if the X_i or the α_i according to this identification are independent, then the matrix of coefficients in (2-13) is symmetric, viz.

$$L_{ik} = L_{ki} \quad (2-26)$$

As Coleman and Truesdell (1959) point out, an arbitrary set of fluxes and forces will not produce the Onsager reciprocal relations. However, when a set of independent forces and fluxes, matched to the invariants of the system, are chosen on the basis of (2-24) and (2-25) then the reciprocal relations are valid. (De Groot (1952) presents several alternate choices of acceptable forces and fluxes.) The experimental evidence cited by Miller (1960) supports this contention.

Onsager derived the reciprocal relations by considering fluctuations (i.e., $\alpha_i \neq 0$) in an "aged" system, i.e., a system which has been isolated for a sufficient time to be near equilibrium. He then assumed that deviations from equilibrium (i.e., the α_i) have a probability distribution $W(\alpha_i)$ of the Boltzmann form

$$W(\alpha_1 \dots \alpha_r) d\alpha_1 \dots d\alpha_r = \frac{e^{(\Delta S/K_B)} d\alpha_1 \dots d\alpha_r}{\int_{-\infty}^{\infty} \dots \int_{-\infty}^{\infty} d\alpha_1 \dots d\alpha_r} \quad (2-27)$$

where K_B is the Boltzmann constant and ΔS is defined by (2-21). For a system fluctuating about equilibrium it was assumed that the principle of microscopic reversibility holds. That is, under equilibrium conditions, any molecular process and the reverse of the process occur at the same rate. Finally, Onsager made the key conjecture that on the average, the

laws of decay of fluctuations are identical with the macroscopic laws of relaxation (i.e., equation (2-13)), and that the fluctuating molecular variables are even functions of particle velocities. The argument then leads directly to (2-26).

In the presence of an external magnetic field \vec{B} or in a system rotating with angular velocity, \vec{W} , the reciprocal relations (2-27) must be modified to read

$$L_{ik}(\vec{B}, \vec{W}) = L_{ki}(-\vec{B}, -\vec{W}) \quad (2-28)$$

Casimir (1945) generalized Onsager's treatment to include odd as well as even variables. Thus, if α_i and α_k are both even or both odd functions of the molecular velocities, then the reciprocal relations are given by (2-28). In the event that one variable is odd and one even, the reciprocal relations gain a minus sign. The most general form of the reciprocal relations can be written

$$L_{ik}(\vec{B}, \vec{W}) = \epsilon_i \epsilon_j L_{ki}(-\vec{B}, -\vec{W}) \quad (2-29)$$

where $\epsilon_i = 1$ for α_i even and $\epsilon_i = -1$ for α_i odd.

De Groot and Mazur (1954) extended Onsager's proof (which is strictly valid only for scalar processes such as chemical reactions or relaxation processes) to include vector processes (heat conduction, diffusion) and tensorial processes (viscous flow). It should be noted that in isotropic systems processes which interact through non-zero cross-coefficients must have the same tensorial character

(Curie's Theorem, e.g., De Groot and Mazur, 1962).

2.3.4 Onsager's Variational Principle (Onsager, 1931)

The kinetic entropy balance equation of an open system in which dissipative processes are occurring is usually written (De Groot and Mazur, 1962) as

$$\frac{dS}{dt} = - \int_V \vec{J}_S \cdot \vec{n} \, dA + \frac{d_i S}{dt} \quad (2-30)$$

where the entropy flux, \vec{J}_S , is directly related to the flow of energy, mass, momentum and charge across the surface bounding the system, and the source term $d_i S/dt$ is designated as "the rate of entropy production" (usually abbreviated to "entropy production" or "dissipation") which is directly related to the irreversible processes (i.e., production of low quality heat) which is occurring within the system. In the linear phenomenological scheme of Onsager, the entropy production per unit volume, σ , is a positive definite bilinear function of the independent forces and fluxes, viz.

$$\sigma = \sum_i J_i X_i \quad (2-31)$$

where

$$\frac{d_i S}{dt} = \int_V \sigma \, dV \quad (2-32)$$

and the fluxes and forces are related by the linear relations with constant coefficients

$$X_i = \sum_j R_{ij} J_j \quad (2-33)$$

where the inverse form of the reciprocal relations

$$R_{ij} = R_{ji} \quad (2-34)$$

are assumed to hold. Onsager noted that this physical behaviour could be summarized completely in the variational principle

$$\delta \int_V (\sum_i J_i X_i - 1/2 \sum_i \sum_k R_{ik} J_k J_i) dV = 0 \quad (2-35)$$

(maximum)

where the variation is performed about equilibrium under the constraints $X_i = \text{constant}$. That is, subject to (2-34), the Euler-Lagrange equation for (2-35) is equation (2-33). The variation is to be understood physically as due to fluctuations in the fluxes which transiently violate the relations (2-33).

Following Onsager, further constraints can be imposed on (2-35) to define the steady state ($dS/dt = \text{constant}$). If the boundary fluxes are fixed so that

$$\delta \int_V \vec{J}_S \cdot \vec{n} dA = 0 \quad (2-36)$$

then in view of $X_i = \text{constant}$ and (2-30) the variational principle becomes

$$\delta \int_V (\sum_i \sum_k R_{ij} J_k J_i) dV = 0 \quad (2-37)$$

(minimum)

which is a microscopic form of the principle of minimum dissipation.

Onsager also noted that under constraints on the internal fluxes such that

$$\int_V (\sum_i J_i X_i) dV = \int_V (\sum_i \sum_k R_{ij} J_k J_i) dV \quad (2-38)$$

and holding $X_i = \text{constant}$, the variational principle (2-35) becomes

$$\delta \int_V (\sum_i J_i X_i) dV = 0 \quad (2-39)$$

(maximum)

Interpreting this macroscopically, Onsager states that "Restrictions (on the internal fluxes) can only decrease the rate of entropy production or cause no change" (ibid).

In summary, a macroscopic initial condition which can be constructed out of cumulative fluctuations of one or more of the fluxes, with no change in the forces at the system boundary, will be followed by a relaxation of the system to a minimum in the entropy production rate. At the same time, a system with internal constraints on fluxes, such as provided by sluggish transient metastable states (Onsager illustrated this kind of constraint by a crack in a crystal which is conducting heat) may tend toward a

maximum in the entropy production as the internal constraints slowly relax toward internal stability (for example as the crack, due to surface tension, spheroidizes and anneals out). Thus the evolutionary path of a system which is prepared at time $t = 0$, with appropriate internal and external constraints will relax, within these constraints, along a path which lies in general on a saddle surface of the entropy production rate (Kirkaldy, 1964 IV; and 1965 a, b).

2.3.5 Prigogine's Formulation of the Minimal Principle

One of the most interesting reasons for studying the properties of steady states comes from the realization that the state of an adult living organism is that of a steady open system. Bertalanffy (1950) maintained that living systems do not operate in violation of the second law of thermodynamics since they are "open" and thus able to surrender their excess entropy to their surroundings. The entropy maximum principle does not apply to the living system alone, but rather to the totality of the living system and its environment. Prigogine and Wiame (1946) have proved that:

- (1) steady states in open systems are not defined by maximum entropy but rather by the approach to minimum entropy production,
- (2) the entropy may decrease in such systems and
- (3) that steady states with minimum entropy production are usually stable.

This tendency to a minimum in the entropy production rate (concomitant with an increase in the order of a system) has been designated as

"dynamic efficiency" by Prigogine. In contrast to Onsager, Prigogine has offered a proof of the principle of minimum entropy production* in a continuum (macroscopic) formulation.

Consider a materially closed discontinuous (Prigogine, 1967) system in which there are two independent irreversible processes, the simultaneous diffusive flow of matter and heat in a thin membrane. If the system is not too far from equilibrium we can write

$$J_q = L_{qq} X_q + L_{qm} X_m \quad (2-40)$$

and

$$J_m = L_{mq} X_q + L_{mm} X_m \quad (2-41)$$

where J_q and J_m are the heat and mass fluxes, respectively, and where X_q and X_m are their conjugate forces. The L_{qq} , etc., are assumed to be constant.

Following (2-14), we can write the entropy production as

$$\frac{d_i S}{dt} = J_q X_q + J_m X_m > 0 \quad (2-42)$$

Utilizing the linear relations (2-40) and (2-41) and Onsager's reciprocal relations $L_{qm} = L_{mq}$, we can write (2-42) as

* The Principle of Minimum Entropy Production, hereafter, P.M.E.P.

$$\frac{d_i S}{dt} = L_{qq} X_q^2 + 2L_{mq} X_q X_m + L_{mm} X_m^2 > 0 \quad (2-43)$$

Now let us assume that the force X_q is constrained to some non-zero value. Differentiation of (2-43) with respect to X_m leads to

$$\begin{aligned} \frac{\partial}{\partial X_m} \left(\frac{d_i S}{dt} \right) &= 2(L_{mq} X_q + L_{mm} X_m) \\ &= 2J_m = 0 \end{aligned} \quad (2-44)$$

Since $J_m = 0$ for the stationary state (recalling that X_m is unconstrained and the system is closed for mass), the conditions

$$J_m = 0 \quad \text{and} \quad \frac{\partial}{\partial X_m} \left(\frac{d_i S}{dt} \right) = 0 \quad (2-45)$$

are completely equivalent provided the linear relations (2-40) and (2-41) hold.

In the case of n forces $X_1 \dots X_n$ of which $X_1 \dots X_k$ are kept constant and where the system is closed for flows $J_{k+1} \dots J_n$, we have for the stationary state (De Groot, 1952)

$$J_{k+1} = \dots = J_n = 0 \quad (2-46)$$

These conditions are equivalent to the minimum conditions on the entropy production

$$\frac{\partial}{\partial X_j} \left(\frac{d_i S}{dt} \right) = 0 \quad (j = k + 1 \dots n) \quad (2-47)$$

The theorem can easily be rewritten in integral form for continuous systems. The optimum is, in general, a minimum since $d_i S/dt$ is a positive definite quadratic form (e.g., (2-43)).

The P.M.E.P. has been examined by many authors. Gyarmati (1967) has shown that the Prigogine principle is an alternative formulation of Onsager's principle valid for the stationary case. Callen (1957) studied the principle from the viewpoint of a microscopic density matrix and concluded that "in the steady state of an irreversible process the density matrix is such as to minimize the rate of entropy production". Klein and Meijer (1954); and Klein (1955, and 1958) examined the validity of the P.M.E.P. by the use of specific models. They too concluded that if the system is not too far from equilibrium, the P.M.E.P. predicts the steady state. Denbigh (1952) demonstrated that in general the stationary state of an open system is a state of minimum entropy production only as an approximation when the system is very close to equilibrium. Trincher (1961), although appreciating the usefulness of Prigogine's Theorem, advises that care be taken in its application. In particular, the P.M.E.P. is not valid during the phase of embryogenesis of a warm blooded animal. In fact, in this phase there is a continuous increase in the heat generated per unit mass of the differentiating organism (i.e., $d/dt(d_i S/dt) > 0$).

Kirkaldy (1964 IV) has suggested that since Onsager's steady state minimax principle of dissipation and Prigogine's P.M.E.P. share a

common Euler-Lagrange equation, their configuration spaces may be combined to form a single potential surface. Thus, a stable steady state may be characterized by a saddle point in a configuration space including both fluctuations and macroscopic relaxation.

Although we have sampled some of the areas of linear irreversible thermodynamics, we are still hampered by the constraint of linear force-flux relations. In the next section we briefly discuss the non-linear regime.

2.4 THE NON-LINEAR REGIME

Most advances in this area are due to Prigogine and his associates so the reader is referred to the bibliography of the book by Glansdorff and Prigogine (1971) for supplementary references.

A great deal of effort has been expended in trying to find a variational principle free of the restrictions on the P.M.E.P. Kikuchi (1961) and Kikuchi and Gottlieb (1961) have defined a function called the "persistence" which takes a maximum in the steady state. Their method of specifying the steady state (based on the path probability method of Onsager and Machlup, 1953) is valid for non-linear systems far from equilibrium provided the stable steady state exists.

Li, in a series of papers (1962 a, b, c), has defined a "Thermokinetic Potential" which takes a minimum at the steady state in non-linear systems. It is again specified that a stable steady state of the system exists. Li (1962 d) also showed that the "persistence" of Kikuchi and his own "thermokinetic potential" agree with each other to within a constant numerical factor.

Following Prigogine let us examine the entropy production in detail. We define the rate of entropy production, P , as

$$P = \frac{d_i S}{dt} = \int_V \sigma dV = \int_V \sum_i J_i X_i dV \geq 0 \quad (2-48)$$

and following Glansdorff and Prigogine (1954) we decompose the time change $d\sigma$ into two parts, namely

$$\begin{aligned} d\sigma &= d_X \sigma + d_J \sigma \\ &= \sum_k J_k dX_k + \sum_k X_k dJ_k \end{aligned} \quad (2-49)$$

Under the restrictive conditions of the previous section, it is a trivial result that

$$d_X \sigma = d_J \sigma = \frac{1}{2} d\sigma \quad (2-50)$$

Thus, in the linear regime, we have the evolution principle

$$d_X \sigma = d_J \sigma = \frac{1}{2} d\sigma \leq 0 \quad (2-51)$$

Postulating mechanical equilibrium and time independent boundary conditions, Glansdorff and Prigogine (ibid) showed that the inequality

$$d_X P = \int_V d_X \sigma dV \leq 0 \quad (2-52)$$

holds for the entire range of validity of the T.I.P. We will not here give the complete proof. Rather we will illustrate the theorem with a specific example. In particular, we choose the case of heat conduction in a solid. Using the standard definition of heat flux $J_q \equiv W$ and $X_q \equiv \nabla \left(\frac{1}{T}\right)$ we write

$$\begin{aligned} \frac{\partial X^P}{\partial t} &= \int_V \vec{W} \cdot \frac{\partial}{\partial t} (\text{grad } T^{-1}) dV \\ &= \int_V \vec{W} \cdot \text{grad} \left(\frac{\partial T^{-1}}{\partial t}\right) dV \end{aligned} \quad (2-53)$$

Integrating (2-53) by parts, where the surface integral is over the surface Ω which bounds the system of volume V , we get the result that

$$\frac{\partial X^P}{\partial t} = \oint_{\Omega} W_n \frac{\partial T^{-1}}{\partial t} d\Omega - \int_V \left(\frac{\partial T^{-1}}{\partial t}\right) \text{div } \vec{W} dV \quad (2-54)$$

Since we are assuming time independent boundary conditions the surface integral in (2-54) vanishes.

The equation of conservation of energy is

$$\rho C_v \frac{dT}{dt} + \text{div } \vec{W} = 0 \quad (2-55)$$

where ρ is the density and C_v the specific heat. Substituting for $\text{div } \vec{W}$ in (2-54) we then obtain

$$\frac{\partial X^P}{\partial t} = - \int_V \rho \frac{C_V}{T^2} \left(\frac{dT}{dt} \right)^2 dV \leq 0 \quad (2-56)$$

which is the required result since the specific heat C_V is positive in the entire range of validity of the T.I.P.

We should emphasize that although the change in entropy production associated purely with the time rate of change of the forces is negative, nothing has been said about dP itself. While the statement that $d_X P \leq 0$ is an interesting criterion for the direction of change, $d_X P$ is not a total differential (and hence a true potential function). Thus unless an integrating factor can be found the result has little practical significance. Li (1963), however, has succeeded in finding an integrating factor for an interesting class of problems in heat conduction.

Glansdorff (1960) has generalized the result (2-52) to include the possibility of steady fluid flow in addition to the processes of chemical reaction, heat flow and diffusion, which were considered in the earlier contribution (Glansdorff and Prigogine, 1954).

In 1964, Glansdorff and Prigogine constructed a general (and more practical) evolution criterion by showing that they could find a quantity ϕ such that

$$d\phi = \int dV \sum_i J_i dX_i \leq 0 \quad (2-57)$$

where the J_i and X_i include mechanical processes as well as the usual fluxes and forces. The important point of this contribution is that while

$d\phi$ is not, in general, a total differential, it is possible to transform (2-57) into a total differential in the neighborhood of the steady state. The associated "local potentials" depend not only on the thermodynamic variables such as temperature and velocity but also on the steady state variables. Prigogine and co-workers have demonstrated the application of this principle to the variational solution of problems in fluid dynamics and heat flow (e.g., Schechter and Himmelbau, 1965; and Glansdorff, 1966). Since there are classical methods available for obtaining the same results, we must regard these contributions as of essentially mathematical interest.

2.5 ON A GENERALIZED MINIMAX PRINCIPLE FOR ANALYTIC SYSTEMS (J.S. Kirkaldy, 1972)

The P.M.E.P. and its various generalizations for non-linear systems, which contain the restrictions to local equilibrium conditions, are completely inadequate for the description of the broadest class of self-organizing systems. A general principle, which allows excursions outside of local equilibrium, will almost certainly have a mini-max character. This was clearly suggested in the application of Onsager's Microscopic Fluctuation Dissipation Theorem to the steady state. Reviewing that theorem, as presented in section 2.3.4, we recognized two classes of regression paths: those which occur when all fluxes are fixed at the boundaries so relaxation must always be into the internal heat bath, and those which occur without the boundary constraints but under internal constraints which violate local equilibrium so relaxation must be at least in part into the external heat baths. These two classes of paths led to

minima and maxima in the dissipation, respectively.

The macroscopic principles like P.M.E.P. assume unique flux-force relations (or equivalently, local equilibrium) and thereby insist that the regression is always into the internal heat baths. Hence their unique minimal character.

The minimax imperative outlined above can be attributed, in general, to every system's competitive tendency to simultaneously equilibrate with its internal heat sources and sinks and with the external sources and sinks. The local equilibrium condition, which is by no means general, tends to block any paths of relaxation into the external sources and sinks.

If we conjecture that a generalized potential function of mini-max character exists on the basis that very broad classes of stable steady states exist, then its construction is essentially determined by its tautologous character (an optimum must be either a maximum or a minimum) and the mathematical analyticity (infinite differentiability) which should characterize a multivariate potential function defining stability in the sense of the Le Chatelier Perturbation Principle (J.S. Kirkaldy, unpublished M.S., 1972).

Specifically, for a system represented by the set of system variables (x_i, y_i) there must exist a multivariate complex function of the variables $x_i + iy_i$, of the form

$$\pi = \xi + i\eta \quad (2-58)$$

which is analytic (i.e., satisfying the Cauchy-Riemann (C-R) or Laplace

differential equations). If the variables x_i, y_i are measured from an origin at the steady state ($^{\circ}$) then both ξ and η are potential functions of the form

$$\xi = \xi^{\circ} + \Delta^2 \xi = \frac{\partial^2 \xi}{\partial x_i^2} x_i^2 + 2 \frac{\partial^2 \xi}{\partial x_i \partial y_i} x_i y_i + \frac{\partial^2 \xi}{\partial y_i^2} y_i^2 + \dots \quad (2-59)$$

and

$$\eta = \eta^{\circ} + \Delta^2 \eta = \frac{\partial^2 \eta}{\partial x_i^2} x_i^2 + 2 \frac{\partial^2 \eta}{\partial x_i \partial y_i} x_i y_i + \frac{\partial^2 \eta}{\partial y_i^2} y_i^2 + \dots \quad (2-60)$$

subject to

$$\Delta \xi = \Delta \eta = 0 \quad (2-61)$$

In view of the C-R or the corresponding Laplace equations, (2-59) and (2-60) represent a complementary pair of saddle surfaces, with the stable steady state defined by the saddle point at the origin.

We emphasize that this is an existence theorem only. In practice it will be very difficult to identify the variables x_i, y_i which compliment the functions ξ, η . Nonetheless, as we shall demonstrate in this thesis via exact solutions for a number of specific radiation-absorbing systems, this basic analytic pattern is generated.

2.6 NON-ANALYTIC SELF-ORGANISING SYSTEMS

For the thermodynamic description of the most general type of evolutionary processes (morphogenesis or evolution in the biological world,

for example) a further generalization is required. The most successful early theoretical discussion of morphogenesis is due to Turing (1952), who investigated the stability of the non-linear differential equations describing certain diffusive autocatalytic reactions. Prigogine and co-workers (e.g., 1969) have expanded this development substantially during the past few years. It has been found that for certain critical values of the rate parameters that the solution of the differential equations branches.

• The new branch (or branches), when attained as through a fluctuation, necessarily involves a break in the symmetry of the main branch. Such symmetry-breaking transitions have long been recognized in hydrodynamics (e.g., Chandrasekhar, 1961) and in the field of phase transformations (Kirkaldy, 1962). More recently, transitions of the type conceived by Turing have been observed by Zhabotinski (1964), and Herschkowitz-Kaufman (1970). Prigogine and co-workers have recently suggested the relevance of this approach to the description of biological evolution (Nicolis, 1971; Prigogine and Nicolis, 1971; and Prigogine et al., 1972).

Kirkaldy conjectured in 1965 that the hierarchy of symmetry-breaking steps and intermediate relaxation processes which characterize morphogenesis or biological evolution can be represented as a discontinuous path on a saddle surface of the entropy production rate. The discontinuities are conceived as dissipation-increasing steps which carry the path upwards towards the saddle point while the intermediate relaxation processes carry the path towards a succession of local minima. A somewhat analogous description might be imposed on the analytic representation given above by associating the symmetry-breaking events with singularities in the potential

surfaces.

We have searched without success for a comprehensive model of a radiation-absorbing system which generates symmetry-breaking transitions of the type described here. However, a three-level model to be described, which is capable of masing action, does appear to generate certain qualitative features of such transitions.

CHAPTER 3

QUANTIFICATION OF ORGANISATION

3.1 INTRODUCTION

The meaning of the term "organisation" is both familiar and elusive. Examples of organisations are the federal government, General Motors and the Rotary Club. Biological systems from unicellular algae to man are examples of organised systems of a different variety. It may be said that atoms can be organised into molecules and that molecules can be organised into multi-molecular complexes. These examples are all familiar and it is intuitively recognized that the systems are "organised" in some fashion. Yet it is not at all obvious what features of the systems suggest this designation. Furthermore, it is not obvious how one should measure the relative "organisation" of the different systems.

3.2 DEFINITION OF ORGANISATION

We first point out the fact that "organisation" and "order" are not synonymous (although they are related). The disorder of a system is indexed by its entropy (or the order is indexed by its negentropy). A highly ordered system will have a small entropy (e.g., a crystal) while a disordered system will have a large entropy (e.g., a gas). Klein (1953) has pointed out that "organisation" and "negentropy" are rarely equivalent

from considerations of the third law of thermodynamics, viz., "at absolute zero all (perfect crystalline) states of the same thermodynamic system have the same entropy". For example, a mixture of atoms of H, C, O, and S, may at zero degrees be in the form of a simple crystalline solid, or alternatively the same atoms may be arranged in a biochemical molecular crystal. The bio-molecular thermodynamic state is more "organised" according to our conventional notions than is the simple solid system. Klein also shows that a large entropy does not exclude the possibility of a high degree of organisation. Reconsider the difference between the "organisation" of the thermodynamic state of a bio-molecule and that of its crystallized constituent atoms when considered at absolute zero. Since the entropies of the states are the same the missing factor must lie elsewhere. Considering the bond energies required to maintain a complex biochemical structure it is easily seen that there will be a large difference in the zero point energies of the two systems. It seems reasonable therefore to include an energy term in the definition of organisation. In an isothermal system at constant volume, the logical candidate for the measure of organisation is the Helmholtz free energy of the system

$$A = U - TS \quad (3-1)$$

where U is the internal energy, S is the entropy and T is the absolute temperature. At absolute zero the organisation is to be measured purely by the energy term while for non-zero temperatures the organisation is measured by the sum of the energy and T times the negentropy. In other

words, organisation is defined as the available energy of an isothermal system. Because it includes the negentropy, it is a non-conservative quantity.

3.3 SELF-ORGANISATION

Self-organisation implies a spontaneous increase in the free energy of a system under fixed external conditions. In general, the term applies to thermally and materially open systems irreversibly interacting with fixed environments. Schroedinger (1944) long ago pointed out the significance of a flow of negative entropy from the environment into a biological system in order to maintain its viability and also suggested the importance of an energy flow via the energy content of food.

For a simple input-output irreversible system the entropy balance can be written (Kirkaldy, 1964 a, b)

$$\frac{dS}{dt} = J_S^{\text{in}} - J_S^{\text{out}} + \frac{d_1 S}{dt} \quad (3-2)$$

where the J's represent total fluxes of entropy. Similarly, we can write a free energy balance

$$\frac{dA}{dt} = J_A^{\text{in}} - J_A^{\text{out}} + \frac{d_1 A}{dt} \quad (3-3)$$

where $d_1 A/dt$ represents the rate of creation of free energy within the system. Since energy U is conserved in the universe, we also have

$$\frac{dU}{dt} = J_U^{\text{in}} - J_U^{\text{out}} \quad (3-4)$$

Combining (3-2), (3-3) and (3-4) we obtain

$$\begin{aligned} \frac{dS}{dt} &= \left(\frac{J_U^{\text{in}} - J_A^{\text{in}}}{T} \right) - \left(\frac{J_U^{\text{out}} - J_A^{\text{out}}}{T} \right) - \frac{1}{T} \frac{d_i A}{dt} \\ &= J_S^{\text{in}} - J_S^{\text{out}} - \frac{1}{T} \frac{d_i A}{dt} \end{aligned} \quad (3-5)$$

Accordingly, the rate of dissipation of free energy

$$- \frac{d_i A}{dt} = T \frac{d_i S}{dt} \quad (3-6)$$

In words, the dissipation of free energy is associated with a loss of information, the energy part of A always being conserved.

The very general definitional relation (3-6) is not to be confounded with the thermodynamic relation for systems which are isothermal with their surroundings (Denbigh, 1951), viz.,

$$- \frac{dA}{dt} = T \frac{d_i S}{dt} \quad (3-7)$$

for here there is the further condition that all

$$J_U = - T J_S \quad \text{or} \quad J_A = 0 \quad (3-8)$$

The meaning of the free energy balance for an open system can be clarified further by means of the schematic flow diagram shown in Fig. 3.1.

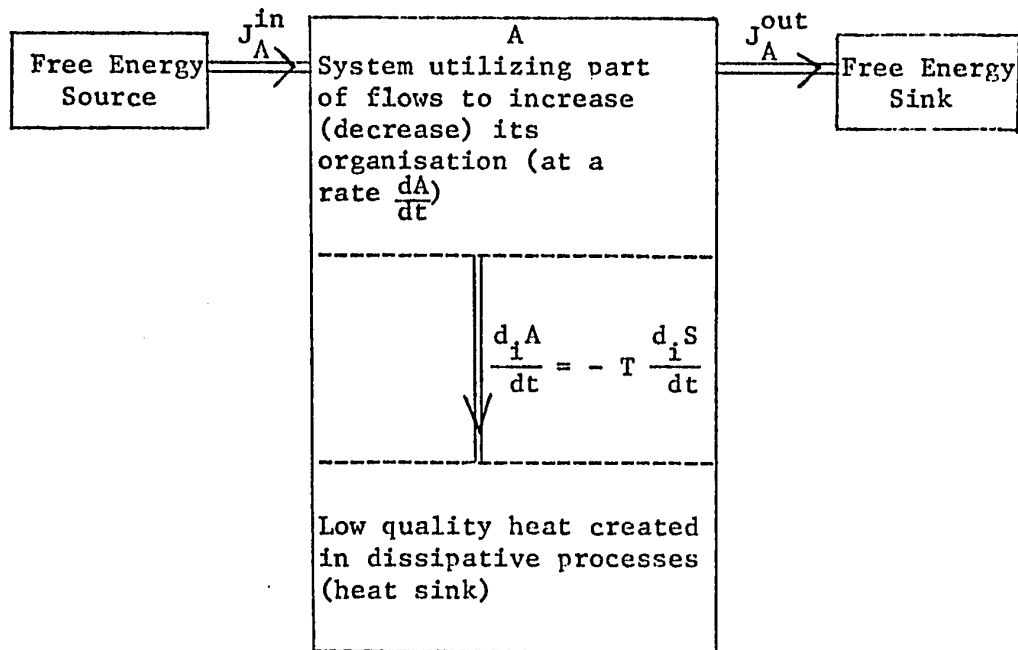


Fig. 3.1 Schematic Diagram of Self-Organising System

This figure, in agreement with equation (3-3), states that the system utilizes part of the incoming free energy (J_A^{in}) to increase its own organisation (at a rate $\frac{dA}{dt}$) returning excess free energy and other waste material to the surroundings (J_A^{out}) while depositing low quality heat ($-T \frac{d_i S}{dt}$) into the heat sink. It is clear from this that the complete description of the state of a self-organising system requires the specification of two internal quantities: the free energy ($A(t)$),

which measures the evolution of organisation, and the dissipation rate (the rate of entropy production in the universe due to processes occurring within the system).

These ideas are consistent with those of Schroedinger (1944), von Bertalanffy (1950), and Blum (1951). The latter regards the basic source of free energy of nourishment for the biological world as the free energy contained in the solar radiation which is "fixed" or trapped on earth by the green plants.

3.4 COMPLEXITY AND DIFFERENTIATION

We anticipate that some readers will find our definition of organisation as too restrictive since it seems at first sight to be incapable of dealing quantitatively with morphogenesis and differentiation and the resulting changes in complexity of the system. In our view, the problem arises through a misunderstanding of the operational meaning of the term complexity. Complexity arises through progressive morphogenesis and differentiation and can be indexed by the progressive loss of microscopic symmetry elements. This concept, like the number of symmetry elements in crystallography, does not map monotonically into any of the state functions. The crystallographic state of simple isothermal equilibrium systems can, in principle, be uniquely defined by the free energy minimum principle. The symmetry is in this context a derivable quantity. Note, however, that conjectured symmetries are an essential aid for minimization of the amount of computation required in predicting stable and metastable thermodynamic states.

Analogously, we suppose that optimization of our proposed complex state function (of two variables) is, in principle, sufficient to uniquely define stable and metastable steady states, including the symmetry elements. Again, however, conjectured symmetries will be a necessary part of economic and tractable solutions to problems of kinetic stability. Indeed, in approaching the problems of biological morphogenesis and differentiation, it would appear necessary to invoke empirical rules of symmetry evolution. For example, evolutionary progress might, in the broadest sense, be regarded as a monotone function of the decrement of microscopic symmetry (differentiation). Such developments are beyond the scope of this thesis.

In conclusion, it is our program to describe organisation and self-organisation in terms of the evolution of free energy ($A(t)$) and of the dissipation rate (or rate of entropy production).

CHAPTER 4

LINEAR* RADIATION ABSORPTION PROCESSES

4.1 INTRODUCTION

This chapter is concerned with the thermodynamic behaviour of an interesting class of radiation absorbing systems. A general model is first introduced along with a series of definitions and short derivations. The properties of this general class are then explored by a systematic study of two, three and four level systems. The model is finally extended to include the effects of a non-constant number of particles. The connections with a number of physio-chemical and biological phenomena are explored. The treatment is patterned after Klein's (1958) elementary quantum-mechanical description of a two-level radiation absorption process.

4.2 DESCRIPTION OF THE SYSTEM

We consider an ensemble of N identical systems (or particles), each system having an average bounded energy. Furthermore, each system has a finite set of quantized states which are accessible to it, and it

* Here, linearity refers to the order of the differential equations, not to the order of the flux-force relations. By-and-large, these models correspond to non-linearity in the thermodynamics of irreversible processes.

is immersed in a heat bath which is maintained at a temperature T . The ensemble is irradiated with radiation including resonant frequencies, $\nu = (E_j - E_k)/h$, where h is Planck's constant and E_j and E_k are the energies of any two allowed states of each particle. Particles are assumed to be non-interacting, which is to say that, the ensemble is dilute in the sense that the volume available to each particle is large compared to the range of interparticle forces.

After Thomsen (1953), we introduce the following definitions:

(1) Probabilities The probability that a system (particle), which is in state k , chosen at random from the ensemble at any instant is denoted as P_k . Each particle must be in some allowed state so

$$\sum_k P_k = 1 \quad (4-1)$$

It follows, therefore, that the average energy of the ensemble is given by

$$\bar{E}_{\text{System}} = N (\sum_k P_k \epsilon_k) \quad (4-2)$$

where the ϵ_k are the energies of the allowed particle states as measured from the lowest lying state.

(2) Transition Probabilities Each particle undergoes transitions between different allowed states due to interactions with the heat bath or interaction with the radiation. In this section we use the symbol, $\lambda_{ij} (\geq 0)$, to denote the conditional transition probability per unit time

of a particle going from state i to state j , due to interactions with the heat bath. Thus, $P_i \lambda_{ij} dt$ is the probability of a particle originally in state i going to state j in the time dt . λ_{ii} is defined as zero for all i . Similarly, we use the symbol $\Gamma_{ij} (\geq 0)$ to denote the conditional transition probability per unit time of a particle going from state i to state j due to interactions with the radiation. Γ_{ii} is defined as zero for all i . It is understood that the numerical specification of the transition probabilities requires the computation of matrix elements (first order theory) of the form $|\langle j | V_{int}^{op} | i \rangle|^2$ where V_{int}^{op} is the operator representing the interaction between states $| i \rangle$ and $| j \rangle$.

Following Fermi's Golden Rule (Baym, 1969), it is assumed that the interactions with the radiation field are symmetric, i.e.

$$\Gamma_{ij} = \Gamma_{ji} \quad (4-3)$$

and that the principle of microscopic reversibility yields

$$\lambda_{ij} e^{-\beta \epsilon_i} = \lambda_{ji} e^{-\beta \epsilon_j} \quad (4-4)$$

where $\beta = 1/k_B T$ and ϵ_i, ϵ_j are the energies of the states involved (see for example, Klein and Meijer, 1954; Cox, 1950 and 1955; Mathews et al., 1960). The assumption that the reservoir is maintained in equilibrium at temperature T (the reservoir is assumed to be so large that interactions with the particle system do not significantly affect its equilibrium) guarantees the result (4-4) for Fermi-Dirac and

Bose-Einstein statistics as well as Maxwell-Boltzmann statistics (Mathews et al., *ibid*).

4.3 THE RATE EQUATIONS

From the definitions given above it follows that the probability of a transition out of state i , in time dt , is given by summing* $P_i(\lambda_{ij} + \Gamma_{ij})dt$ over all j . Similarly, the probability of a transition into state i is given by summing, $P_j(\lambda_{ji} + \Gamma_{ji})dt$ over all j . Thus the net change in P_i in dt is

$$dP_i = \sum_j P_j(\lambda_{ji} + \Gamma_{ji})dt - \sum_j P_i(\lambda_{ij} + \Gamma_{ij})dt$$

or

$$\dot{P}_i \equiv \frac{dP_i}{dt} = \sum_j [P_j(\lambda_{ji} + \Gamma_{ji}) - P_i(\lambda_{ij} + \Gamma_{ij})] \quad (4-5)$$

Equation (4-5) may be written in matrix form as

$$\dot{\underline{P}} = \underline{\Lambda} \underline{P} \quad (4-6)$$

* It is implicit in the definitions that the particles are of the Maxwell-Boltzmann type (Mathews et al., *ibid*; and Meijer, 1956); however, for systems of independent particles (e.g., dilute system of electrons) such a result is still valid.

or

$$P_i = \sum_j (\Lambda_{ji} P_j - \Lambda_{ij} P_i) \quad (4-7)$$

where

$$\underline{P} \equiv \begin{bmatrix} P_1 \\ \vdots \\ P_M \end{bmatrix} \quad (4-8)$$

and the matrix elements of Λ are given by

$$\Lambda_{ji} = \lambda_{ji} + \Gamma_{ji} \quad (4-9)$$

and

$$\Lambda_{ij} = \lambda_{ij} + \Gamma_{ij} \quad (4-10)$$

This system of equations may, with appropriate initial conditions, be solved by the method of characteristics (cf. Appendix 1).

In the steady state all \dot{P}_i are zero and the set of linear differential equations (4-6) reduces to a set of M linear algebraic equations of the form

$$\Lambda \underline{P} = 0 \quad (4-11)$$

which may be solved for the steady values of the probabilities.

Equation (4-1) reduces (4-6) to a set of $M - 1$ linearly independent differential equations.

Condition (4-11) is equivalent to the statement that in the steady state transitions between any two states occur with equal frequency in both directions. That is, for every i and j

$$\Lambda_{ji}P_j = \Lambda_{ij}P_i \quad (4-12)$$

This condition (4-12) is commonly referred to as detailed balance.

4.4 THERMODYNAMIC FUNCTIONS

The definition and construction of the thermodynamic functions requires some care. We begin with the usual definition of the entropy (configurational part) per particle

$$S_C = -K_B \sum_j P_j \ln P_j \quad (4-13)$$

where it is recognized that

$$\lim_{P_j \rightarrow 0} P_j \ln P_j \rightarrow 0 \quad (4-14)$$

It is readily seen that when one of the $P_j = 1$, the entropy assumes its minimum value, namely zero. Evidently, the entropy is a maximum when all P_j are equal.

To calculate the Helmholtz free energy, A , arbitrarily define the energy of the lowest lying state to be the zero reference state, and evaluate the free energy per particle as

$$A = U - TS_C \quad (4-15)$$

where S_C is the configurational entropy, T is the absolute temperature (temperature of the reservoir) and the internal energy per particle is

$$U = \sum_i P_i \epsilon_i \quad (4-16)$$

where the sum is taken over all states. This may be rewritten as

$$U = K_B T \sum_i P_i \ln \alpha_i \quad (4-17)$$

where α_i is the Boltzmann factor for transitions from level i to the lowest level and is given by

$$\alpha_i = e^{\epsilon_i \beta} \quad (4-18)$$

where $\beta = 1/K_B T$. Using (4-18), we can rewrite (4-4) as

$$\lambda_{ij} = e^{-\beta(\epsilon_j - \epsilon_i)} \lambda_{ji}$$

or

$$\lambda_{ij} = \alpha_{ji} \lambda_{ji} \quad (4-19)$$

The simplest case we can consider is pure relaxation into the heat bath (i.e., $\lambda_{ij} \neq 0$, $\Gamma_{ij} = 0$). Then, in the steady state we require, as usual, that equation (4-11) be valid. For an example, consider a two level model. In the steady state the condition holds that

$$\lambda_{21} P_1 = \lambda_{12} P_2 \quad (4-20)$$

and employing (4-19), we have the result that

$$\alpha_{12} \lambda_{12} P_1 = \lambda_{12} P_2 \quad (4-21)$$

or

$$P_1 = 1/\alpha_{21} P_2 = e^{\beta(\epsilon_2 - \epsilon_1)} P_2 = \alpha_{12} P_2 \quad (4-22)$$

which is just the result we would get if the system were in equilibrium with the heat bath. (Of course, in the absence of external forces, i.e., $\Gamma_{ij} = 0$, the system will try to equilibrate with the heat bath and when all $\dot{P}_i = 0$ the system will have equilibrated.)

The free energy for the system is now written as

$$\begin{aligned}
A &= N(U - TS_C) \\
&= N(K_B T \sum_i P_i \ln \alpha_i + K_B T \sum_i P_i \ln P_i) \\
&= N K_B T \sum_i P_i \ln \alpha_i P_i
\end{aligned} \tag{4-23}$$

The calculation of the entropy production rate is carried out for a system of particles with two levels. The generalisation to multi-level systems is obvious from the form of the solution. Recalling that $\Gamma_{ij} = \Gamma_{ji}$ we set

$$\Gamma_{12} = \Gamma_{21} = \Gamma \tag{4-24}$$

and from (4-19) we have

$$\lambda_{21} = \alpha_{12} \lambda_{12} \tag{4-25}$$

or

$$\alpha_{12} = e^{\beta(\epsilon_2 - \epsilon_1)} \tag{4-26}$$

Thus, we may write the equations for the time evolution as

$$\begin{aligned}
\frac{dP_1}{dt} &= -(\lambda_{12} + \Gamma)P_1 + (\lambda_{21} + \Gamma)P_2 \\
&= -(\lambda_{12} + \Gamma)P_1 + (\alpha_{12}\lambda_{12} + \Gamma)P_2 \\
&= -\frac{dP_2}{dt}
\end{aligned} \tag{4-27}$$

The rate of entropy production of the system, \dot{S}_i , is evaluated as the rate of change of entropy of the universe attributable to processes occurring within the system, viz.,

$$\dot{S}_i = \left(\frac{dS}{dt}\right)_{\text{particles}} + \left(\frac{dS}{dt}\right)_{\text{Bath}} \tag{4-28}$$

Proceeding to evaluate these two terms separately we have

$$\begin{aligned}
\frac{d}{dt} (S_C) &= -NK_B \frac{d}{dt} (P_1 \ln P_1 + P_2 \ln P_2) \\
&= -NK_B \dot{P}_1 \ln(P_1/P_2)
\end{aligned} \tag{4-29}$$

Secondly, the heat bath gains an entropy

$$\Delta S = \frac{\epsilon_2 - \epsilon_1}{T} \equiv \frac{\Delta \epsilon}{T} \tag{4-30}$$

for each transition down in the particle system and this has a probability $P_2 \alpha_{12} \lambda_{12} \Delta t$ in time Δt . Similarly, the heat bath loses an entropy

$$\Delta S = \frac{\Delta \epsilon}{T} \quad (4-31)$$

for each upward transition in the particle system with a probability $P_1 \lambda_{12} \Delta t$ in time Δt . The net entropy gain in the heat bath is

$$\Delta S = N \frac{\Delta \epsilon}{T} (\alpha_{12} \lambda_{12} P_2 - \lambda_{12} P_1) \Delta t \quad (4-32)$$

In the limit as Δt becomes small

$$\left(\frac{dS}{dt}\right)_{\text{Bath}} = N \frac{\Delta \epsilon}{T} (\alpha_{12} \lambda_{12} P_2 - \lambda_{12} P_1) \quad (4-33)$$

Adding (4-29) and (4-33) and substituting (4-27) we get

$$\begin{aligned} \dot{S}_i &= \left(\frac{dS}{dt}\right)_{\text{Bath}} + \frac{d(S_C)}{dt} \\ &= N \frac{\Delta \epsilon}{T} (\alpha_{12} \lambda_{12} P_2 - \lambda_{12} P_1) - NK_B [-(\lambda_{12} + \Gamma) P_1 \\ &\quad + (\alpha_{12} \lambda_{12} + \Gamma) P_2] \ln(P_1/P_2) \end{aligned} \quad (4-34)$$

After rearrangement we obtain

$$\begin{aligned} \dot{S}_i &= NK_B \left\{ \lambda_{12} P_1 \left(\frac{\alpha_{12} P_2}{P_1} - 1 \right) \ln \left(\frac{\alpha_{12} P_2}{P_1} \right) \right. \\ &\quad \left. + \Gamma P_1 \left(\frac{P_2}{P_1} - 1 \right) \ln(P_2/P_1) \right\} \end{aligned} \quad (4-35)$$

It is evident that \dot{S}_i is positive definite since it is the sum of terms of the form $(X - 1)\ln X > 0$ for $X > 0$.

It is obvious that for a multilevel system (4-35) generalizes to

$$\begin{aligned} \dot{S}_i = NK_B \{ \sum_{j>k} [\lambda_{kj} P_k \left(\frac{\alpha_{kj} P_j}{P_k} \right) - 1] \ln \left(\frac{\alpha_{kj} P_j}{P_k} \right) \right. \\ \left. + \Gamma_{kj} P_k (P_j/P_k - 1) \ln(P_j/P_k) \right\} \end{aligned} \quad (4-36)$$

Further results will be derived as they are required for the discussion of each particular model.

4.5 DETAILED BEHAVIOUR OF THE TWO LEVEL MODEL

4.5.1 Introduction

This model of an irreversible process was originally proposed and investigated by Klein (1958) with a view to testing the range of validity of the principle of minimum entropy production. We have found it to be a very useful vehicle for investigating the minimax principle, as described in Chapter 2, and the relationship between the self-organising properties and the dissipative properties of a "photo-synthetic" system. Extensions to more realistic models will be introduced in later sections.

Referring to Figure 4.1, we have a system consisting of $n_1 + n_2 = N$, weakly interacting particles and each particle is in one of two possible energy states which are separated by an energy $\Delta\epsilon$. It is assumed that the entire system is in good thermal contact with a heat bath at temperature

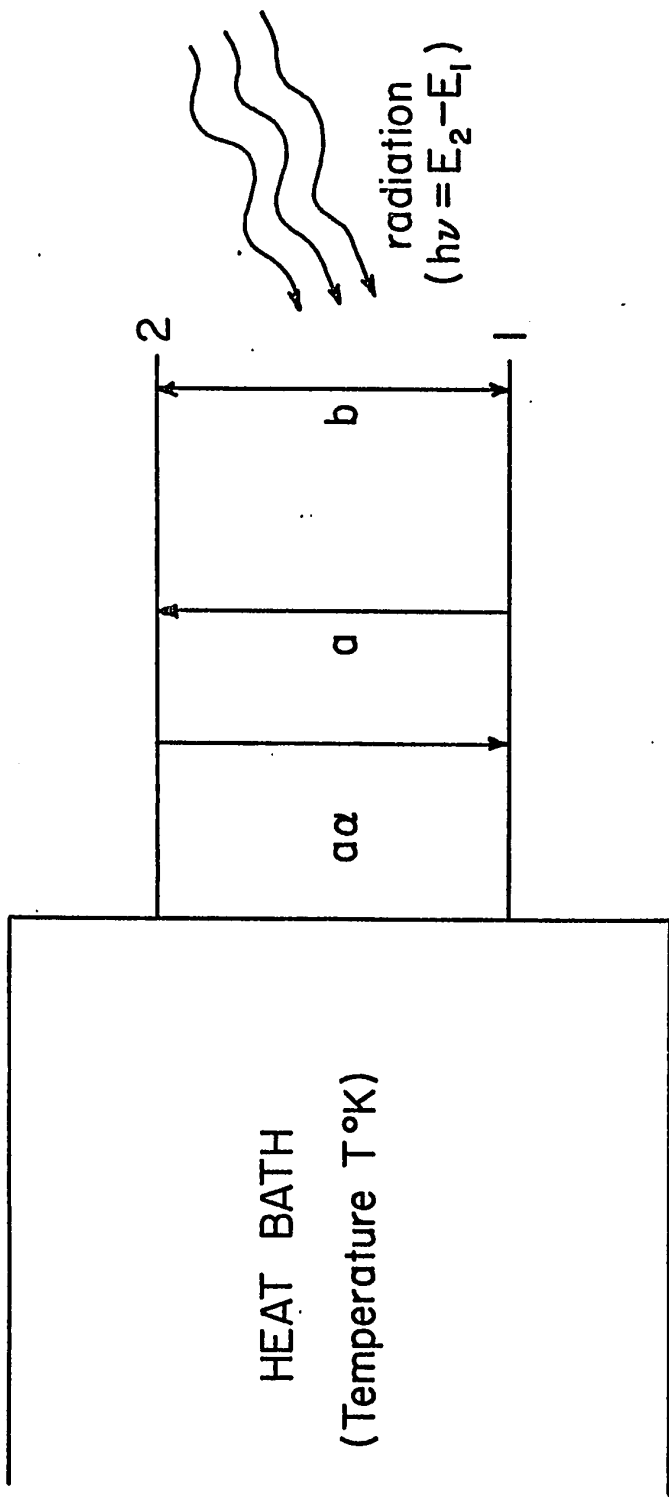


Fig. 4.1 Schematic of Two Level Model

T, and is irradiated with monochromatic radiation of the resonant frequency ν such that

$$h\nu = \Delta\varepsilon \quad (4-37)$$

The various transition probabilities are defined in Table 4-1, with the usual Boltzmann factor

$$\alpha = e^{\Delta\varepsilon/K_B T} \quad (4-38)$$

K_B being the Boltzmann constant. b may be controlled by changing the intensity of the radiation. Note that in the table the probability of coupling between the particles and the radiation is symmetric in accord with Fermi's Golden Rule (ibid).

The occupation probabilities are defined as

$$P_i = n_i/N \quad (4-39)$$

or

$$P_1 + P_2 = 1 \quad (4-40)$$

thus

$$\frac{dP_1}{dt} = \dot{P}_1 = -\dot{P}_2 = -\frac{dP_2}{dt} \quad (4-41)$$

The time evolution of the occupation probabilities is evidently defined by the conservation equation

$$\begin{aligned}\dot{P}_1 &= \frac{dP_1}{dt} = (\alpha a + b)P_2 - (a + b)P_1 \\ &= -\dot{P}_2\end{aligned}\quad (4-42)$$

which has the obvious solution

$$\begin{aligned}P_1(t) &= P_1(0) e^{-Kt} + P_1^S (1 - e^{-Kt}) \\ &= P_1^S + (P_1(0) - P_1^S) e^{-Kt}\end{aligned}\quad (4-43)$$

where $K = \alpha a + a + 2b$, $P_1(0) = P_1(t = 0)$, and P_1^S is the steady value of P_1 .

It is easily shown that P_1 (and hence P_2) are monotonic functions of time, the actual evolution being determined by the initial conditions as shown in Table 4-2.

4.5.2 Thermodynamic Functions

The rate of entropy production of the system is

$$\dot{S}_i \equiv \frac{d_i S}{dt} = \left(\frac{dS}{dt}\right)_{\text{particles}} + \left(\frac{dS}{dt}\right)_{\text{Bath}}\quad (4-44)$$

Table 4-1

Transition Probabilities Two Level Model

Transitions from levels	Probability per unit time of transition between levels, due to interaction with	
	Heat Bath	Radiation
1 → 2	a	b
2 → 1	aα	b

Table 4-2

Sign of \dot{P}_1 and \dot{P}_2

As Function of Initial Conditions

Initial Condition	Sign of \dot{P}_1 or \dot{P}_2
$P_1^O > P_1^S$	$\dot{P}_1 < 0 < \dot{P}_2$
$P_1^O < P_1^S$	$\dot{P}_1 > 0 > \dot{P}_2$

where

$$\begin{aligned} \left(\frac{dS}{dt}\right)_{\text{Bath}} &= NK_B \left(\frac{\Delta E}{K_B T}\right) (\alpha P_2 - a P_1) \\ &= NK_B (\ln \alpha) (\alpha P_2 - a P_1) \end{aligned} \quad (4-45)$$

and

$$\begin{aligned} \left(\frac{dS}{dt}\right)_{\text{particles}} &= \frac{d}{dt} (S_C) \\ &= -NK_B \frac{d}{dt} (P_1 \ln P_1 + P_2 \ln P_2) \end{aligned} \quad (4-46)$$

or combining (4-45) and (4-46) (see section 4.4)

$$\begin{aligned} \dot{S}_i &= NK_B [a P_1 (\alpha P_2 / P_1 - 1) \ln(\alpha P_2 / P_1) \\ &\quad + b P_1 (P_2 / P_1 - 1) \ln(P_2 / P_1)] \geq 0 \end{aligned} \quad (4-47)$$

In the steady state all $\dot{P}_i = 0$, so solving (4-40) and (4-42), we obtain the steady values

$$\begin{aligned} P_1^S &= (\alpha + b) / (\alpha + a + 2b) \\ \text{and} \\ P_2^S &= (a + b) / (\alpha + a + 2b) \end{aligned} \quad (4-48)$$

The steady state rate of entropy production is

$$\begin{aligned} (\dot{S}_1)^S &= N \left(\frac{\Delta E}{T} \right) (a\alpha P_2 - aP_1) \\ &= N \left(\frac{K_B}{T} \right) \left(\frac{ab}{a\alpha + a + 2b} \right) (\alpha - 1) \ln \alpha \geq 0 \end{aligned} \quad (4-49)$$

which is an increasing (and bounded) function of the radiation of intensity b .

The Helmholtz free energy (organisation) of the system is from section 4.4

$$A = NK_B (P_1 \ln P_1 + P_2 \ln \alpha P_2) \quad (4-50)$$

The steady value of A is also a monotonically increasing (and bounded) function of the radiation intensity b . From the above, it can be seen that if the radiation to the system is increased, both the steady state dissipation and the stored free energy will increase. It can be concluded that the system utilizes part of the available energy from the environment to increase its internal organisation.

Table 4-3 is a summary of the behaviour of the system variables, P_1 , \dot{S}_1 , and A as functions of the system coupling parameters a and b .

It should be noted from Table 4-3, that the saturation value of the free energy, which is the maximum possible value

$$\begin{aligned} A_{b \rightarrow \infty} &= NK_B T/2 \ln (\alpha/4) \\ &\text{a constant} \end{aligned} \quad (4-51)$$

Table 4-3

Values of System Variables at Limiting Values of Parameters

Steady values	Values of Coupling Parameters*		
	$a \rightarrow 0$	$a \rightarrow \infty$	$b \rightarrow \infty$
P_1	1/2	$\alpha/\alpha+1$	1/2
\dot{S}_i	0	$NK_B b(\alpha-1/\alpha+1) \ln \alpha > 0$	$NK_B (\frac{a}{2})(\alpha-1) \ln \alpha > 0$
A	$NK_B T/2 \ln (\frac{\alpha}{4})$	$NK_B T \ln (\alpha/\alpha+1)$	$NK_B T/2 \ln (\alpha/4)$

* " \rightarrow " means approaches or "in the limit"; the entries in Table 4-3 are also to be taken in that sense. When one parameter is varied the other is assumed to be fixed and finite.

will be positive for $\alpha > 4$. Thus, if the level spacing $\Delta\epsilon$ is such that $\Delta\epsilon > 2K_B T \ln 2$, the saturation free energy will be positive. The equilibrium free energy is given by

$$A_{b \rightarrow 0} = NK_B T \ln (\alpha/\alpha + 1) \quad (4-52)$$

a constant

and is always negative. Thus at saturation, the system will always accumulate free energy with respect to the equilibrium state and the free energy will be positive if $\Delta\epsilon > 2K_B T \ln 2$. (This is a kind of statistical uncertainty principle since, if levels one and two are separated by a $\Delta\epsilon < K_B T$, their fluctuations will ensure that they are always equally populated. It is therefore only meaningful to talk about increasing the population of level two when it is possible to distinguish between the two levels.) The evolution of A as it approaches the steady state (increasing or decreasing) is indicated in Table 4-4.

The behaviour of the time evolution of the entropy production rate is given in Table 4-5.

These Tables 4-4 and 4-5 show that in the range, $P_1^{eq} > P_1 > P_1^S$, the free energy, A, is a monotonically increasing function of time and concomitantly the time rate of change of the entropy production rate can be either positive or negative. The final approach to the steady state is often characterized by an increasing entropy production rate.

4.5.3 The Free Energy Balance

The time rate of change of the free energy dA/dt , and hence A, may

Table 4-4

Evolutionary Behaviour of A
As a Function of Initial Condition

Range of P_1	Sign of $\frac{d}{dt}$ (A)
$P_1 > P_1^{eq}$	negative
$P_1^{eq} \geq P_1 \geq P_1^S$	positive
$P_1 < P_1^S$	negative

Table 4-5

Evolutionary Behaviour of \dot{S}_1
As a Function of Initial Condition

Range of P_1	Sign of $\frac{d}{dt} (\dot{S}_1)$
$P_1 > P_1^{eq} **$	negative
$P_1^{eq} > P_1 \geq P_1^S$	* either + or -
$1/2 \leq P_1 < P_1^S$	* either + or -
$P_1 < 1/2$	negative

* by "either" we mean that the actual sign of the time rate of change of the entropy production rate depends upon the actual values of the parameters, a, b, and until these values as well as P_1 are known, nothing precise may be said about the "sign" of $\frac{d}{dt} (\dot{S}_1)$

** P_1^{eq} = equilibrium value of P_1 ; P_1^S = steady value of P_1 .

be alternatively calculated from the balance equation for the free energy equation

$$\frac{dA}{dt} = - \int_{\text{surface}} \vec{J}_A \cdot d\vec{S} + \frac{d_i A}{dt} \quad (4-53)$$

where \vec{J}_A is the outward flow of free energy and $\frac{d_i A}{dt}$ is the free energy produced within the system. We have

$$- \int_{\text{surface}} \vec{J}_A \cdot d\vec{s} = N(\Delta\epsilon)b(P_1 - P_2) \quad (4-54)$$

and

$$\frac{d_i A}{dt} = - T \frac{d_i S}{dt} = - T \dot{S}_i \quad (4-55)$$

where (\dot{S}_i) is given by (4-47). Substituting (4-47) and (4-54) into (4-55) and performing the time integration (it is assumed that this is a legitimate procedure as A is defined for all t), we obtain

$$\begin{aligned} \Delta A &= \int_0^t \left(\frac{dA}{dt} \right) dt = A(t) - A(t=0) \\ &= N K_B T \{ P_1(t) \ln P_1(t) + P_2(t) \ln \alpha P_2(t) \\ &\quad - P_1(t=0) \ln P_1(t=0) \\ &\quad + P_2(t=0) \ln \alpha P_2(t=0) \} \end{aligned} \quad (4-56)$$

which agrees with (4-50) up to a constant term. This result is consistent with the conclusions of Chapter 3 concerning free energy dissipation.

4.5.4 The Force-Flux Relations and the Mini-Max Principle

Let us now examine in more detail the behaviour of the terms in (4-47). It is usual to regard the entropy production rate as the sum of two, or more, bilinear terms of the form

$$\frac{d_1 S}{dt} \equiv \sigma = J_1 X_1 + J_2 X_2 \quad (4-57)$$

where J_i , X_i are the generalized fluxes and forces, respectively. In our model we may consider the term

$$N K_B a P_1 (\alpha P_2 / P_1 - 1) \ln (\alpha P_2 / P_1) \quad (4-58)$$

as describing a process of pure thermal relaxation into the heat bath with a flux

$$N K_B a P_1 (\alpha P_2 / P_1 - 1) \quad (4-59)$$

and a driving force

$$\ln (\alpha P_2 / P_1) \quad (4-60)$$

which expresses the deviation from the equilibrium populations of levels one and two. Similarly we may consider the term

$$NK_B b P_1 \left(\frac{P_2}{P_1} - 1 \right) \ln (P_2/P_1) \quad (4-61)$$

as a radiation-induced diffusion process. In this case we have as a flux

$$NK_B b P_1 \left(\frac{P_2}{P_1} - 1 \right) \quad (4-62)$$

and as the driving force

$$\ln (P_2/P_1) \quad (4-63)$$

which measures the deviation from the saturation populations.

The distinctive behaviour of these two terms in the entropy production rate is illustrated by the typical example shown in Figure (4.3). We see that for the initial condition chosen (equilibrium) the diffusion term is monotonically increasing and the thermal term is monotonically decreasing. Thus, the dissipation rate may be regarded as a competition between the two processes mentioned above, one tending towards a maximum and one tending towards a minimum, the sum function taking, in general, a maximal or minimal steady state. (This helps to explain the equivocal character of \dot{S}_1 as shown in Table 4-5.) The behaviour of the free energy for the same example is also indicated in Figure 4.3. The free energy can be decomposed into two terms

$$A = A_1 + A_2 \quad (4-64)$$

such that

$$A_1 = NK_B (P_1 \ln P_1) \quad (4-65)$$

$$A_2 = NK_B (P_2 \ln \alpha P_2) \quad (4-66)$$

From the figure it is evident that the processes which increase the population of level two also increase the free energy.

The foregoing lends itself to a new and rather profound thermodynamic interpretation of the steady state (Kirkaldy, 1972). It is a balance between forces trying to simultaneously equilibrate the system with the free energy sources and with the heat sink. Note that at saturation, $P_1 = P_2$, so $X_2 = \ln \frac{P_2}{P_1} = 0$, and at equilibrium $P_1 = \alpha P_2$ so $X_1 = \ln \alpha \frac{P_2}{P_1} = 0$. Balanced, non-zero values of these two competing forces characterize the steady state, and this must lie between the two extremes irrespective of the initial conditions. The sign and relative strengths of the two forces during evolution, leading from the initial conditions, specify the minimal or maximal character of the steady state.

When $\alpha \rightarrow 1$ (i.e., $\Delta\epsilon/K_B T \rightarrow 0$) expression (4-47) can be linearized to yield the conventional quadratic form of the linear theory of irreversible thermodynamics, viz.

$$\dot{S}_i \approx NK_B \left\{ aP_1 \left(\alpha \frac{P_2}{P_1} - 1 \right)^2 + bP_1 \left(\frac{P_2}{P_1} - 1 \right)^2 \right\} \quad (4-67)$$

It is readily seen by differentiating (4-67) with respect to time that the

mini-max character of \dot{S}_i is retained in the linear limit, viz., for systems close to equilibrium (i.e., $b \ll 1$) the time derivative of (4-67) becomes

$$\frac{d}{dt} (\dot{S}_i) \approx NK_B \left\{ a \left(\alpha \frac{P_2}{P_1} - 1 \right) [2(\alpha - 1) + P_1] \right\} \dot{P}_2 \quad (4-68)$$

which can be either positive or negative.

It is worth noting from equation (4-68) and the $P_i(t)$ that if the initial condition is $P_1^O > P_1^S$ (in the direction of equilibrium with the heat sink, then the subsequent relaxation is maximal. If $P_1^O < P_1^S$ (in the direction of equilibrium with the source) then the relaxation is minimal. These initial conditions are equivalent to those which appear in Onsager's mini-max theorem (2.3.4) and Prigogine's minimal theorem (2.3.5). This can be seen by first preparing the system with b fixed and $a = 0$ which specifies an initial state at saturation. Returning a to its non-zero value, the system relaxes towards a minimum in the entropy production. These two operations are equivalent to an internal fluctuation towards upper level occupancy and $\delta \int \text{div } \vec{J} \cdot \vec{n} \, dA = 0$ (Onsager) or X_n unconstrained (Prigogine) during subsequent relaxation. On the other hand if the system is momentarily prepared with $b = 0$, which is the incremental equivalent of Onsager's continuum constraint (2-38), then the subsequent relaxation is towards a maximum in the entropy production.

4.5.5 Numerical Calculations

The time evolution of the above model was studied in detail for many sets of parameters and initial conditions. We find, with Klein, that for many combinations of parameters and initial conditions, the steady state rate of entropy production assumes a minimum or very nearly

minimum value. However, there are also many arrangements where the system tends to a maximum in the entropy production rate as the system approaches the steady state. The behaviour of the free energy curves is found in most instances to complement that of the entropy production curves.

It is seen from an examination of Fig. 4.2 (a) and Fig. 4.2 (b) that quite different behaviour results from the different initial conditions. In case (3) of Fig. 4.2 (a), a purely minimal approach to the steady state is obtained while in cases (1) and (2), the final approach to the steady state is along a maximal path. The curves for the free energy in Fig. 4.2 (b) show a similar behaviour. These particular results are, of course, consistent with the general statements made in Table 4-4 and Table 4-5. We conclude that in any case where the magnitude of P_2 increases towards its steady value, both the entropy production rate and the accumulation of free energy assume maximal behaviour.

Fig. 4.3 shows the competitive tendency of the two terms in the entropy production rate. In this example, the thermal relaxation term shows maximal behaviour and the diffusion term shows minimal behaviour as the system approaches the steady state. For the free energy decomposed into two terms, one term increases and one term decreases as the system approaches the steady state.

Fig. 4.4 illustrates another interesting property of the two level system. We see that there is a minimum ratio of b/a necessary in order that the system have a positive free energy in the steady state. The larger is b , the further is the system away from equilibrium, which must be the case for a positive free energy.

Table 4-6 contains the steady values of the entropy production

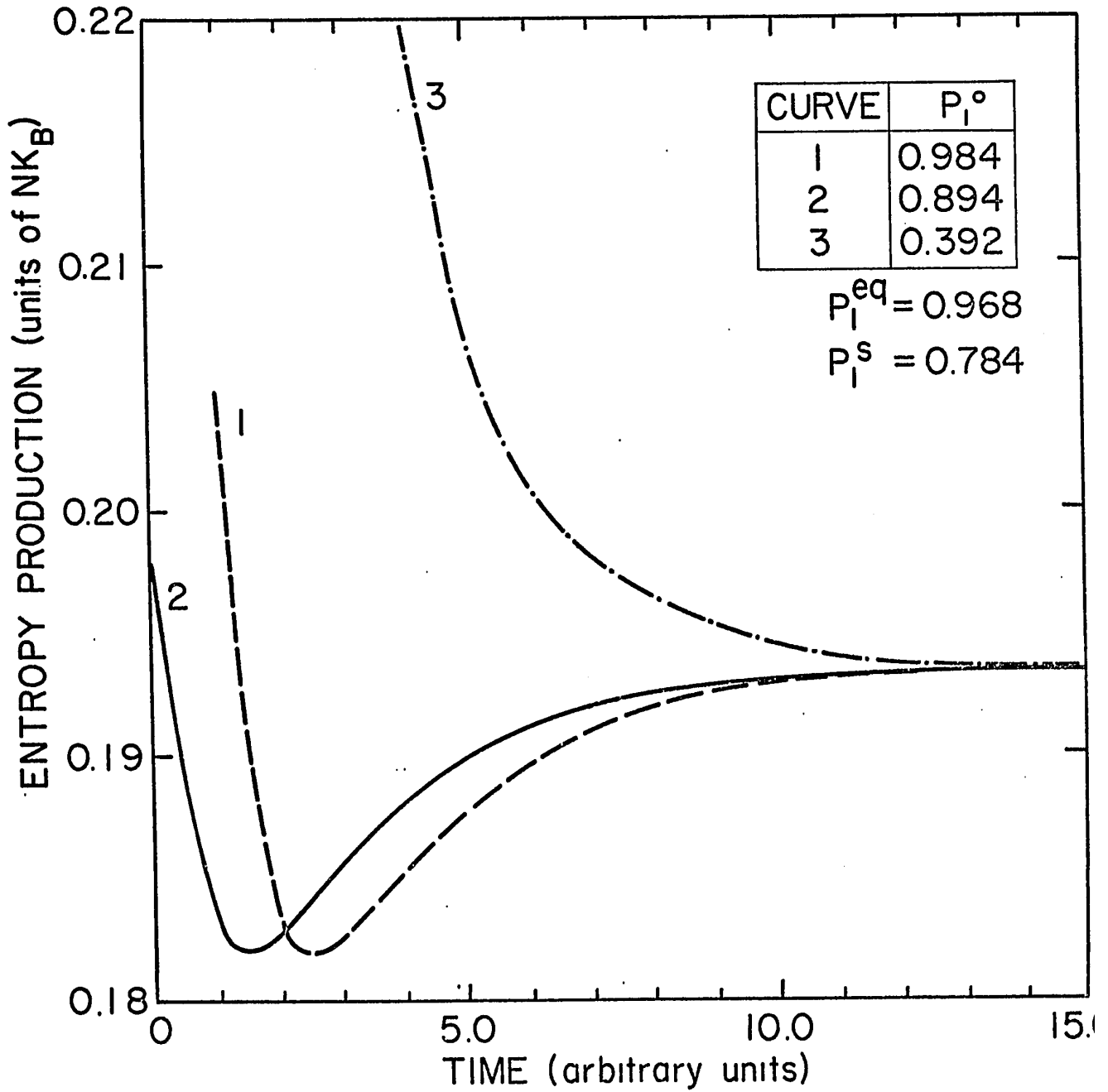


Fig. 4.2 (a) Entropy production versus time for various initial conditions.

The parameters were $a = .01$, $\alpha = 30.$, and $b = .1$.

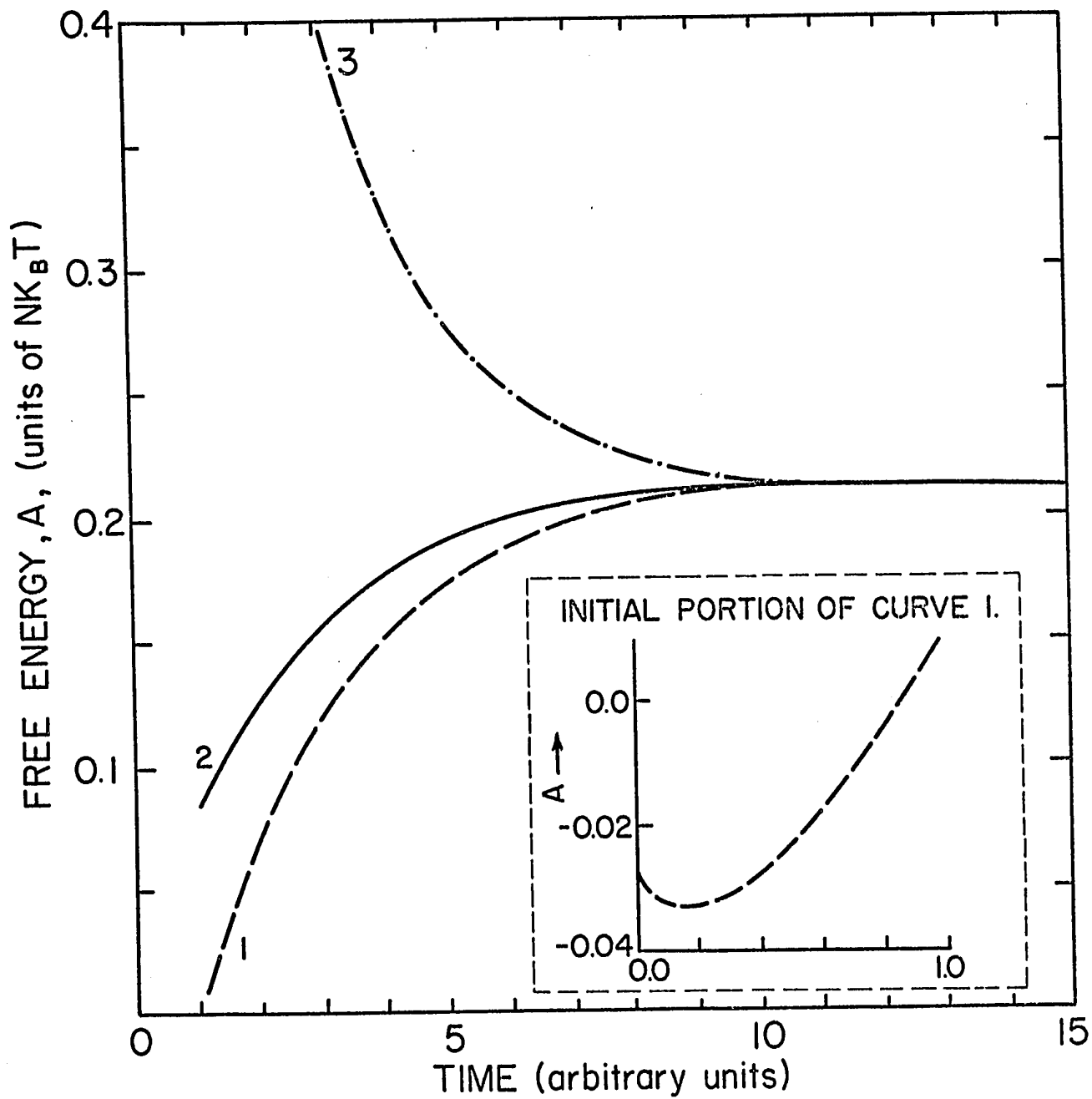
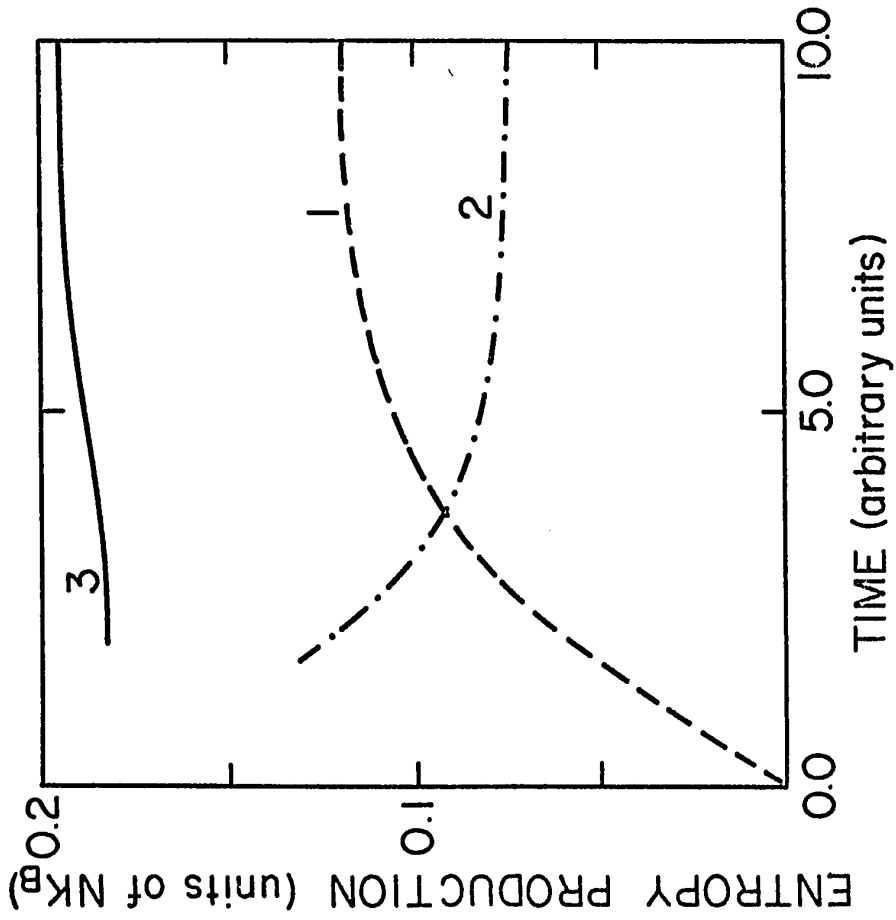
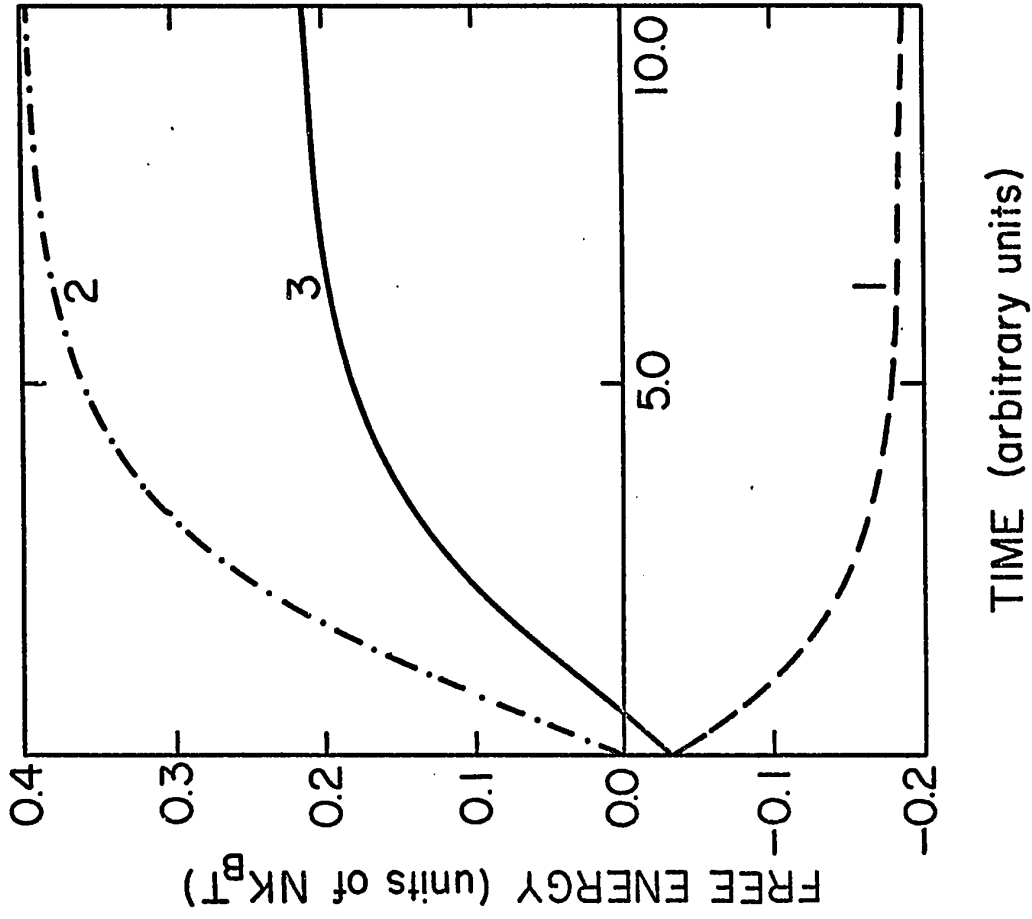


Fig. 4.2 (b) Free energy versus time. Conditions same as in 4.2 (a).



(a)



(b)

Fig. 4.3 (a) Entropy production versus time. (b) Free energy versus time. System was initially

in equilibrium and the parameters were $a = .01$, $\alpha = 30.$, and $b = .1.$

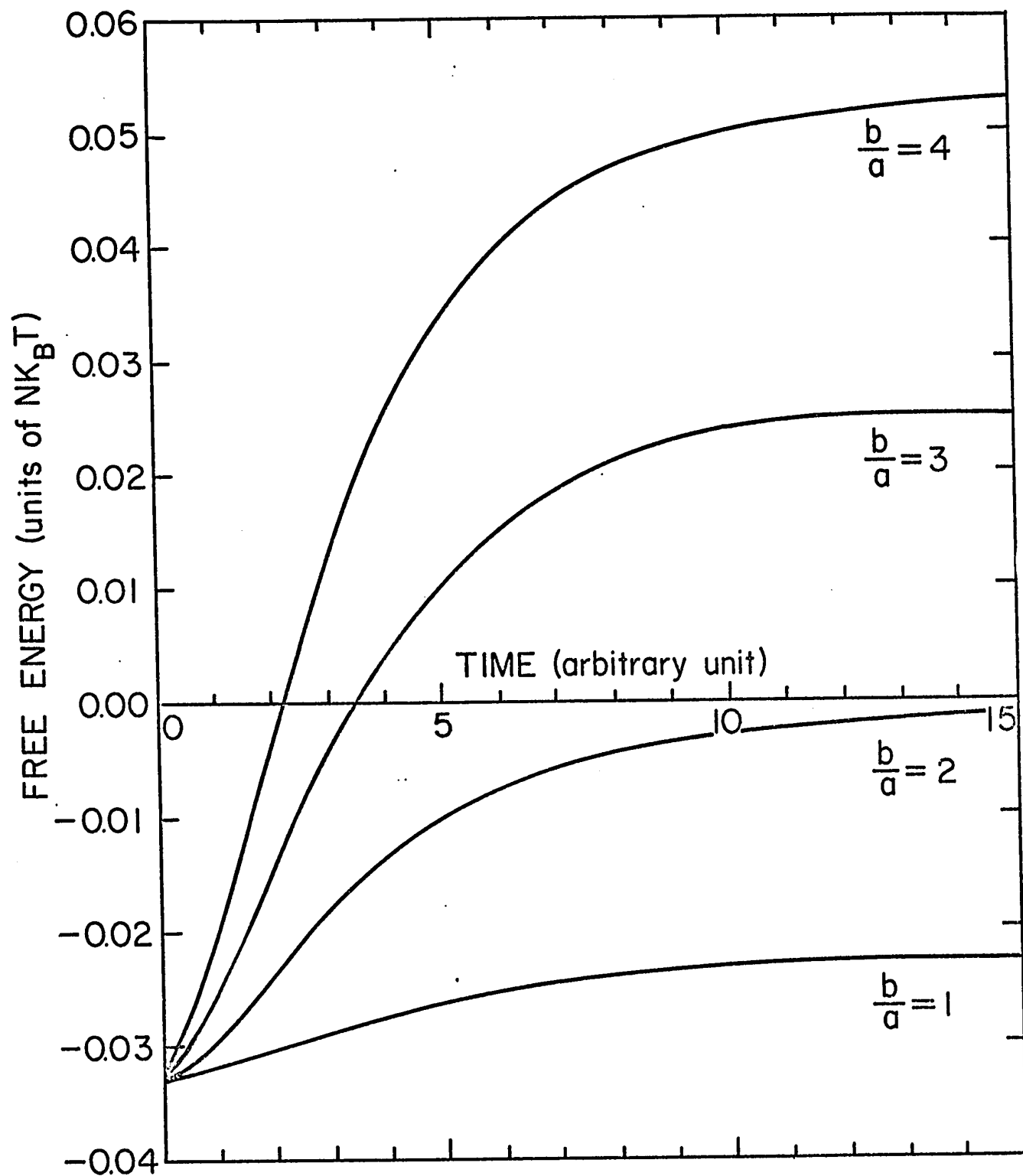


Fig. 4.4 Critical b/a . Free energy versus time for system initially in equilibrium. Parameters were $a = .01$, $\alpha = 30.$, and $b/a = 1, 2, 3$ and 4 .

Table 4-6

Two Level Model: Steady Values

Parameters			Steady Values							
α	a	b	P_2/P_1	σ_1	σ_2	σ	A_1	A_2	A	
↑ 30.0 ↓	.01	.001	.0365	.000083	.0031	.0031	-.035	+.0019	-.033	
	.01	.005	.0492	.0035	.0136	.017	-.046	.016	-.030	
	.01	.01	.0645	.0058	.024	.03	-.059	.036	-.0225	
	.01	.015	.0794	.011	.032	.043	-.071	.058	-.013	
	.01	.05	.146	.043	.070	.113	-.135	.216	+.081	
	.01	0.1	.275	.120	.073	.193	-.191	.403	.212	
	.01	0.5	.638	.327	.050	.377	-.301	.957	.656	
	.01	1.0	.777	.395	.032	.427	-.32	1.12	.80	
	.01	10.0	.972	.481	.0041	.486	-.34	1.33	.98	
		.001	0.1	.777	.0395	.0032	.0427	-.32	1.12	.80
		.01	0.1	.275	.120	.073	.193	-.191	.403	+.212
		.05	0.1	.0938	.086	.196	.282	-.082	.081	-.0011
		0.1	0.1	.0645	.058	.241	.30	-.059	.036	-.0225
	0.15	0.1	.0543	.044	.261	.305	-.051	.022	-.028	
	0.5	0.1	.0397	.0161	.298	.314	-.0375	.005	-.0325	
	1.0	0.1	.0365	.0085	.308	.316	-.0347	+.0019	-.0328	
	10.0	0.1	.0336	.0009	.317	.318	-.032	-.00082	-.033	
5.0	.01	.1	.733	.02	.0048	.0248	-.317	.175	-.142	
125.0	.01	.1	.0815	.012	.213	.225	-.0742	.169	.097	

rate and the free energy for a wide range of parameters. It is apparent that both the rate of entropy production and the free energy increase with increasing b/a ratio, at fixed a . For decreasing the ratio b/a with fixed b , the rate of entropy production increases but the free energy decreases.

In Fig. 4.5, we see again the effect of changing the b/a ratio for fixed b . The results are in agreement with the conclusions of Table 4-6. It is worth noting that for $b/a = 100$ the system is virtually in equilibrium with the energy source and we have a purely minimal approach to the steady state. Indeed, we can say, in general, that processes of relaxation toward complete equilibrium with either the energy source or the heat sink result in a purely minimal behaviour of the entropy production rate.

We see in Fig. 4.6 the effect of changing the level spacing while maintaining a constant b/a ratio. While the entropy production rate increases with increasing spacing, the free energy does not. Indeed, the free energy is maximized for an intermediate value of the level spacing.

In Fig. 4.7 and Fig. 4.8, we see the effect of changing the b/a ratio during the time evolution of the system. From Fig. 4.7 (a) (b), we see that increasing b/a (fixed a) gives rise to subsequent maximal behaviour of both the rate of entropy production and the free energy while decreasing b/a (fixed a) gives rise to subsequent minimal behaviour. In contrast, we see from Fig. 4.8 (a) that increasing b/a (b fixed) gives rise to subsequent maximal behaviour for both the entropy production rate and the free energy. The entropy production, however,

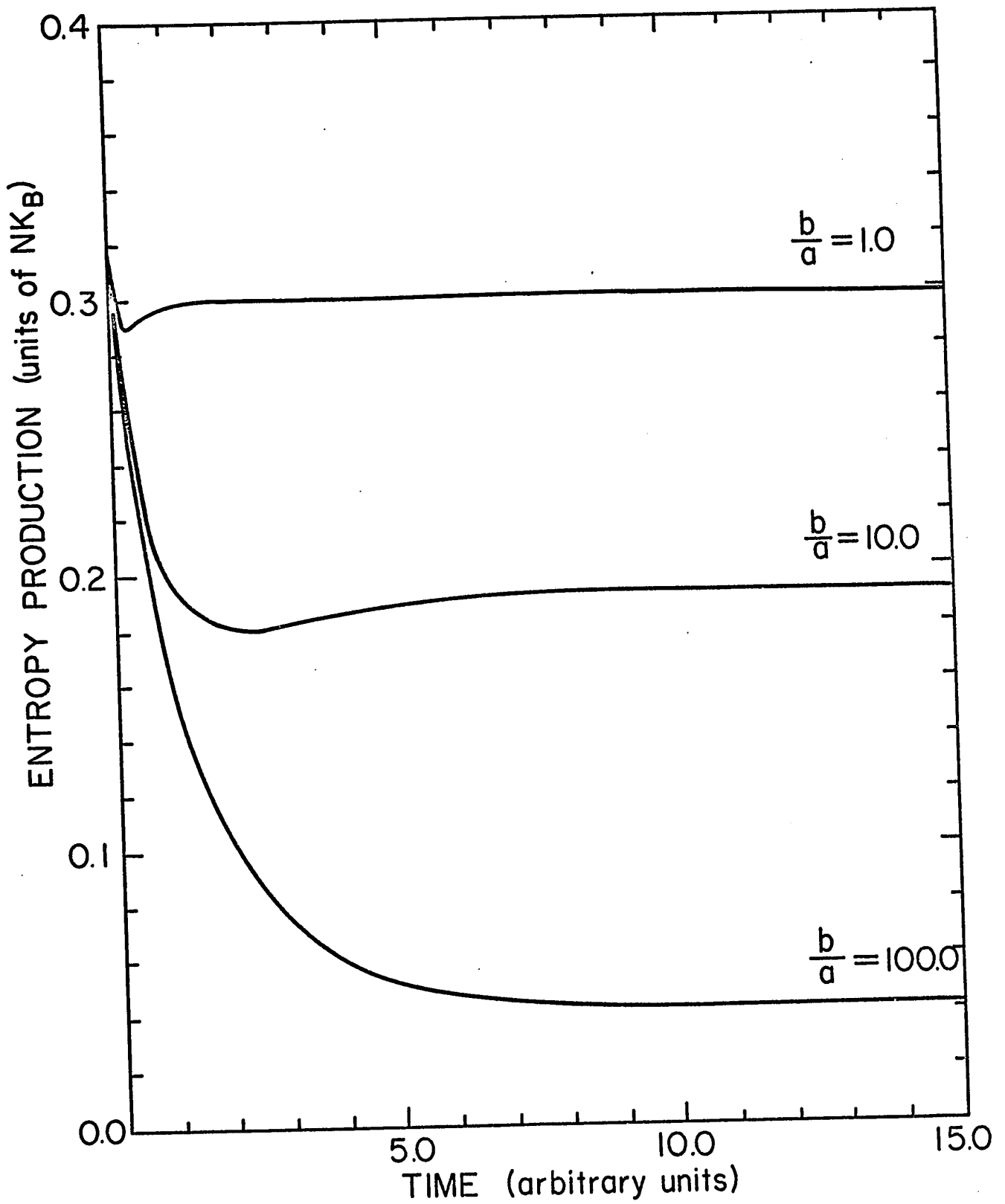


Fig. 4.5 (a) Effect of changing b/a . Entropy production versus time. System was initially in equilibrium. Parameters were $\alpha = 30.$, $b = .1$, and $b/a = 1., 10., 100.$

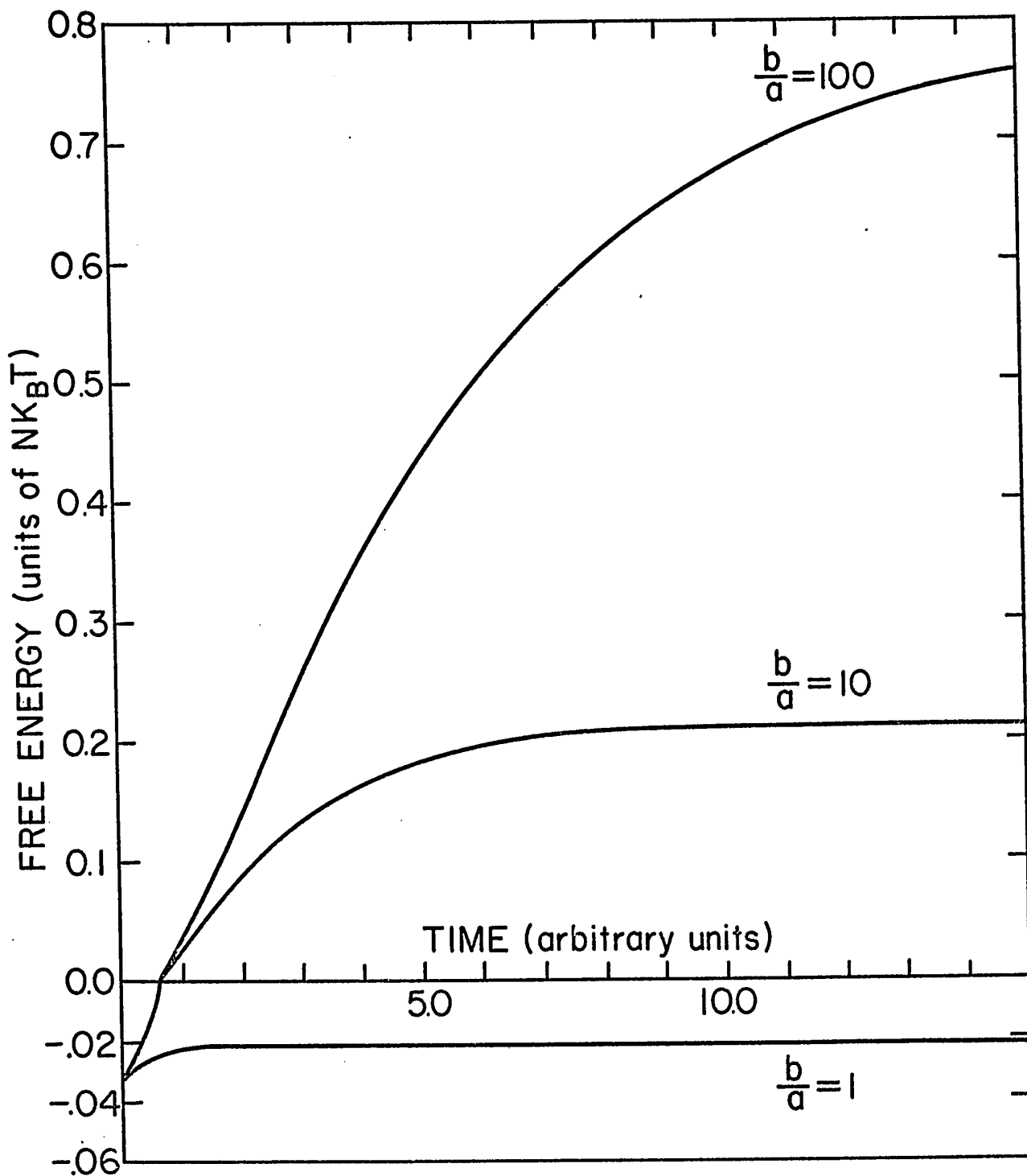


Fig. 4.5 (b) Free energy versus time. Note the change of scale for negative Λ . Conditions as in 4.5 (a).

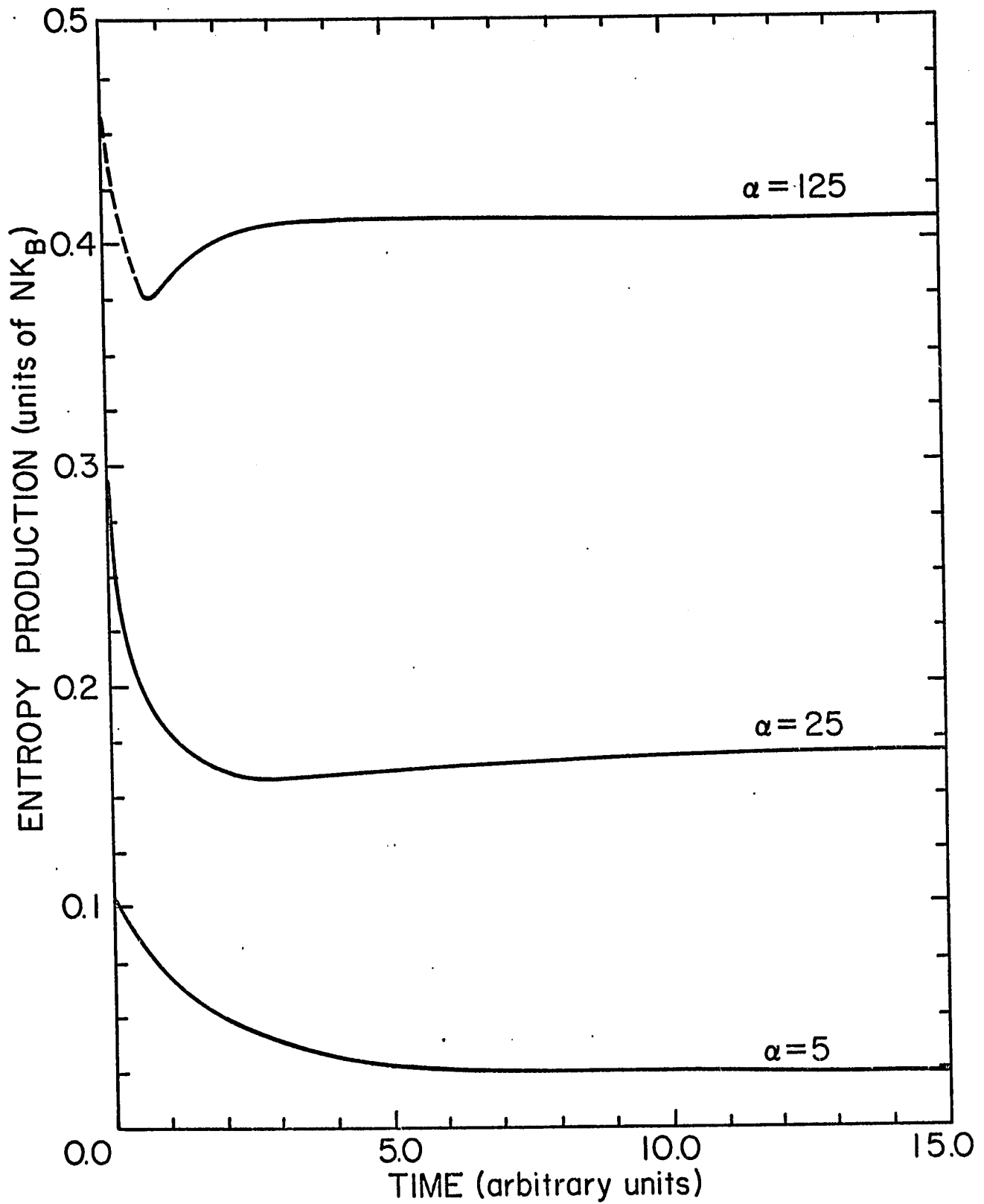


Fig. 4.6 (a) Change of level spacing. Entropy production versus time for system initially in equilibrium. The parameters were $a = .01$, $b = .1$, $\alpha = 5., 25., 125.$

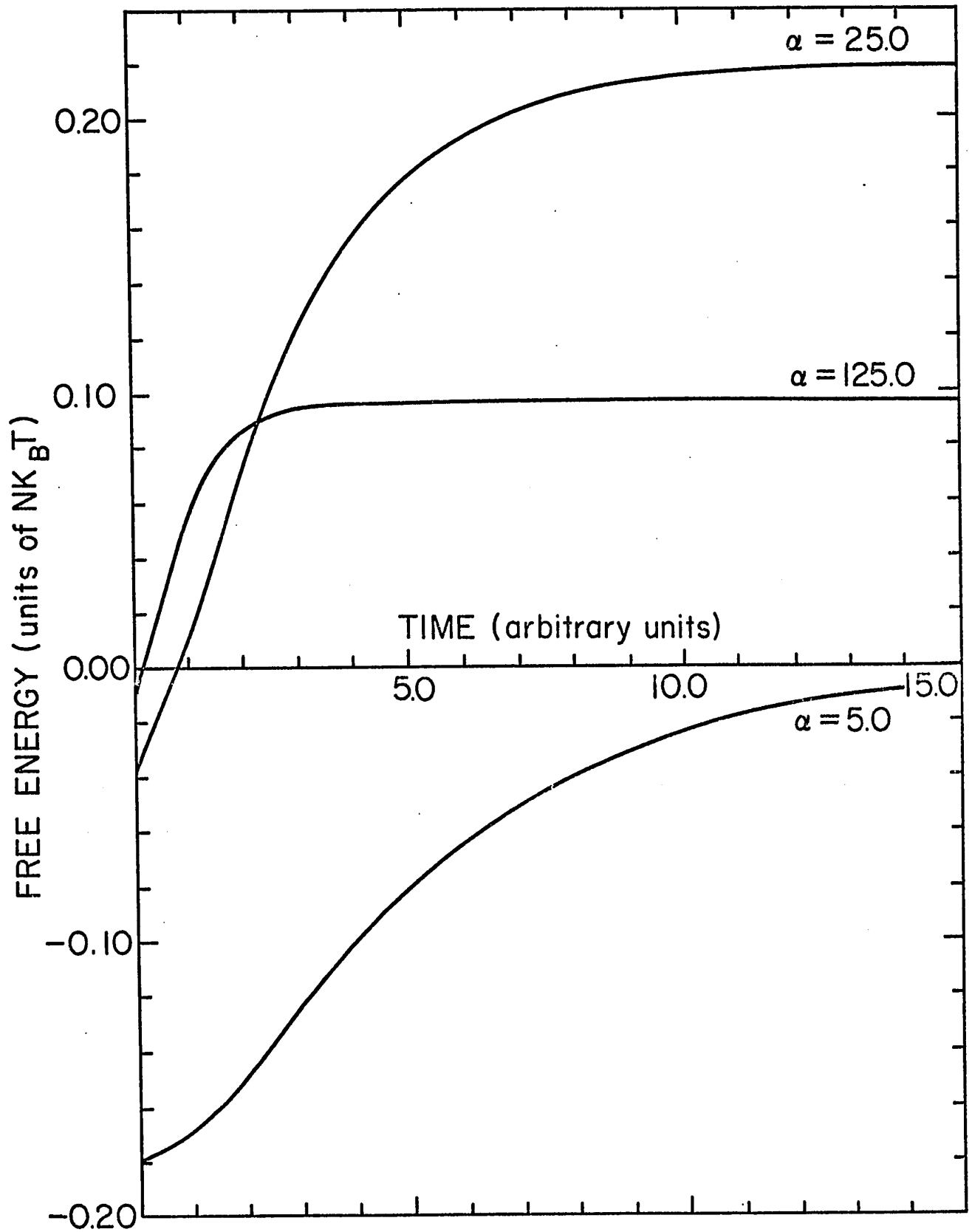


Fig. 4.6 (b) Free energy versus time. Conditions as in 4.6 (a).

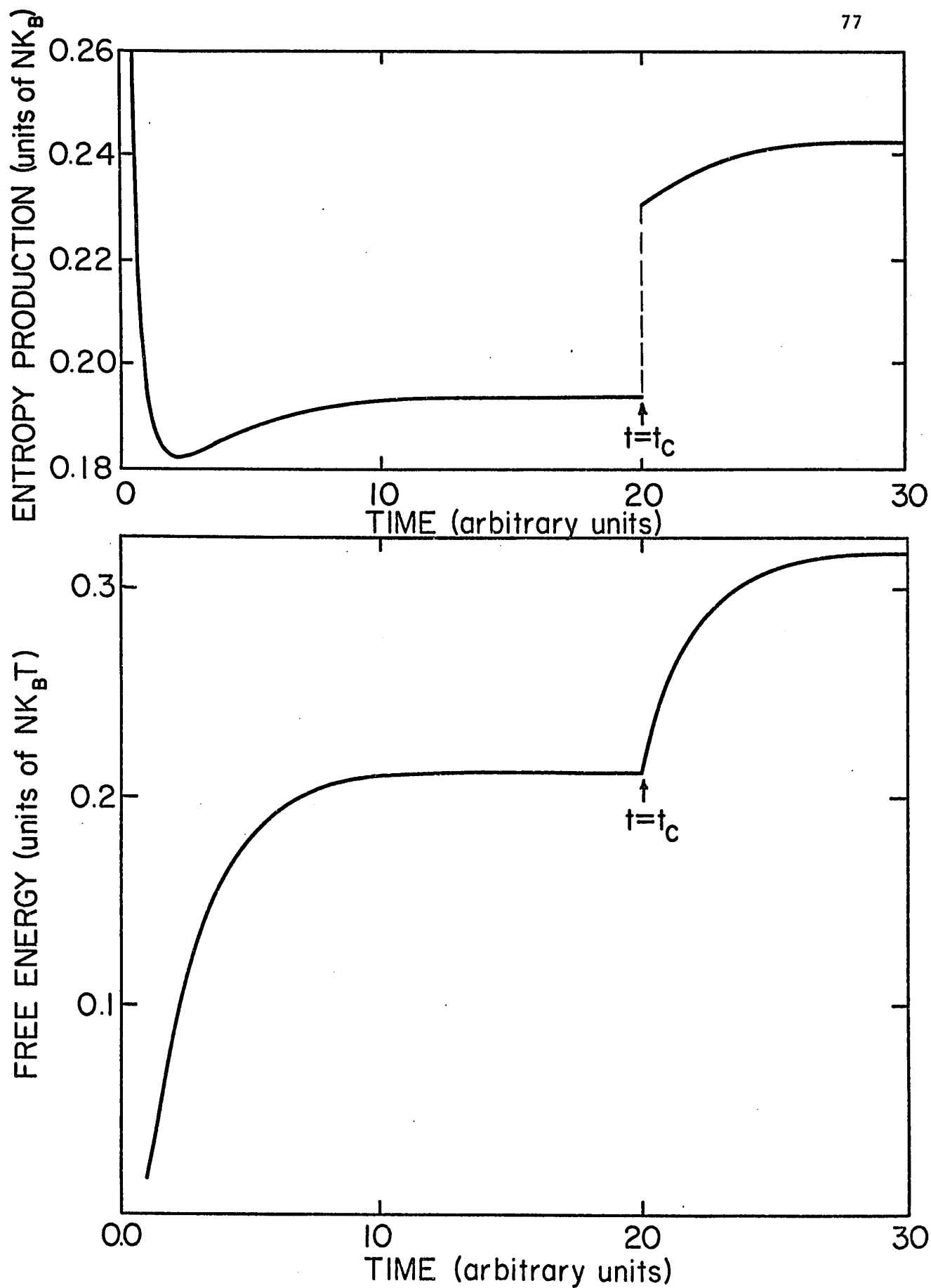


Fig. 4.7 (a) Entropy production and free energy versus time. At $t = t_c$ b changes from .1 to .15. System was initially in equilibrium. Parameters were $a = .01$, $\alpha = 30.0$.

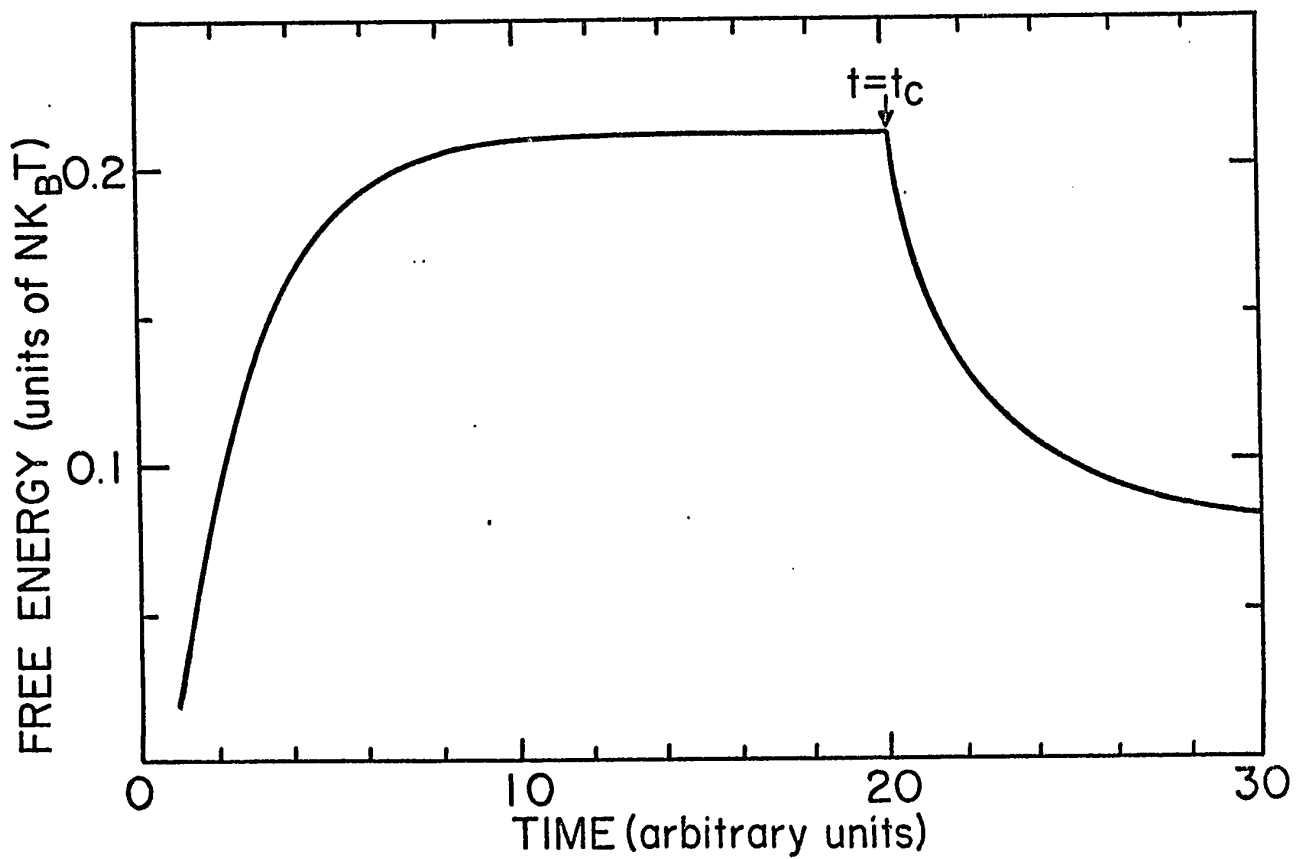
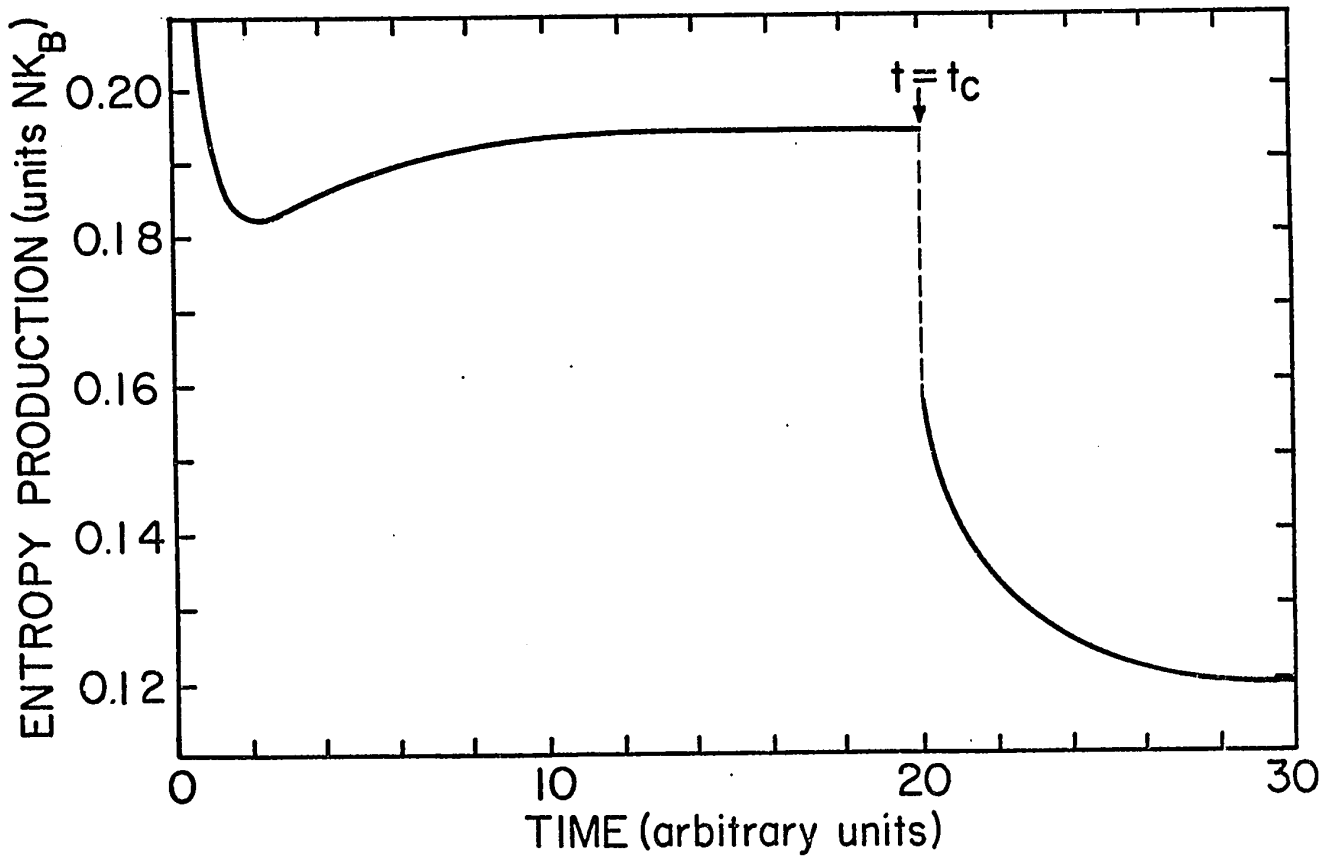


Fig. 4.7 (b) Entropy production and free energy versus time. At $t = t_c$ b changes from .1 to .05. System was initially in equilibrium. Parameters were $a = .01$, $\alpha = 30.0$.

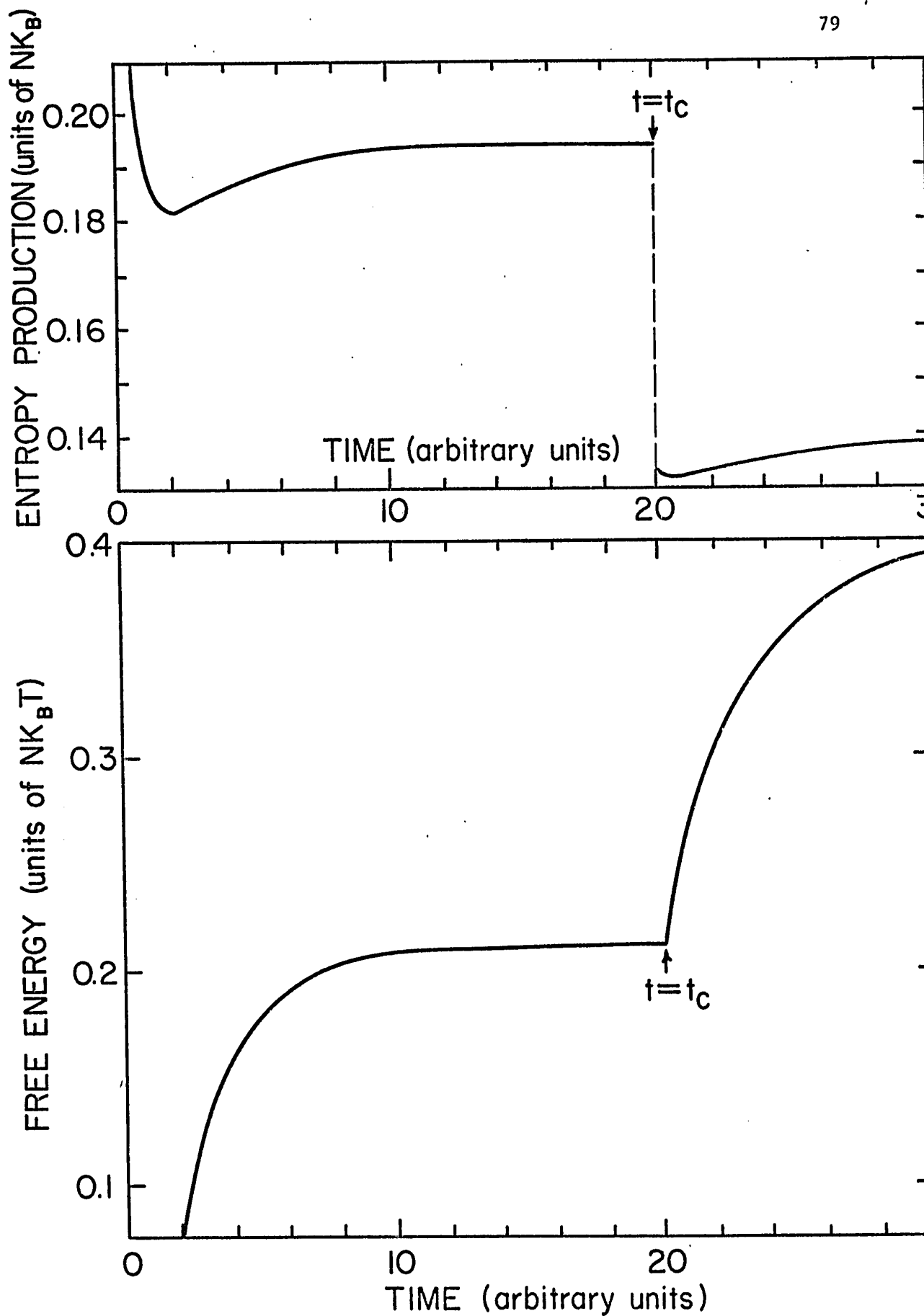


Fig. 4.8 (a) Entropy production and free energy versus time. At $t = t_c$ a changes from .01 to .005. System was initially in equilibrium. Parameters

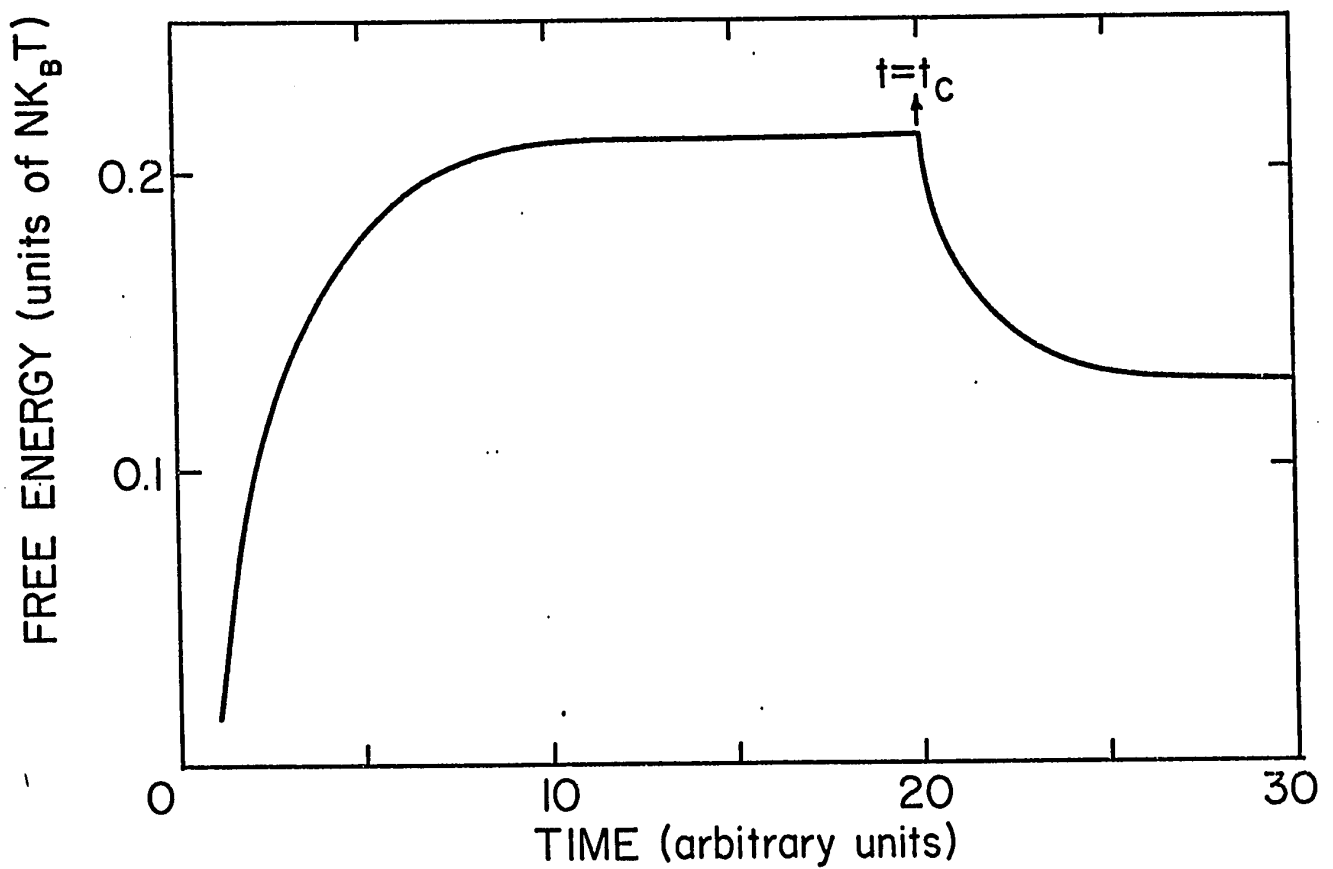
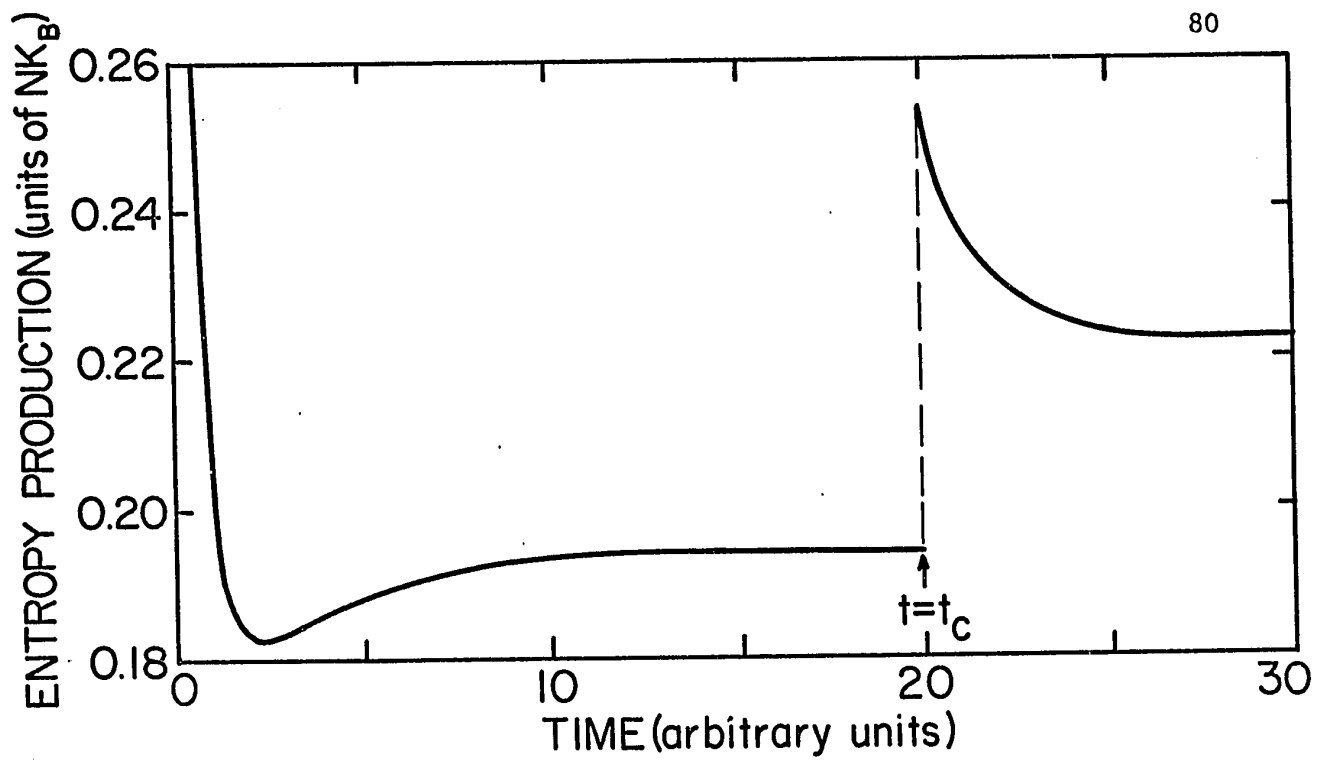


Fig. 4.8 (b) Entropy production and free energy versus time. At $t = t_c$ a changes from .01 to .015. System initially in equilibrium. Parameters were $b = .1$, $\alpha = 30$.

shows a net decrease. From Fig. 4.8 (b), we see that decreasing the ratio b/a (b fixed) leads to subsequent minimal behaviour for both the entropy production rate and the free energy.

Fig. 4.9 shows a plot of the entropy production rate and the free energy in "natural" coordinates. These coordinates are a measure of the deviation of the system variables from their steady state values. The origin representing the steady state. Both curves attempt to give a three dimensional representation. The coordinates for the entropy production curve are

$$[\dot{S}_1 - (\dot{S}_1)^S]/(\dot{S}_1)^S, \ln (P_1/P_1^S) \text{ and } e^{-Kt}$$

where $K = a\alpha + a + 2b$. The coordinates for the free energy are

$$(A - A^S)/A^S, \ln (P_1/P_1^S) \text{ and } e^{-Kt}$$

where K is as previously defined. It is seen that for varying initial conditions the functions \dot{S}_1 and A may follow either minimal or maximal paths which lie on a kind of saddle surface. From an examination of the corresponding curves in Fig. 4.9 (a) and Fig. 4.9 (b), we see that the entropy production rate and the free energy behave in the same fashion. Here we have obtained maximal behaviour for increasing P_2 as the system approaches the steady state in agreement with earlier conclusions.

4.5.6 Discussion of Two Level Model

Although the model is very elementary, it nonetheless exhibits

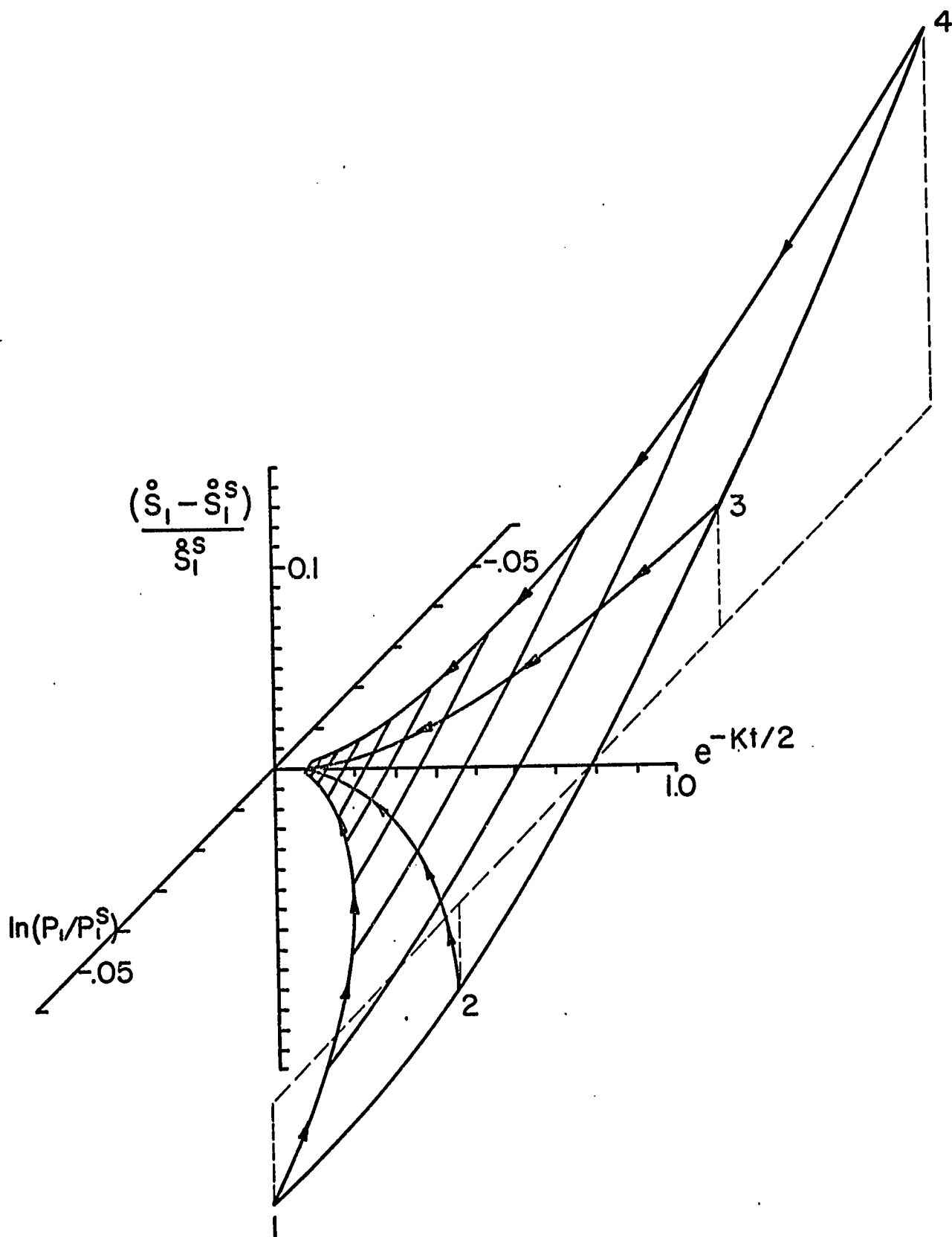


Fig. 4.9 (a) Entropy production in natural coordinates. Parameters were $a = .01$, $b = .1$, and $\alpha = 30.0$. The steady occupation $P_1 = .784$. Initial conditions were: curve 1, $P_1 = .676$; curve 2, $P_1 = .741$; curve 3, $P_1 = .827$ and curve 4, $P_1 = .893$.

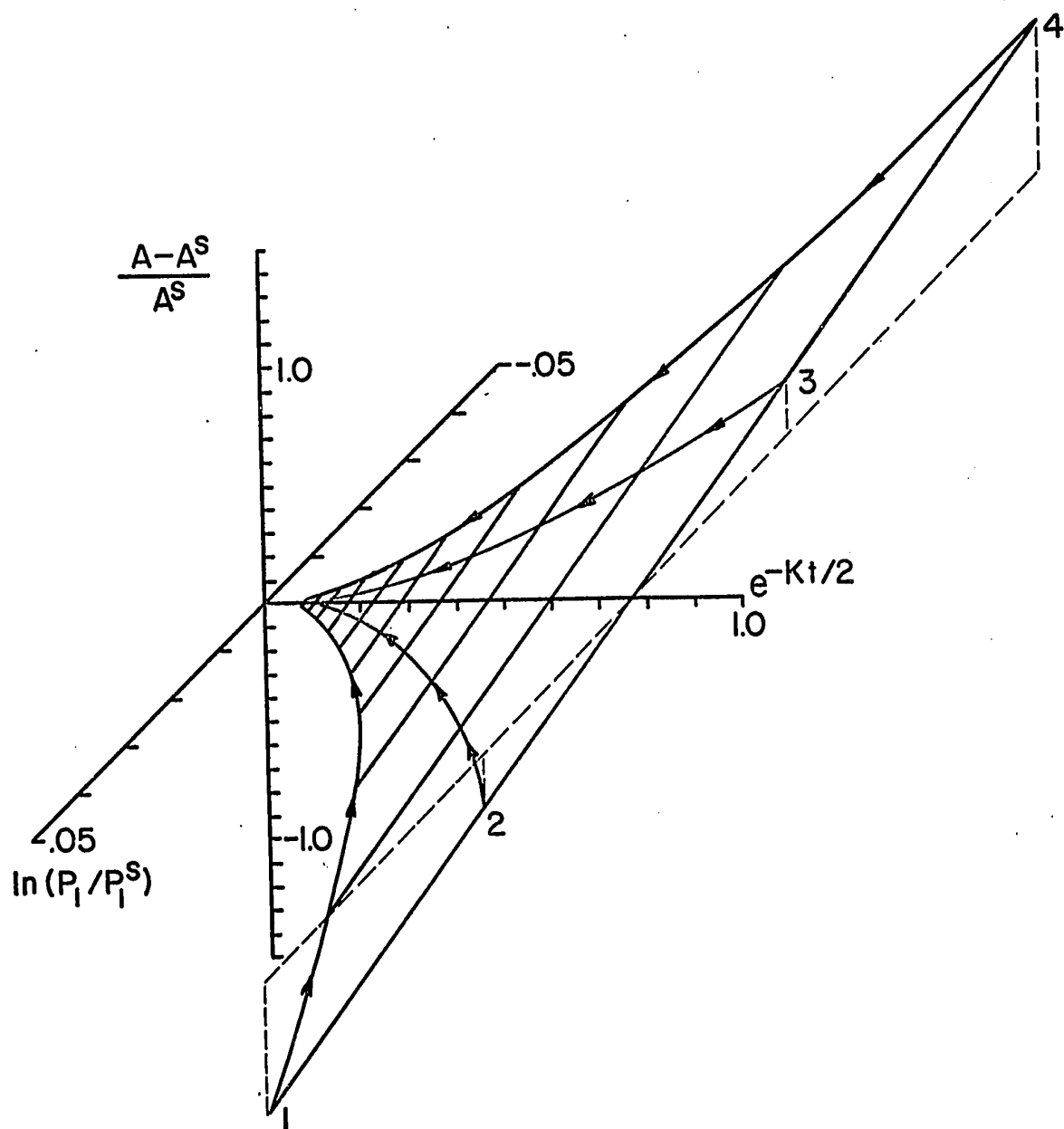


Fig. 4.9 (b) Free energy in natural coordinates. Conditions are the same as in Fig. 4.9 (a).

many qualitative features of a photosynthetic system. The primary process in photosynthesis may be represented schematically by the equation



where the radiation field creates a high energy product (A^*) from a low free energy reactant (A). The material A^* is then used to drive chemical reactions which produce the carbohydrates necessary for the growth of the green plant (Rabinowitch and Govindjee, 1969). The production of A^* in (4-69) represents an increase in the free energy content of the photosynthetic system which is, of course, supplied by the radiation field. The entropy production of our model corresponds to the heat-producing processes occurring as the reaction (4-69) proceeds.

Two further interesting features of the model are, that it requires a minimum radiation intensity before it can accumulate free energy, and it shows saturation effects, both of which have analogies in photosynthetic systems.

There are many non-biological examples of processes corresponding to our system. We might, for example, consider a dilute solid solution of a paramagnetic ion which is placed in a magnetic field and then irradiated. For a more concrete illustration let us examine Fig. 4.10. Fig. 4.10 (a) is a copy of Bloembergen's Fig. 4 (1949) in which a crystal of CaF_2 has been placed in a constant magnetic field and irradiated with an r.f. field. At time zero, the power of the r.f. field is reduced and Fig. 4.10 (a) represents the r.f. absorption by the F^{19} spins as the system relaxes toward equilibrium with the heat bath. Fig. 4.10 (b) shows

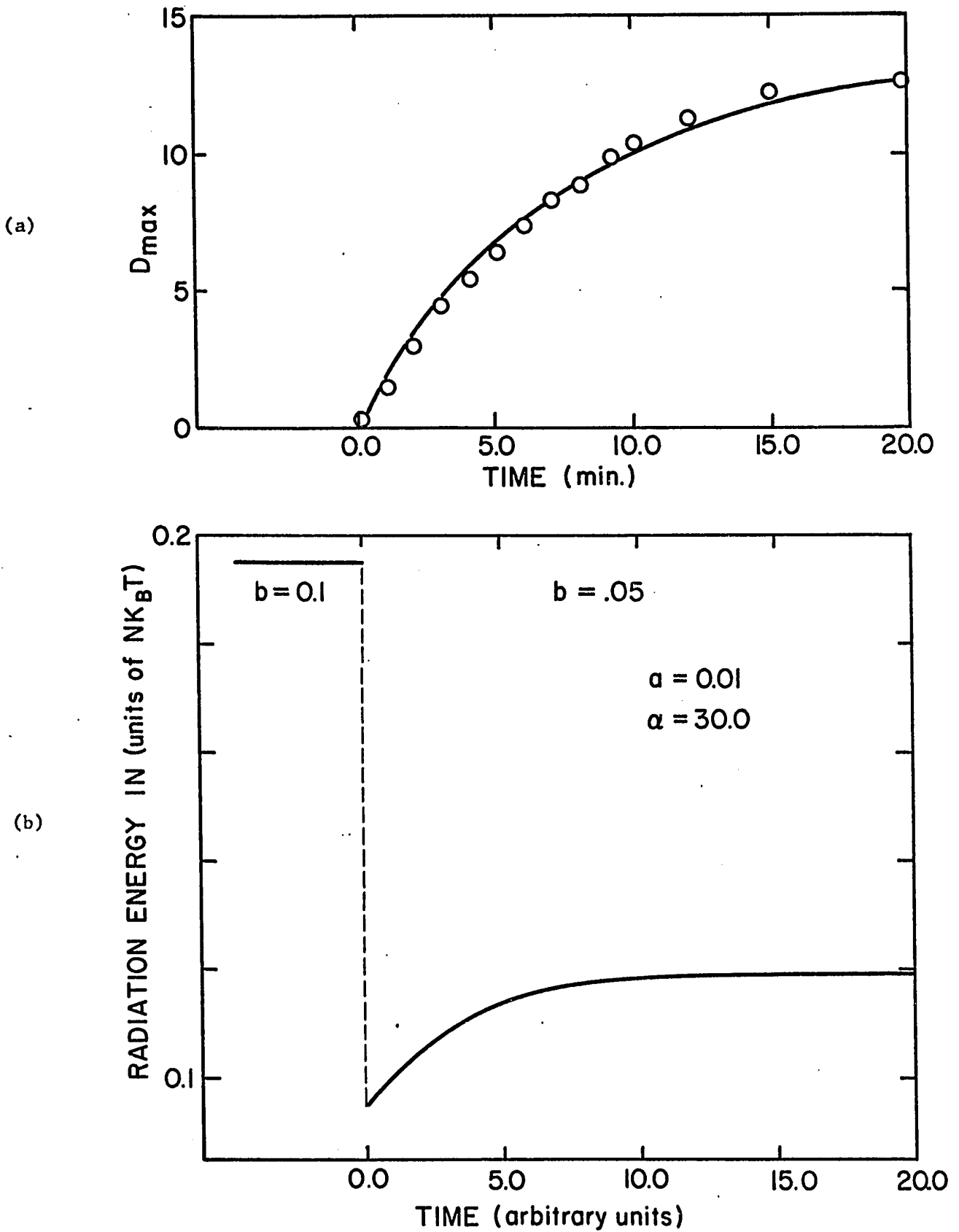


Fig. 4.10 Radiation absorption versus time. (a) Absorption versus time after decrease in r.f. signal at $t = 0$ (Bloembergen Fig. 4, 1949), (b) Absorption versus time after decrease in b . System was in steady state $t < 0$.

the analogous behaviour of our two level model. At time zero, the radiation coupling is halved. Then the graph shows the subsequent absorption of radiation as the system relaxes toward thermal equilibrium.

The main results of this section are the following:

- (i) the entropy production has a mini-max character; that is, it may either increase or decrease as the system approaches the steady state
- (ii) for certain sets of parameters and initial conditions, an increasing rate of dissipation parallels an increasing free energy
- (iii) in order that the system have a positive free energy (self-organisation) the ratio b/a must exceed some minimum value (i.e., the system must tend to a state far from equilibrium)
- (iv) for a fixed b/a ratio the free energy optimizes for an intermediate value of the level spacings.

4.6 THE THREE LEVEL MODEL

4.6.1 Introduction

This is an extension of the two level model discussed in section 4.5. The model is analysed in two parts: the first part deals with a restricted number of transitions, the second part removes this restriction.

The model is represented schematically in Fig. 4.11. For clarity the only radiative transitions shown couple levels one and three. The transition probabilities indicated in Fig. 4.12 are defined in Table 4-7. The model is composed of a system of N weakly interacting particles which are in good thermal contact with a heat bath at temperature $T^\circ(K)$. Each particle has three accessible energy states and in the general model transitions are possible between any pair of states. The system is irradiated with monochromatic beams of radiation of a resonant frequency, ν , where $h\nu = E_3 - E_1$, etc., and is allowed to evolve in time for various initial conditions and sets of parameters.

If n_i represents the number of particles in energy state i , we may write

$$n_1 + n_2 + n_3 = N \quad (4-70)$$

The occupation probabilities of the various levels may then be defined as

$$P_i = n_i/N \quad (4-71)$$

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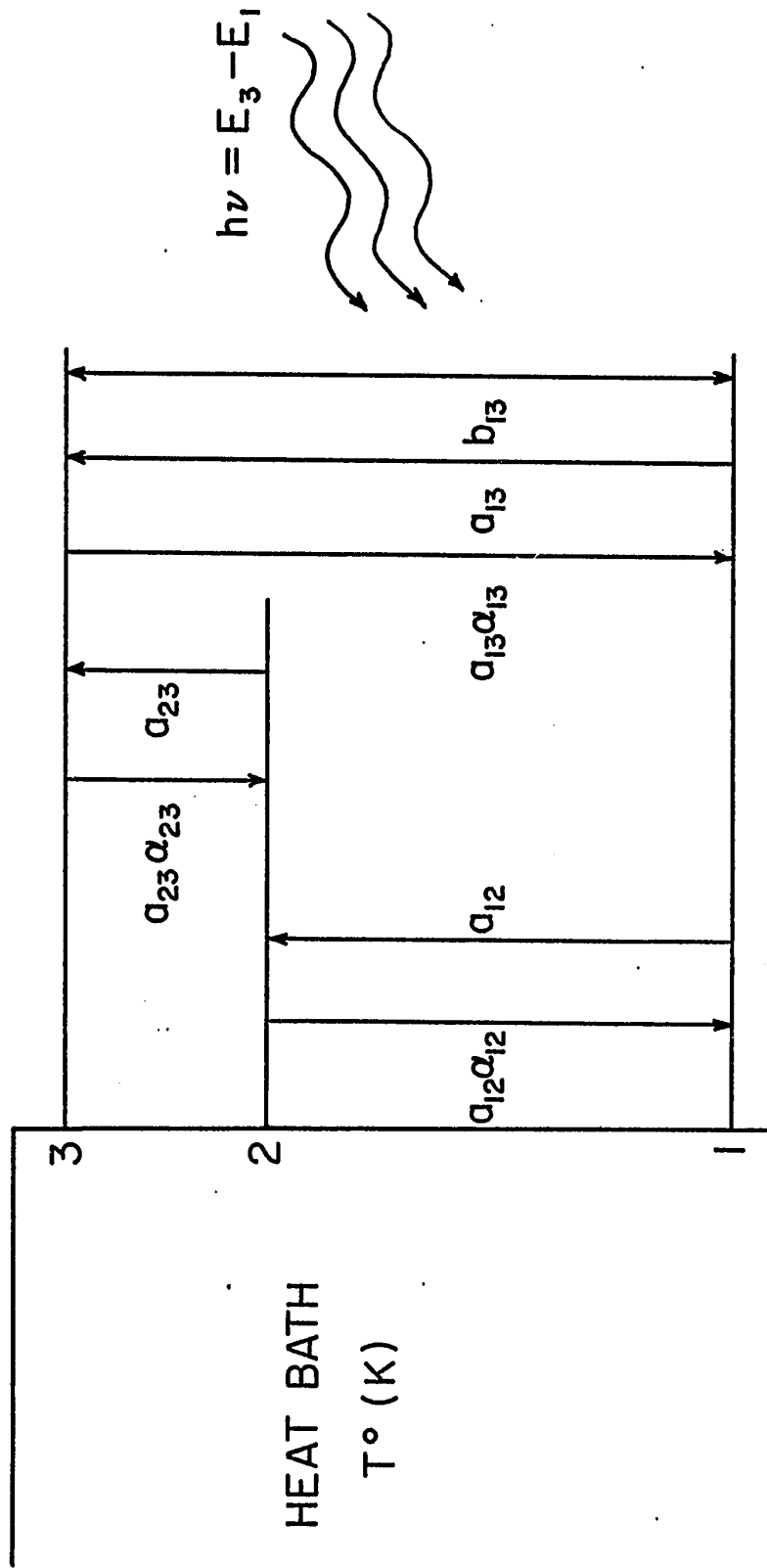


Fig. 4.11 Schematic of Three Level Model. The symbols are defined in the text.

Table 4-7

Transition Probabilities Three Level Model

Transitions from levels	Probability per unit time of transition between levels, due to interaction with	
	Heat Bath	Radiation
1 → 2	a_{12}	b_{12}
2 → 1	$a_{12}\alpha_{12}^*$	b_{12}
2 → 3	a_{23}	b_{23}
3 → 2	$a_{23}\alpha_{23}$	b_{23}
1 → 3	a_{13}	b_{13}
3 → 1	$a_{13}\alpha_{13}$	b_{13}

* α_{ij} are Boltzmann factors, such that

$$\alpha_{ij} = \exp((E_j - E_i)/K_B T)$$

with

$$P_1 + P_2 + P_3 = 1 \quad (4-72)$$

and

$$\frac{dP_1}{dt} + \frac{dP_2}{dt} + \frac{dP_3}{dt} = 0 \quad (4-73)$$

4.6.2 The Restricted Three Level Model

We first specialize the model to one where

$$b_{23} = b_{13} = a_{12} = 0 \quad (4-74)$$

Utilizing these restrictions in Table 4-7, we can write the rate equations which govern the time evolution as

$$\begin{aligned} \dot{P}_1 \equiv \frac{dP_1}{dt} &= (-a_{12} - a_{13} - b_{13}) P_1 + (a_{12}\alpha_{12}) \\ &+ (a_{13}\alpha_{13} + b_{13}) P_3 \end{aligned} \quad (4-75)$$

$$\dot{P}_2 \equiv \frac{dP_2}{dt} = (a_{12}) P_1 + (-a_{12}\alpha_{12}) P_2 \quad (4-76)$$

$$\dot{P}_3 \equiv \frac{dP_3}{dt} = (a_{13} + b_{13}) P_1 + (-a_{13}\alpha_{13} - b_{13}) P_3 \quad (4-77)$$

The exact solution of equations (4-75 to 4-77) is given in Appendix 1 in terms of arbitrary initial conditions and parameters (transition probabilities). These solutions show that all the occupation probabilities approach their steady state values asymptotically with the time.

The steady state occupations P_i^S are found by setting $dP_i/dt = 0$ in 4-75 to 4-77 and solving the resulting algebraic equations. We obtain for these steady state values

$$\left. \begin{aligned} P_1^S &= \alpha_{12} (a_{13}\alpha_{13} + b_{13})/K \\ P_2^S &= (a_{13}\alpha_{13} + b_{13})/K \\ P_3^S &= \alpha_{12} (a_{13} + b_{13})/K \end{aligned} \right\} \quad (4-78)$$

where $K = \alpha_{12} (a_{13}\alpha_{13} + b_{13}) + (a_{13}\alpha_{13} + b_{13}) + \alpha_{12} (a_{13} + b_{13})$.

It is interesting to note that in the steady state

$$\frac{P_1^S}{P_2^S} = \alpha_{12} \quad (4-79)$$

which is just the ratio that would obtain at equilibrium. This states that the degrees of freedom not coupled directly to the external driving force are effectively decoupled from that force (i.e., b_{13}) at the steady state. The values P_1^S and P_2^S are not, however, the equilibrium values.

It is apparent that the steady state occupation of level three (P_3^S) has increased over its equilibrium value (equilibration with the heat bath with $P_1^{eq} = \alpha_{13}/(1 + \alpha_{23} + \alpha_{13})$), while P_1^S and P_2^S have decreased from their equilibrium values. Thus the radiation has pushed particles into the highest energy state and depleted levels one and two.

Utilizing the evaluations introduced earlier in this chapter, we write the rate of entropy production \dot{S}_i as

$$\begin{aligned} \dot{S}_i = & NK_B \{ a_{12} P_1 \left(\frac{\alpha_{12} P_2}{P_1} - 1 \right) \ln \left(\frac{\alpha_{12} P_2}{P_1} \right) \\ & + a_{13} P_1 \left(\frac{\alpha_{13} P_3}{P_1} - 1 \right) \ln \left(\frac{\alpha_{13} P_3}{P_1} \right) \\ & + b_{13} P_1 \left(\frac{P_3}{P_1} - 1 \right) \ln \left(\frac{P_3}{P_1} \right) \} \end{aligned} \quad (4-80)$$

and the Helmholtz free energy as

$$A = NK_B T \{ P_1 \ln P_1 + P_2 \ln \alpha_{12} P_2 + P_3 \ln \alpha P_3 \} \quad (4-81)$$

Using (4-78) it is seen that \dot{S}_i , given by (4-80), reduces at the steady state to

$$\begin{aligned} (\dot{S}_i)^S = & NK_B \{ a_{13} P_1^S \left(\frac{\alpha_{13} P_3^S}{P_1^S} - 1 \right) \ln \left(\frac{\alpha_{13} P_3^S}{P_1^S} \right) \\ & + b_{13} P_1^S \left(\frac{P_3^S}{P_1^S} - 1 \right) \ln \left(\frac{P_3^S}{P_1^S} \right) \} \end{aligned} \quad (4-82)$$

That is to say the entropy production associated with the uncoupled transition vanishes at the steady state.

Table 4-8 summarizes the steady state values of the system variables, namely, the occupation probabilities, the entropy production rate and the free energy, for various limiting values of the system parameters. We note from the Table that even in the case of saturation between levels 1 and 3 it is necessary to add the additional sufficient restriction that $\alpha_{13} > 9$ to assure that the steady free energy be positive.

Exact solutions for many sets of parameters and initial conditions have been evaluated and a selection of results will now be presented. The mini-max behaviour of this model is shown clearly in Table 4-9. Initially the system was in equilibrium with the heat bath. After illumination the system immediately begins to store free energy (gained from the radiation field) and the various terms in the entropy production rate begin to change. It is apparent that terms which couple directly to the driving force are unambiguous in their behaviour. The term, D2, which results from coupling to the heat bath, increases steadily as the system moves further from equilibration with the heat bath. On the other hand, the term D3, resulting from coupling to the radiation field, decreases as the system approaches equilibrium with the energy source. The remaining term which couples with the heat bath but not directly with the energy source is ambiguous in nature, first increasing and then decreasing (it is zero in the steady state). Thus, it is apparent that evolutionary paths exist along which the entropy production rate may increase or decrease as the system approaches its steady state.

Table 4-8

Steady System Variables for Limiting Parameters

Variable	Values of Coupling Parameters			
	$a_{13} \rightarrow 0$	$a_{13} \rightarrow \infty$	$b_{13} \rightarrow 0$	$b_{13} \rightarrow \infty$
P_1	$\frac{\alpha_{12}}{(2\alpha_{12}+1)}$	$\frac{\alpha_{12}\alpha_{13}}{K_a}$ **	$\frac{\alpha_{12}\alpha_{13}}{K_a}$	$\frac{\alpha_{12}}{(2\alpha_{12}+1)}$
P_2	$\frac{1}{(2\alpha_{12}+1)}$	$\frac{\alpha_{13}}{K_a}$	$\frac{\alpha_{13}}{K_a}$	$\frac{1}{(2\alpha_{12}+1)}$
\dot{S}_i / NK_B	0	$b_{13}\alpha_{12} \left(\frac{\alpha_{23}^{-1}}{K_a}\right) \ln\alpha_{23}$	0	$a_{13} \left(\frac{\alpha_{12}}{2\alpha_{12}+1}\right) (\alpha_{13}-1) \ln\alpha_{13}$
$A / NK_B T$	$\ln y + y \ln \alpha_{13}^*$	$\ln \left(\frac{\alpha_{12}\alpha_{13}}{K_a}\right)$	$\ln \left(\frac{\alpha_{12}\alpha_{13}}{K_a}\right)$	$\ln y + y \ln \alpha_{13}^y$

* $y \equiv \frac{\alpha_{12}}{2\alpha_{12}+1}$

** $K_a = \alpha_{12}\alpha_{13} + \alpha_{12} + \alpha_{13}$

NB In order that $A^S > 0$ for $b_{13} \rightarrow \infty$ it is sufficient that $1/3 \ln \left(\frac{\alpha_{13}}{9}\right) > 0$, i.e., $\alpha_{13} > (3)^2$. For comparison, recall that for the two level model $\alpha_{12} > (2)^2$ for $A^S > 0$.

Table 4-9

Demonstration of Mini-Max Behaviour for Restricted Three Level Model*

Time	D 1** (/NK _B)	D 2** (/NK _B)	D 3** (/NK _B)	ΔA ⁺ (/NK _B T)
0	0.0	0.0	.314	0.00
1	0.0	.046	.161	.0559
2	.000009	.085	.125	.106
3	.000012	.106	.113	.134
4	.000014	.117	.104	.148
5	.0000152	.123	.101	.156
6	.0000155	.125	.0994	.159
7	.0000155	.126	.0986	.161
8	.0000155	.127	.0983	.162
9	.0000154	.127	.0982	.163
10	.0000152	.128	.0981	.163

* The system was initially in equilibrium and then at $t = 0$ was illuminated with radiation coupling levels one and three. The system parameters were:
 $a_{12} = .001$; $a_{13} = .01$; $b_{13} = .1$; $\alpha_{12} = 5$; $\alpha_{23} = 10$
 and $\alpha_{13} = 50$

**

$$D1 = a_{12} P_1 (\alpha_{12} P_2 / P_1 - 1) \ln(\alpha_{12} P_2 / P_1)$$

$$D2 = a_{13} P_1 (\alpha_{13} P_3 / P_1 - 1) \ln(\alpha_{13} P_3 / P_1)$$

$$D3 = b_{13} P_1 (P_3 / P_1 - 1) \ln(P_3 / P_1)$$

+ $\Delta A = A(t) - A(t=0)$

In Fig. 4.12 we see the effect of various initial conditions on the temporal evolution of the system. It is apparent that the behaviour is not simple, although certain trends can be identified. With respect to the rate of entropy production (Fig. 4.12 (a)), depending upon the initial conditions, the behaviour can be maximal or minimal as the system approaches the steady state and either maximal, minimal or mixed for shorter times. Indeed, there is no such criterion for anticipating each of these kinds of behaviour. Similar ambiguous behaviour occurs with respect to the free energy, as may be seen in Fig. 4.12 (b). However, it is generally the case that the free energy shows a net increase for initial conditions such that the highest energy state is underpopulated with respect to its steady value. Otherwise, the free energy shows a net decrease. Of particular significance is the purely maximal evolutionary behaviour of the entropy production rate for case (A) of Fig. 4.12 (a). This also occurs with a net increase in free energy and a maximal approach of the free energy to the steady state (case (A) of Fig. 4.12 (b)).

The effect of relative spacing between the levels is to be seen in Fig. 4.13. Both the rate of entropy production and the free energy show an increase when level two is "moved" from near level one to near level three. The evolutionary paths are similar in shape in both cases but the absolute values of the entropy production rate and the free energy have been shifted.

Fig. 4.14 shows the effect on the free energy of changing the ratio of b_{13}/a_{13} . The system was initially in equilibrium and at time zero radiation fields of various strengths were turned on. As in the two level model, a certain minimum b/a ratio is required to obtain a positive

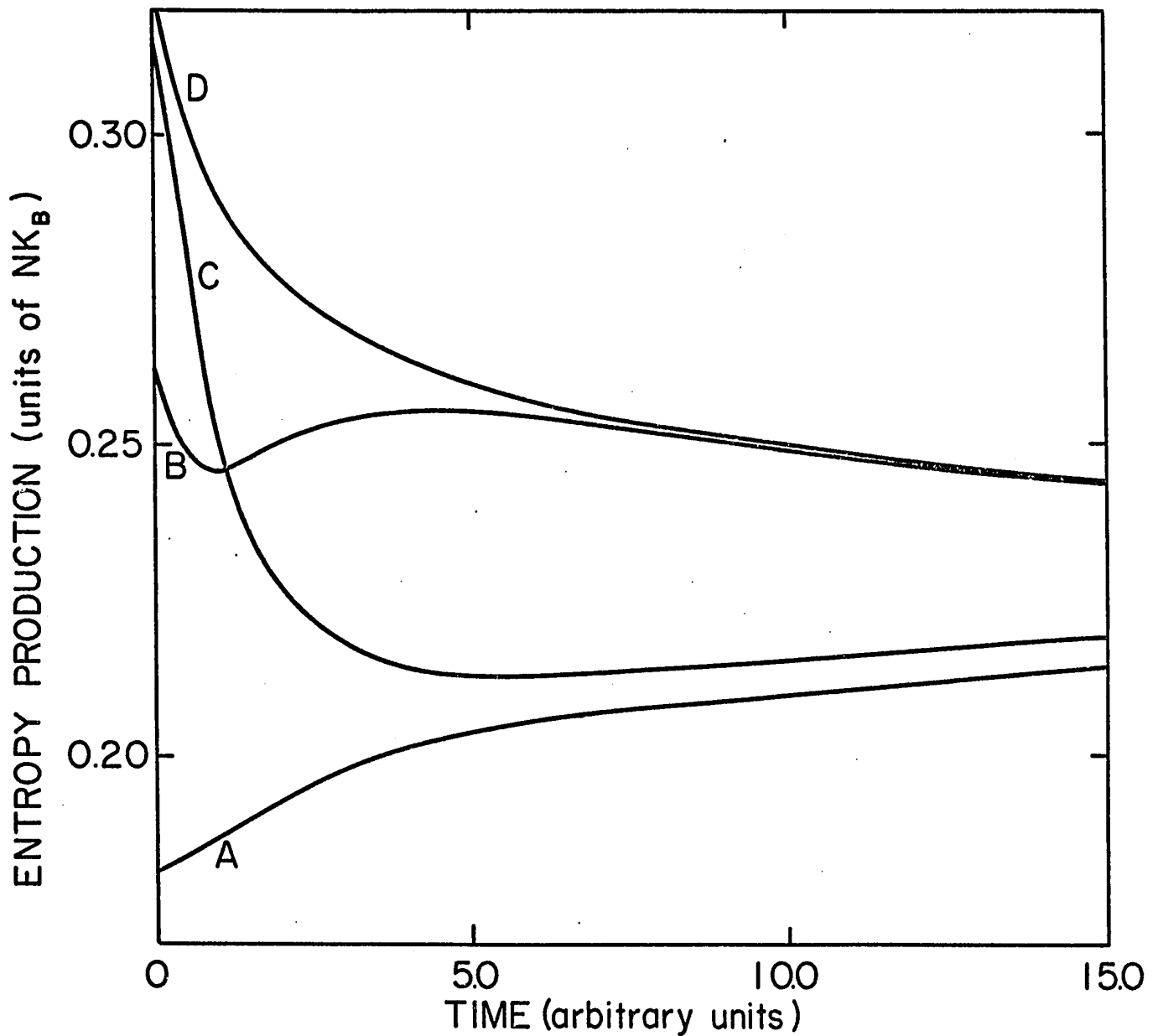


Fig. 4.12 (a) Entropy production versus time for different initial conditions. The parameters were $a_{12} = .01$, $a_{23} = 0.0$, $a_{13} = .01$, $b_{12} = b_{23} = 0.0$, $\alpha_{12} = 5.0$, $\alpha_{23} = 10$. The initial conditions were: curve A, $P_1 = .645$, $P_2 = .288$; curve B, $P_1 = .897$, $P_2 = .036$; curve C, $P_1 = .554$, $P_2 = .248$ and curve D, $P_1 = .770$, $P_2 = .030$.

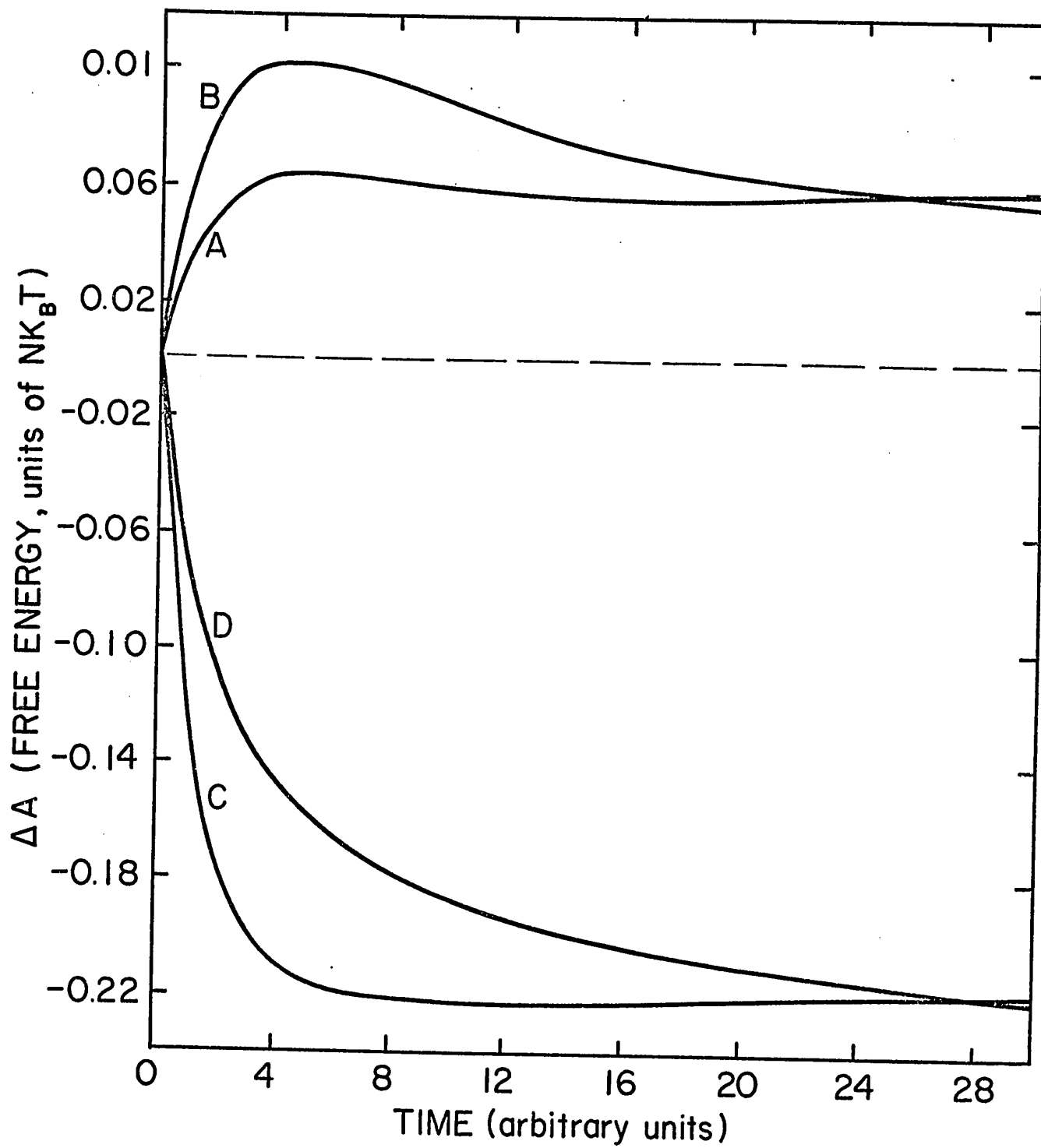


Fig. 4.12 (b) Free energy versus time. Same conditions as in Fig. 4.12 (a).

Note that $\Delta A \equiv A(t) - A(t = 0)$.

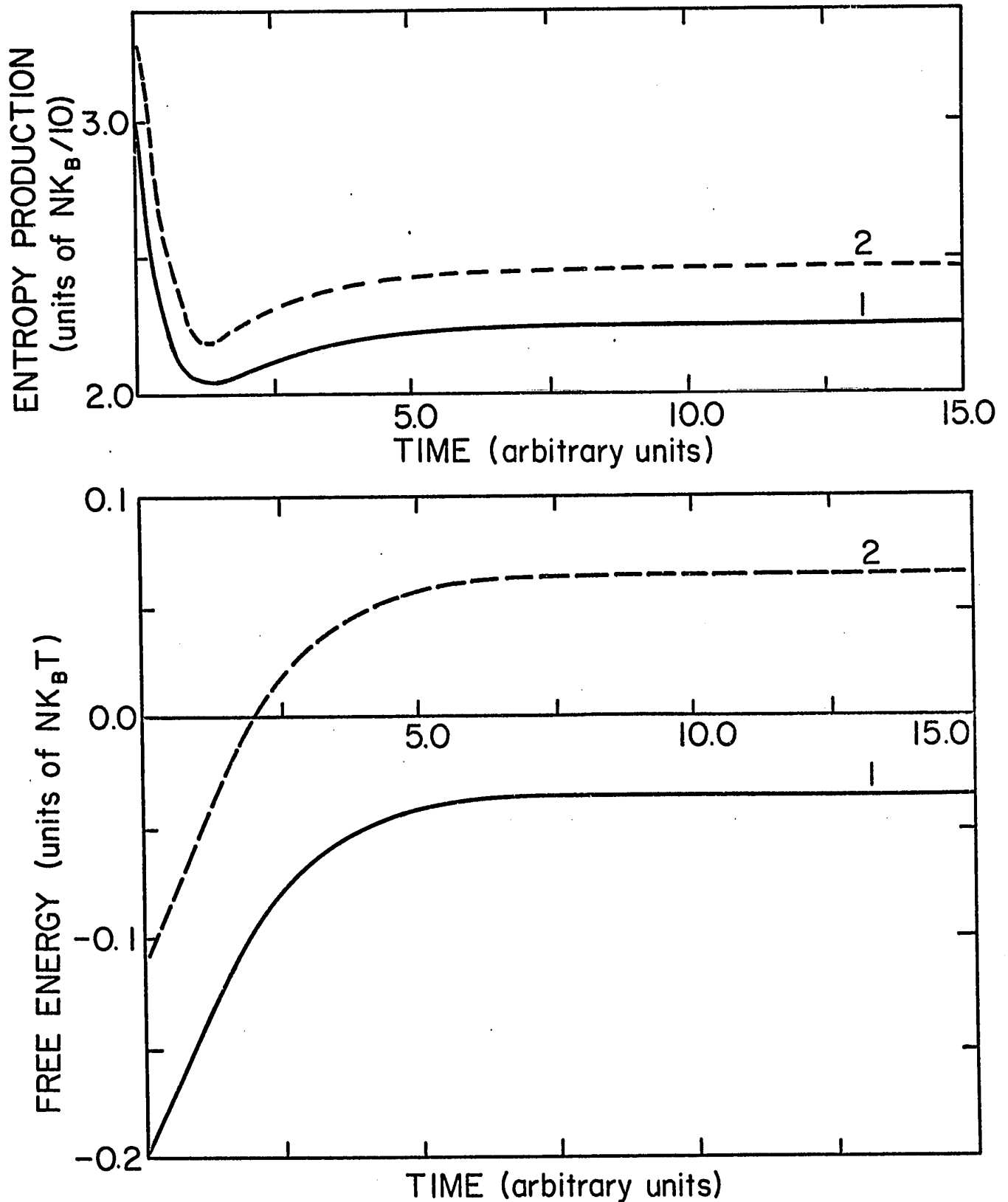


Fig. 4.13 Entropy production and free energy versus time for different level spacings. The system was initially in equilibrium. The parameters were: both curves, $a_{12} = .001$, $a_{23} = 0.0$, $a_{13} = .01$, $b_{12} = b_{23} = 0.0$, and $b_{13} = .1$; curve 1, $\alpha_{12} = 5.$, $\alpha_{23} = 10.$, and curve 2, $\alpha_{12} = 10.$, $\alpha_{23} = 5.$

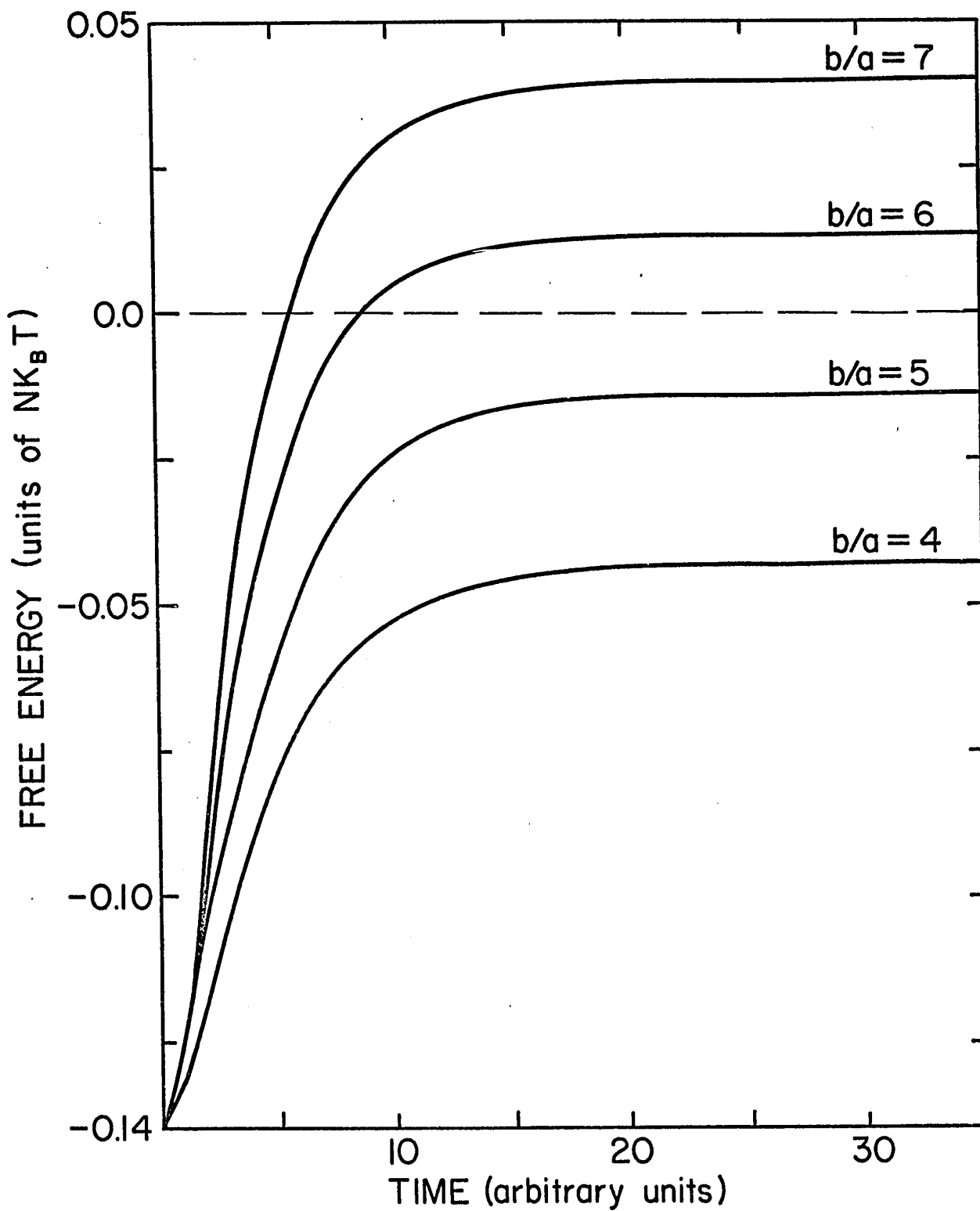


Fig. 4.14 Critical b_{13}/a_{13} . Free energy versus time. The system was initially in equilibrium. The parameters were $a_{12} = .001$, $a_{23} = 0.0$, $a_{13} = .01$, $\alpha_{12} = 10.0$, and $\alpha_{23} = 2.0$. The b_{13}/a_{13} ratios were 4, 5, 6, and 7.

free energy.

Generally speaking, the restricted three level model is similar to the two level model already discussed. The three level model, however, allows for behaviour not possible in the two level model. This will become apparent in the following discussion.

4.6.3 The Complete Three Level Model

In this generalization, we allow the possibility of transitions between any two levels. Then, with the aid of Table 4-7, we can write the equations which govern the time evolution of the occupation probabilities. These equations are

$$\begin{aligned} \frac{dP_1}{dt} = & -(a_{12} + a_{13} + b_{12} + b_{13}) P_1 + (a_{12}\alpha_{12} + b_{12}) P_2 \\ & + (a_{13}\alpha_{13} + b_{13}) P_3 \end{aligned} \quad (4-83)$$

$$\begin{aligned} \frac{dP_2}{dt} = & (a_{12} + b_{12}) P_1 - (a_{12}\alpha_{12} + b_{12} + a_{23} + b_{23}) P_2 \\ & + (a_{23}\alpha_{23} + b_{23}) P_3 \end{aligned} \quad (4-84)$$

and

$$\begin{aligned} \frac{dP_3}{dt} = & (a_{13} + b_{13}) P_1 + (a_{23} + b_{23}) P_2 \\ & - (a_{13}\alpha_{13} + b_{13} + a_{23}\alpha_{23} + b_{23}) P_3 \end{aligned} \quad (4-85)$$

The solutions to equations (4-83 to 4-85) are given in Appendix 1.

Using the methods developed previously, we can write the rate of entropy production, \dot{S}_i , as

$$\begin{aligned} \dot{S}_i = & NK_B \{ a_{12} P_1 \left(\frac{\alpha_{12} P_2}{P_1} - 1 \right) \ln \left(\frac{\alpha_{12} P_2}{P_1} \right) \\ & + a_{23} P_2 \left(\frac{\alpha_{23} P_3}{P_2} - 1 \right) \ln \left(\frac{\alpha_{23} P_3}{P_2} \right) \\ & + a_{13} P_1 \left(\frac{\alpha_{13} P_3}{P_1} - 1 \right) \ln \left(\frac{\alpha_{13} P_3}{P_1} \right) \\ & + b_{12} P_1 \left(\frac{P_2}{P_1} - 1 \right) \ln \left(\frac{P_2}{P_1} \right) \\ & + b_{23} P_2 \left(\frac{P_3}{P_2} - 1 \right) \ln \left(\frac{P_3}{P_2} \right) \\ & + b_{13} P_1 \left(\frac{P_3}{P_1} - 1 \right) \ln \left(\frac{P_3}{P_1} \right) \} \end{aligned} \quad (4-86)$$

Similarly, the free energy may be written as

$$A = NK_B T \{ P_1 \ln P_1 + P_2 \ln(\alpha_{12} P_2) + P_3 \ln(\alpha_{13} P_3) \} \quad (4-87)$$

As usual the energy of level 1 is taken as the free energy reference state and the configuration with $P_1 = 1$ and $P_2 = P_3 = 0$ as the entropy reference state.

At the steady state we have the condition that

$$\frac{dP_i}{dt} = 0 \quad (i = 1, 2, 3) \quad (4-88)$$

This allows us to solve the algebraic equations resulting from (4-83 to 4-85) for the steady state occupations, viz.

$$P_1^S = \frac{\{(a_{12}\alpha_{12} + b_{12})(a_{23}\alpha_{23} + b_{23}) + (a_{13}\alpha_{13} + b_{13})(a_{12}\alpha_{12} + b_{12} + a_{23} + b_{23})\}}{D} \quad (4-89)$$

$$P_2^S = \frac{\{(a_{21}\alpha_{12} + b_{12})(a_{13}\alpha_{13} + b_{13}) + (a_{23}\alpha_{23} + b_{23})(a_{12} + b_{12} + a_{13} + b_{13})\}}{D} \quad (4-90)$$

$$P_3^S = 1 - P_1^S - P_2^S \quad (4-91)$$

with

$$D = (a_{12} + b_{12} + a_{13} + b_{13})(a_{23}\alpha_{23} + a_{23} + 2b_{23}) + (a_{23}\alpha_{23} + b_{23} + a_{13}\alpha_{13} + a_{13} + 2b_{13})(a_{12}\alpha_{12} + b_{12}) + (a_{13}\alpha_{13} + b_{13})(a_{12} + b_{12} + a_{23} + b_{23})$$

Table 4-10 gives the values of the system variables for certain limiting values of the system parameters (transition probabilities). It is to be noted that in each case all parameters not explicitly referred to are to be assumed non-zero and finite. Column II is, of course, identical to the results given for the restricted three level model, with $b_{13} \rightarrow \infty$. We note, however, that $P_3 > P_2$ even though level three is at a higher energy than level two. Thus, if the system is irradiated with a weak radiation of energy

$$h\nu_{23} = E_3 - E_2 \quad (4-92)$$

the system will emit more radiation than it absorbs. This is analogous to stimulated emission from a three level laser. If the external source is weak then the population inversion can be maintained indefinitely by the "pumping" of level three due to radiation coupling between levels one and three. In the two-level model an inverted population can only be maintained transiently as a result of prepared initial conditions, so continuous stimulated emission is not possible.

Column I of Table 4-10 shows the situation where level two is more densely populated than level one. Again, for a weak external radiation of frequency ν_{12} such that

$$h\nu_{12} = E_2 - E_1 \quad (4-93)$$

it is possible to obtain continuous stimulated emission with this set of parameters.

Table 4-10

Steady State Values for Limiting Cases of System Parameters⁺⁺

	I	II	III	IV
Parameters	$a_{12} \approx 0$ $b_{13}/a_{13} \gg 1$	$a_{23} \approx 0$ $b_{13}/a_{13} \gg 1$	$a_{12}/b_{11} \approx a_{23}/b_{11} \gg 1^*$	$b_{12}/a_{11} \approx b_{23}/a_{11} \gg 1^+$
Variables	$(b_{12} \approx b_{23} \approx 0)$	$(b_{12} \approx b_{23} \approx 0)$	(Equilibrium With Sink)	(Equilibrium With Source)
P_1	$\frac{1}{a_{23}+2}$	$\frac{a_{12}}{2a_{12}+1}$	$\frac{a_{13}}{a_{13}+a_{23}+1}$	1/3
P_2	$\frac{a_{23}}{a_{23}+2}$	$\frac{1}{2a_{12}+1}$	$\frac{a_{23}}{a_{13}+a_{23}+1}$	1/3
P_3	$\frac{1}{a_{23}+2}$	$\frac{a_{12}}{2a_{12}+1}$	$\frac{1}{a_{13}+a_{23}+1}$	1/3
S_1/K_1T	$a_{13}(\frac{1}{a_{23}+2})(\alpha_{13}^{-1}) \ln \alpha_{13}$	$a_{13}(\frac{a_{12}}{2a_{12}+1})(\alpha_{13}^{-1}) \ln \alpha_{13}$	$(\frac{1}{a_{13}+a_{23}+1})\{b_{12}(\alpha_{13}^{-1}) \ln(\frac{a_{12}}{a_{23}}) + b_{13}(\alpha_{13}^{-1}) \ln \alpha_{13}\}$	$\frac{1}{3} a_{12}(\alpha_{12}^{-1}) \ln \alpha_{12} + a_{13}(\alpha_{13}^{-1}) \ln \alpha_{13} + a_{23}(\alpha_{23}^{-1}) \ln \alpha_{23}$
A/NK_1T	$(\frac{1}{a_{23}+2})\{\ln(\frac{a_{13}a_{23}}{(a_{23}+2)^2}) + a_{23} \ln(\frac{a_{12}}{a_{23}+2})\}$	$\ln(\frac{a_{12}}{2a_{12}+1}) + (\frac{a_{12}}{2a_{12}+1}) \ln(\alpha_{13})$	$\ln(\frac{a_{13}}{a_{13}+a_{23}+1})$	$\frac{1}{3} \ln \frac{a_{12}a_{13}}{27}$

* the results are the same for any pair of the a_{ij} large (or all three large)

+ the results are the same for any pair of the b_{ij} large (or all three large)

++ see discussion following table

Column III of Table 4-10 shows the case where the system couples strongly to the heat sink. The populations of the levels are their equilibrium values and it is apparent that the free energy is negative.

Column IV of Table 4-10 shows the case where the system is in equilibrium with the radiation (energy) source (saturation). All levels are equally populated and the free energy will be positive if the level spacing is sufficiently great. For positive free energy, we require that $\alpha_{ij} > 3$ or $\Delta\epsilon_{ij} > K_B T \ln 3$. Compare this with $\Delta\epsilon > K_B T(2\ln 2)$ for the saturated two level model.

It is apparent from Table 4-11 that the complete three level model exhibits the mini-max behaviour characteristic of all these models. Three terms behave unambiguously, with two of them increasing monotonically and one decreasing monotonically. The remaining term (D1) is more complicated and initially increases and later decreases. Similar behaviour is observed for additional terms when present. It is usual for terms which couple directly to a single external field to behave in a monotonic fashion.

Since many properties of the complete three level model are the same as those of the restricted three level model only a few important similarities and differences will be discussed in the following paragraphs.

Fig. 4.15 shows the effect of increasing the ratio b_{13}/a_{13} for the complete model. Again a certain minimum ratio is required in order that the steady state free energy is positive. However, a comparison of Fig. 4.15 with Fig. 4.14 shows that stronger external fields are required to ensure positive steady state free energy in the complete three level model than in the restricted three level model. This is due to the fact

Table 4-11

Mini-Max Behaviour of the Three Level Model*

Time	D 1** (/NK _B)	D 2** (/NK _B)	D 3** (/NK _B)	D 4** (/NK _B)	ΔA ⁺ (/NK _B T)
0	0.0	0.0	0.0	.314	0.0
1	.000380	.0012	.00634	.143	.0778
2	.000766	.0028	.0148	.0895	.190
3	.000907	.00428	.0225	.0616	.296
4	.000885	.00557	.0292	.0450	.387
5	.000793	.00665	.0347	.0344	.463
6	.000685	.00755	.0392	.0274	.526
7	.000584	.00828	.0429	.0225	.576
8	.000500	.00878	.0459	.0191	.617
9	.000432	.00936	.0482	.0167	.650
10	.000379	.00975	.0501	.0146	.677

* The system was initially in equilibrium and at $t = 0$ was illuminated with radiation coupling levels one and three. The system parameters were:

$$a_{12} = .1; a_{23} = .001; a_{13} = .001; b_{13} = .1; \alpha_{12} = 5.;$$

$$\alpha_{23} = 10.; \alpha_{13} = 50.$$

$$** D1 = a_{12}(\alpha_{12}P_2 - P_1) \ln(\alpha_{12}P_2/P_1)$$

$$D2 = a_{23}(\alpha_{23}P_3 - P_2) \ln(\alpha_{23}P_3/P_2)$$

$$D3 = a_{13}(\alpha_{13}P_3 - P_1) \ln(\alpha_{13}P_3/P_1)$$

$$D4 = b_{13}(P_3 - P_1) \ln(P_3/P_1)$$

$$+ \Delta A = A(t) - A(t=0)$$

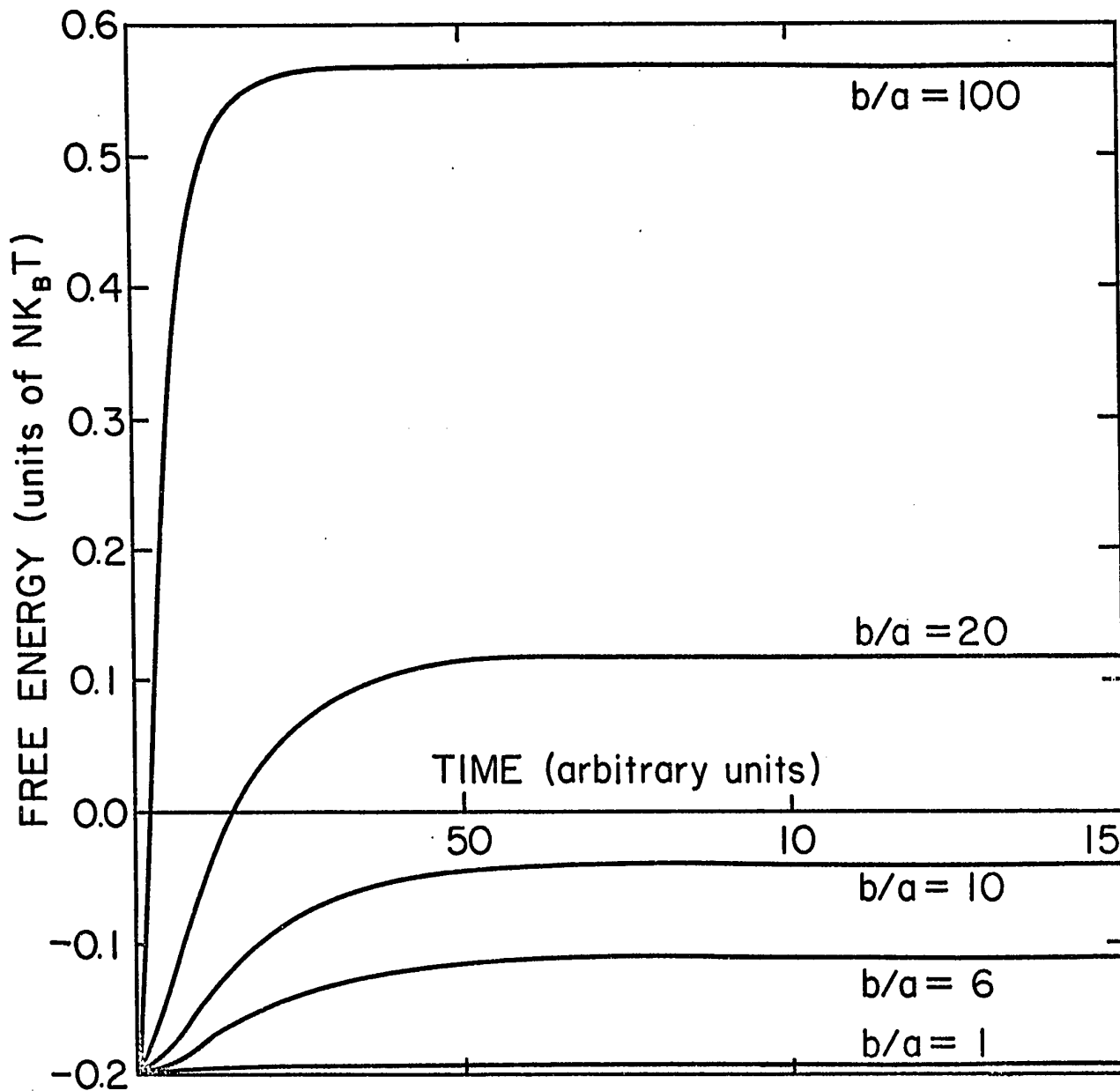


Fig. 4.15 Critical b_{13}/a_{13} . Free energy versus time. The system was initially in equilibrium and the parameters were $a_{12} = .01$, $a_{23} = .001$, $a_{13} = .01$, $b_{12} = b_{23} = \alpha_{12} = 5$, and $\alpha_{23} = 0$. The ratios of b_{13}/a_{13} were 1, 6, 10, 20, and 100.

that the complete three level model allows more energy to be lost to the heat bath and thus more energy (per unit time) must be supplied to the system (per unit time) to maintain the system at a particular free energy level.

Fig. 4.16 shows the effect of turning the radiation (energy source) on or off at a particular instant where the steady state occupation of level two is less than the occupation of level three. The rate of entropy production minimizes in each instance, but we see that when the radiation is present the free energy always increases. The system always increases its organisation (free energy content) when free energy from the radiation is available. It is also apparent that the system attains a larger free energy when level two is near to level three than it does when level two is closer to level one.

Fig. 4.17 describes an example of "stimulated emission". Curve 1 of Fig. 4.17 represents the situation where level three has a larger steady state population than level two. At a certain time after this steady state has been reached a small external radiation, which couples levels two and three, is turned on. We see from Fig. 4.17 (b) that the system loses free energy during the time that b_{23} is non-zero. Further, from Fig. 4.17 (c) we see that the energy is lost in the form of radiation energy of frequency ν_{23} such that

$$h\nu_{23} = E_3 - E_2 \quad (4-94)$$

An incremental time later, the radiation field (b_{23}) is turned off and the system relaxes to its previous steady state.

Fig. 4.16 (a) Entropy production versus time. System was initially in equilibrium. At $t = 20$ the radiation was turned off and at $t = 30$ the radiation was turned on again. The parameters were: both curves, $a_{12} = .1$, $a_{23} = a_{13} = .001$, $b_{12} = b_{23} = 0.0$, and $b_{13} = .1$; curve 1 $\alpha_{12} = 10.$, $\alpha_{23} = 5.$, and curve 2, $\alpha_{12} = 5.$, $\alpha_{23} = 10.$

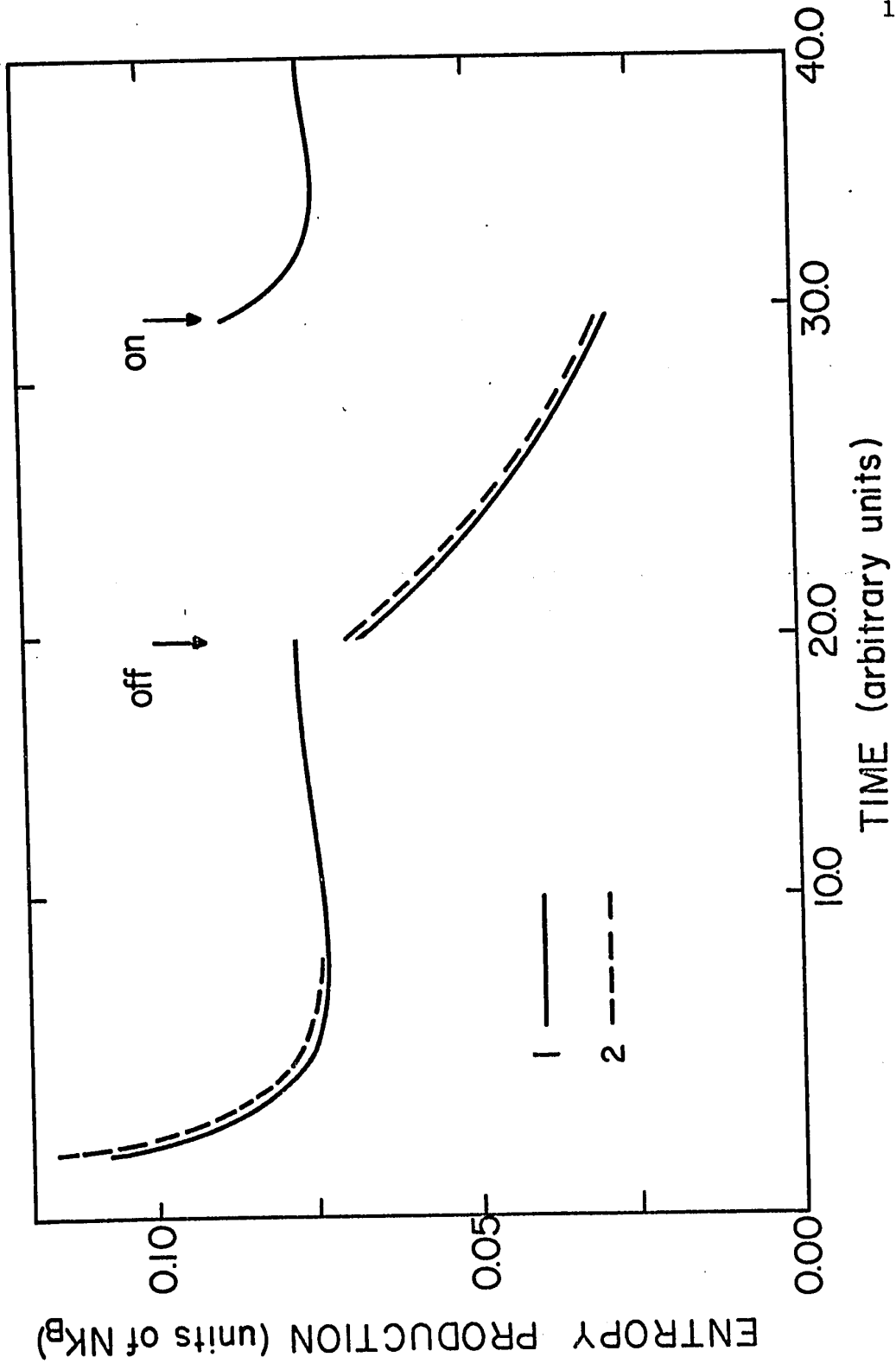


Fig. 4.16 (a)

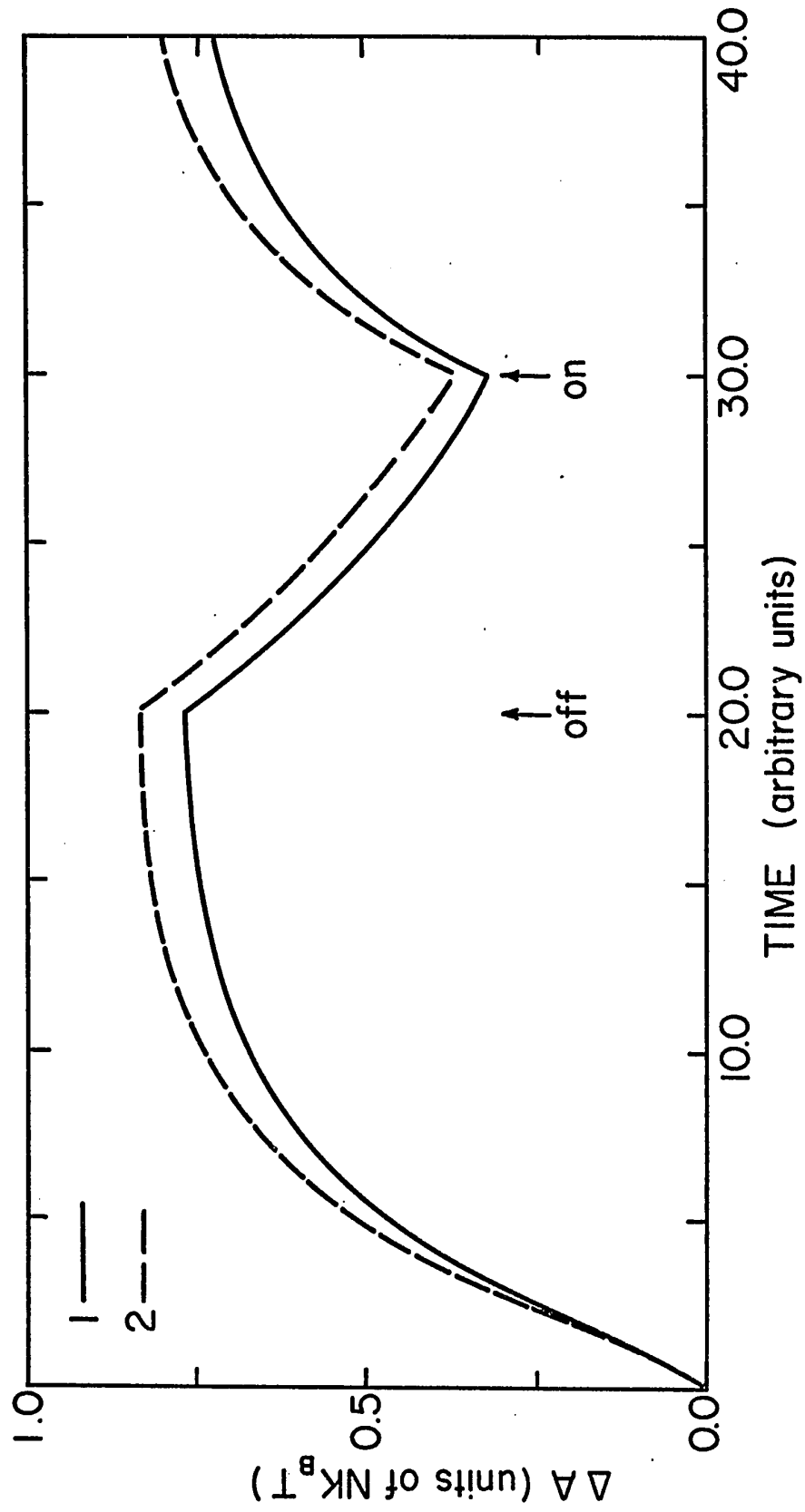


Fig. 4.16 (b) Free energy versus time. Same conditions as in Fig. 4.16 (a). Note that

$$\Delta A \equiv A(t) - A(t = 0).$$

Fig. 4.17 (a) Entropy production versus time. The system was initially in equilibrium. For $20 < t < 30$, $b_{23} = 1.0$ and for all other times, $b_{23} = 0.0$. The parameters were for curve 1: $a_{12} = .1$, $a_{23} = .00001$, $a_{13} = .01$, $b_{13} = 1.0$, $b_{12} = 0$, $\alpha_{12} = 5.$, $\alpha_{23} = 10.$, and for curve 2: $a_{12} = .00001$, $a_{23} = .1$, $a_{13} = .01$, $b_{13} = 1.0$, $b_{12} = 0$, $\alpha_{12} = 5.$, and $\alpha_{23} = 10.$

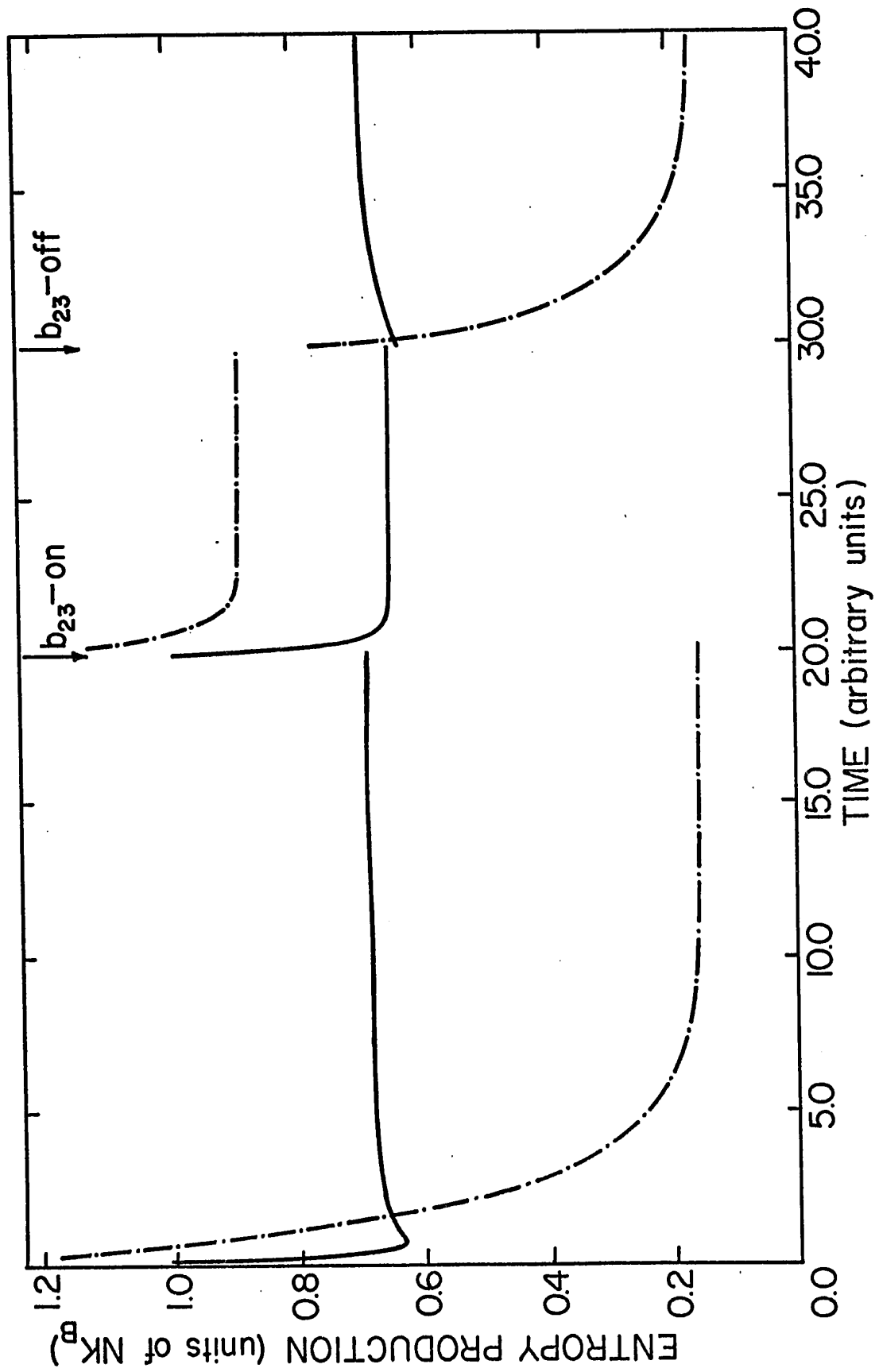


Fig. 4.17 (a)

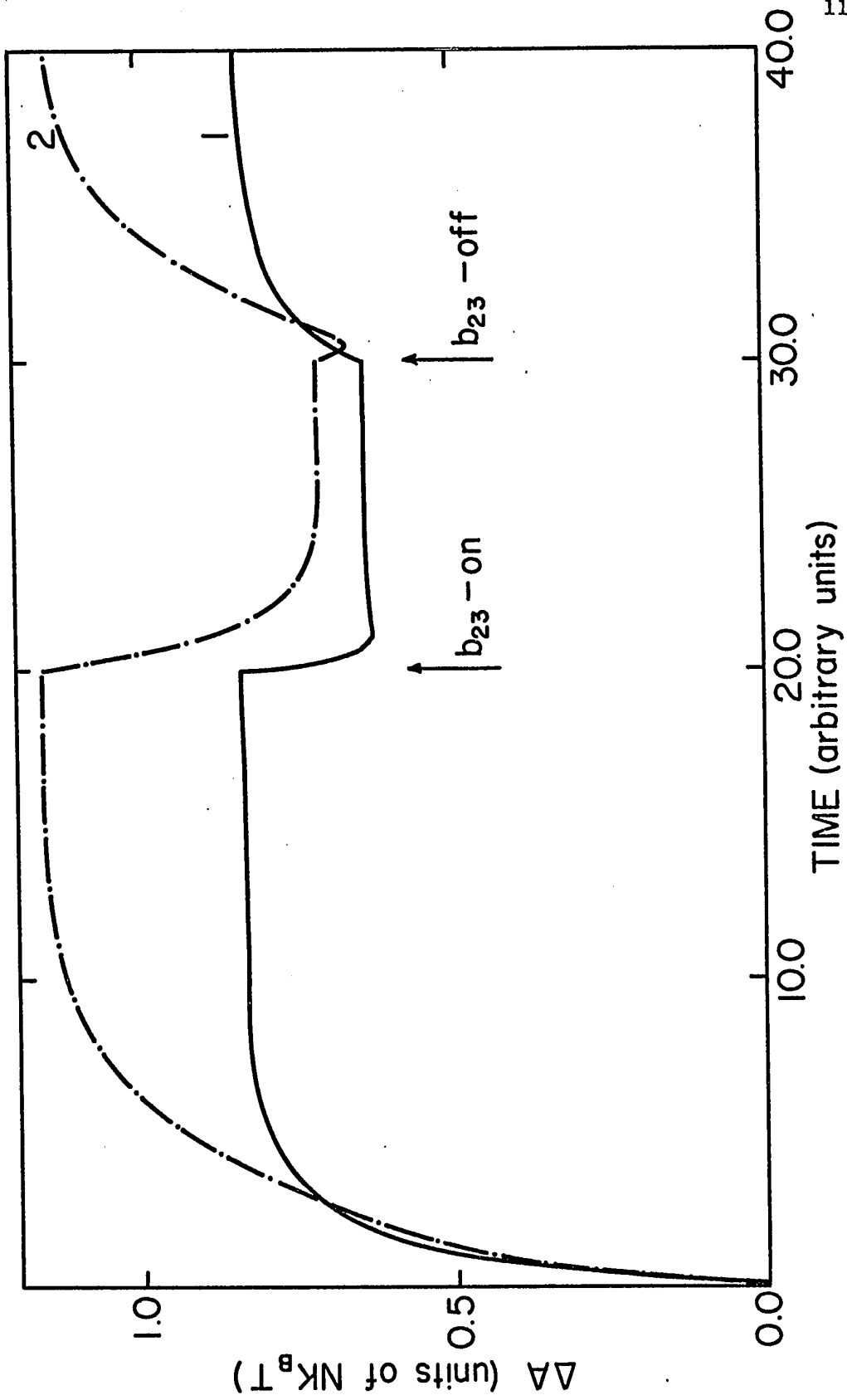


Fig. 4.17 (b) Free energy versus time. Graph 1 and Graph 2 are for the same conditions as in

Fig. 4.17(a). Note that $\Delta A \equiv \Lambda(t) - \Lambda(t = 0)$.

Fig. 4.17 (c) Radiant energy absorption versus time. Graph 1 and Graph 2 are for the same conditions as in Fig. 4.17 (a). J_{ij}^A is the free energy absorbed per unit time due to radiative transitions between levels i and j .

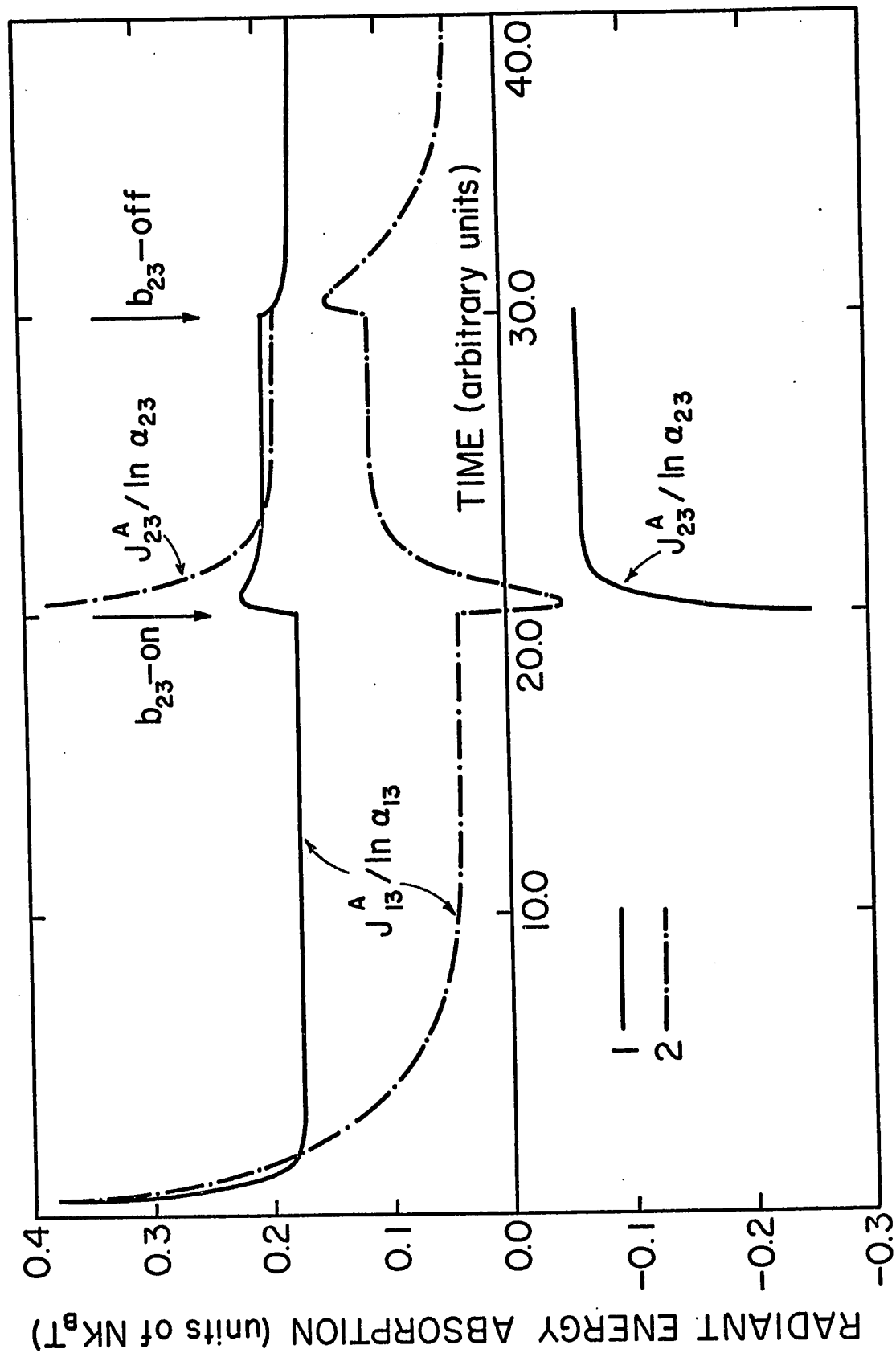


FIG. 4.17 (c)

Curve 2 of Fig. 4.17 represents the situation where the steady state occupations are ordered in the normal fashion, i.e., $P_1 > P_2 > P_3$. In this instance we see that although the system now absorbs radiant energy of frequency ν_{23} in the time interval when $b_{23} \neq 0$, in the same interval the system shows a net decrease in free energy. It is apparent that although the system absorbs more radiant energy, it must be losing an even larger amount to the heat bath.

4.6.4 Discussion of Three Level Model

In many respects the three level model behaves in a similar fashion to the two level model. For example, both the two level model and the three level model exhibit mini-max behaviour in the entropy production rate. In addition, both models require a minimum (critical) b/a ratio in order that the steady state free energy be positive. There are other similarities, but let us now recall one important difference. In the three level model it is possible to maintain a steady state in which one of the high lying levels is more populated than a lower level. In assessing the importance of this population inversion, let us assume that we are interested in a system with the populations of levels three and two inverted (i.e., $P_3 > P_2$). One way of obtaining such a system would be to apply a strong field coupling levels one and three (causing saturation). Then, if the system is such that $a_{12}\alpha_{12} > a_{23}\alpha_{23}$, it is possible to attain $P_3 > P_2$. Thermal transitions would normally empty level two faster than it is being supplied but level three is being maintained at a high population level by the radiation pumping.

If we now apply a weak radiation field which couples levels two

and three, it is readily seen that the system emits more radiant energy of frequency ν_{23} than it absorbs (i.e., stimulated emission). The energy emitted per unit time is given by

$$\begin{aligned} J_A^{23} &= N \epsilon_{23} b_{23} (P_3 - P_2) \\ &= NK_B T (\ln \alpha_{23}) b_{23} (P_3 - P_2) \end{aligned} \quad (4-95)$$

where $N b_{23} (P_3 - P_2)$ is the number of radiative transitions per unit time from level three to level two and ϵ_{23} is the energy emitted per transition. The situation described is of course a simple model of a three level maser (or laser) (Singer, 1959).

It is of interest to compare the predicted rate of energy output of our model with the predictions of Bloembergen (1956) for a similar arrangement. Taking the liberty of rewriting Bloembergen's equation (4) in our notation, we obtain for the emitted power P_m

$$P_m = \frac{N h^2 \nu_{23}}{3K_B T} \frac{(a_{21} \nu_{12} - a_{32} \nu_{23})}{(a_{21} + a_{32} + b_{23})} b_{23} \quad (4-96)$$

If we assume that the power of the stimulating radiation is small ($b_{23} \ll a_{21}, a_{32}$) then (4-96) may be written as

$$\begin{aligned}
 P_m &\approx \frac{N h^2 \nu_{23}}{3K_B T} \frac{(a_{21} \nu_{12} - a_{32} \nu_{23})}{(a_{21} + a_{32})} b_{23} \\
 &= N \left(\frac{h \nu_{23}}{3K_B T} \right) (h \nu_{23}) \left[\frac{(a_{21} \nu_{12} / a_{32} \nu_{23}) - 1}{(a_{21} / a_{32}) + 1} \right] b_{23} \quad (4-97)
 \end{aligned}$$

Expression (4-97) was derived assuming full saturation at the frequency ν_{13} and that the level spacing is small (i.e., that we approximate the Boltzmann factors by their linear terms).

Utilizing the results of Table 4-10, Column II, we can write (4-95) as

$$\begin{aligned}
 J_A^{23} &\approx N K_B T \ln \alpha_{23} [(\alpha_{12} - 1) / (2\alpha_{12} + 1)] b_{23} \\
 &= N (h \nu_{23}) [(\alpha_{12} - 1) / (2\alpha_{12} + 1)] b_{23} \quad (4-98)
 \end{aligned}$$

where we have assumed full saturation at frequency ν_{13} and that level three is metastable with respect to level two (i.e., a_{23} very small ≈ 0). Both (4-97) and (4-98) assume weak radiations at the amplifying frequency ν_{23} . The expressions (4-97) and (4-98), based on similar models, are nearly identical. The differences are due to our retention of the full exponential (more accurate) and the assumption of ideal population inversion (i.e., $a_{23} \approx 0$, less realistic).

To compare the predictions of (4-97) and (4-98), we use the values of McWhorter and Meyer (1958) for a particular three level

system*. We have $N = 3.9 \times 10^{19}$, the population of the upper three levels at 1.25°K, $\nu_{23} = 2800$ Mc/sec., $\nu_{12} = 6600$ Mc/sec., and $a_{21} \approx a_{32} \approx 1/T_1$, where $T_1 = .2$ sec. is the spin lattice relaxation time. In addition, we assume that $b_{23} \sim 1/10 a_{21}$ since we would like the stimulating field to be weak. With the above parameters, we find that

$$P_m \approx 44 \text{ erg/sec.}$$

and

$$J_A^{23} \approx 58 \text{ erg/sec.}$$

These values are both smaller than the theoretical maximum (large b_{23}) value of 87 ergs/sec. output but still very much larger than the measured maximum value of about 40 ergs/sec. McWhorter and Meyer suggest that the discrepancy (50%) can be accounted for by cavity and coupling losses.

Considering the approximate nature of the models, the agreement between our value and Bloembergen's is quite satisfactory. We note that for the value of b_{23} chosen ($b_{23} \approx a_{32}/10$) the steady state emitted power

* The values were measured by McWhorter and Meyer for a three level system consisting of the upper three levels of the Cr^{+++} ion. The "physical" system was a .5% solid solution of a chromium salt in a diluent (potassium chromicyanide).

is between 50% (Bloembergen's value) and 70% (our value) of the theoretical maximum. It is not surprising that our value is the higher one, since our assumptions ensure the maximum possible population inversion.

It is interesting to see from Fig. 4.16 that in the presence of a source of free energy the system tends to increase its organisation (i.e., free energy). It is apparent therefore, that if the system had a mechanism whereby it can continuously store the free energy which it is accumulating then it, or a collection of such systems, can act as an energy reservoir for a second system. The system of three level particles then acts as a transducer, converting the free energy of the radiation into some form of stored free energy (chemical, electromagnetic radiation of a different frequency, etc.). This problem of energy storage will be discussed in a later section.

Another interesting feature of the three level model is the fact that it undergoes a type of phase transformation at the margin where two of the populations become inverted. If we consider inversion between level three and level two then, for $P_3 < P_2$, the system absorbs radiant energy due to radiative transitions between levels 2 and 3, while for $P_3 > P_2$, the system loses energy. If $P_3 = P_2$, the system is neutral, neither gaining nor losing radiant energy. Thus, the system changes character with respect to radiative transitions, as the populations become inverted. This is a kind of symmetry change which will be discussed further in Chapter 6.

Further general discussion of this model will be reserved for the end of this Chapter.

4.7 THE FOUR LEVEL MODEL

4.7.1 Introduction

The model system considered here consists of a collection of free* paramagnetic atoms (ions) which is placed in a strong magnetic field. The energy levels of the paramagnetic atoms are dominated by the Zeeman splitting of the energy levels (Kittel, 1967) but in strong fields the hyperfine interaction (between the magnetic moment of the nuclear and electronic spins) gives rise to an additional small splitting. For electrons in an s state the form of the interaction is

$$V = a \underline{I} \cdot \underline{S}$$

$$\approx a M_S M_I^+ \text{ (strong fields)} \quad (4-99)$$

where I is the nuclear spin in units of h (Kittel, *ibid*).

4.7.2 The Model

If we assume that $S = 1/2$ and $I = 1/2$, then the energy level scheme of a free atom is represented schematically as in Fig. 4.18. The number of allowed transitions is restricted by the fact that electronic transitions must have $\Delta M_I = 0$, and nuclear transitions must have $\Delta M_S = 0$ (Kittel, *ibid*).

* Such a system is equivalent to a dilute solution (solid or otherwise) of paramagnetic ions in a diluent.

+ M_S, M_I are the magnetic quantum numbers

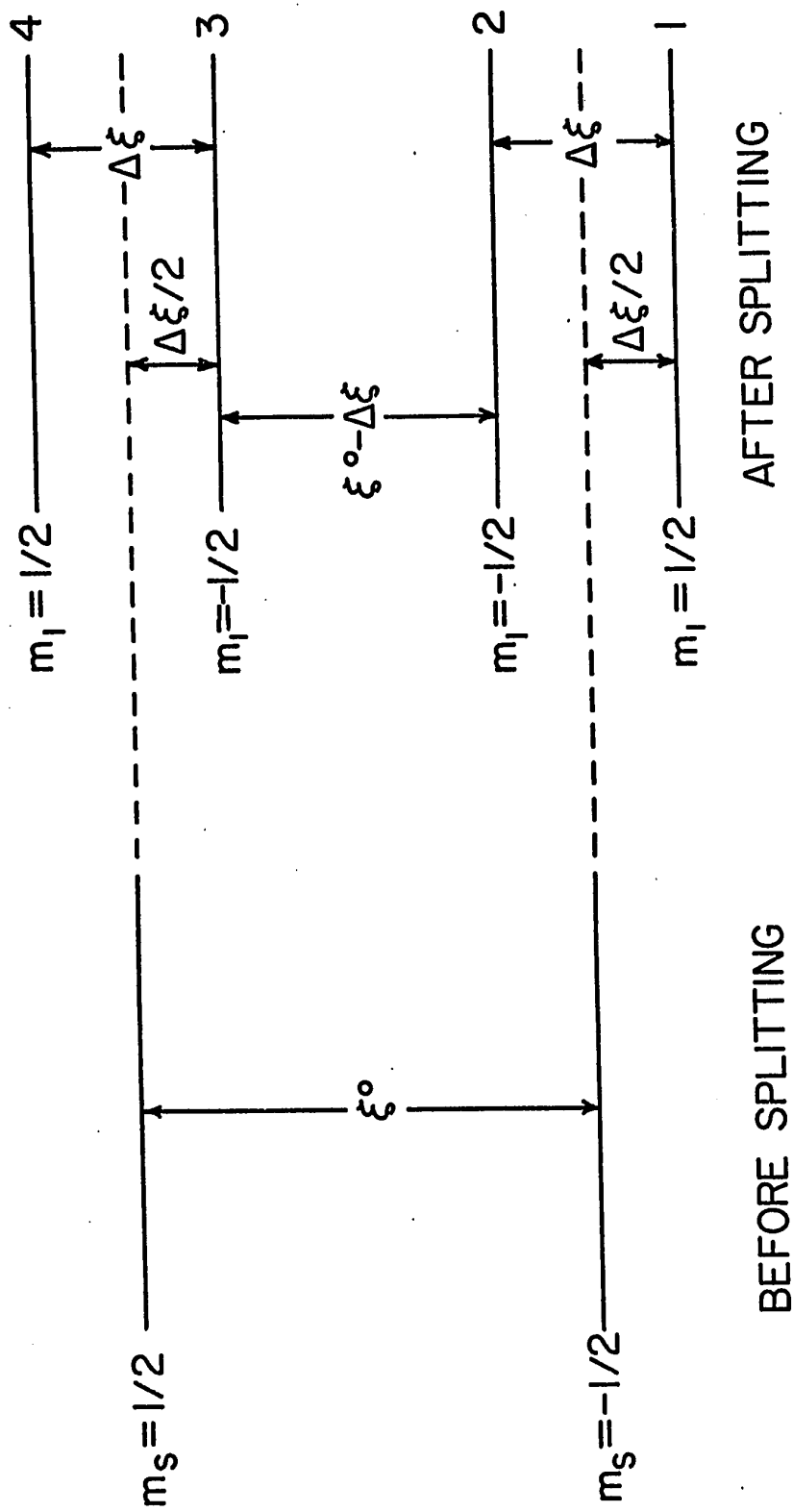


Fig. 4.18 Schematic of Four Level Model.

Let us now imagine that the system consists of a dilute solution of N such paramagnetic atoms each of which is in good thermal contact with a heat bath (lattice) at a temperature of $T^\circ\text{K}$. Then, there are two allowed electronic transitions which may be stimulated by radiation of the resonant frequencies ν_{14} , ν_{23} such that

$$h\nu_{14} = \epsilon^\circ + \Delta\epsilon$$

and

$$h\nu_{23} = \epsilon^\circ - \Delta\epsilon$$

In addition, there are thermal relaxation transitions which couple the spins and the heat bath. With the above restrictions in mind, the allowed transition probabilities can be defined as in Table 4-12.

Kittel states that the frequencies of the nuclear transitions $1 \rightarrow 2$ and $3 \rightarrow 4$ are very nearly equal so we shall set $C_1 = C_2 = C$.

We can now write the equations which govern the occupation probabilities of the levels as

$$\frac{dP_1}{dt} = -(a_{14} + b_{14} + C) P_1 + (\alpha C) P_2 + (a_{14}\alpha_{14} + b_{14}) P_4 \quad (4-100)$$

$$\frac{dP_2}{dt} = (C) P_1 - (a_{23} + b_{23} + C\alpha) P_2 + (a_{23}\alpha_{23} + b_{23}) P_3 \quad (4-101)$$

Table 4-12

Transition Probabilities Four Level Model

Transitions from levels	Probability per unit time of transition between levels, due to interaction with	
	Heat Bath	Radiation
1 → 4	a_{14}	b_{14}
Electronic 2 → 3	a_{23}	b_{23}
3 → 2	$a_{23}\alpha_{23}^*$	b_{23}
4 → 1	$a_{14}\alpha_{14}$	b_{14}
1 → 2	C_1	--
Nuclear 2 → 1	$C_1\alpha$	--
3 → 4	C_2	--
4 → 3	$C_2\alpha$	--

* where the Boltzmann factors are $\alpha_{23} = e^{(\epsilon^\circ - \Delta\epsilon)/K_B T}$,
 $\alpha_{14} = e^{(\epsilon^\circ + \Delta\epsilon)/K_B T}$ and $\alpha = e^{\Delta\epsilon/K_B T}$.

$$\frac{dP_3}{dt} = (a_{23} + b_{23}) P_2 - (a_{23}\alpha_{23} + b_{23} + C) P_3 + (C\alpha) P_4 \quad (4-102)$$

$$\frac{dP_4}{dt} = (a_{14} + b_{14}) P_1 + (C) P_3 - (a_{14}\alpha_{14} + b_{14} + C\alpha) P_4 \quad (4-103)$$

4.7.3 Thermodynamic Functions

If we define the complete occupation of level one as a reference for the entropy we can write, as in previous sections, an expression for the rate of entropy production

$$\begin{aligned} \dot{S}_1 = NK_B \{ & C P_1 (\alpha P_2/P_1 - 1) \ln (\alpha P_2/P_1) \\ & + C P_3 (\alpha P_4/P_3 - 1) \ln (\alpha P_4/P_3) \\ & + a_{14} P_1 (\alpha_{14} P_4/P_1 - 1) \ln (\alpha_{14} P_4/P_1) \\ & + a_{23} P_2 (\alpha_{23} P_3/P_2 - 1) \ln (\alpha_{23} P_3/P_2) \\ & + b_{14} P_1 (P_4/P_1 - 1) \ln (P_4/P_1) \\ & + b_{23} P_2 (P_3/P_2 - 1) \ln (P_3/P_2) \}^* \end{aligned} \quad (4-104)$$

* here we have the Boltzmann factors $\alpha_{14} = e^{(E_4 - E_1)/K_B T} = e^{(\epsilon^\circ + \Delta\epsilon)/K_B T}$ etc.

Using the energy of level one as a reference level for the energy, we can write the free energy A as

$$A = NK_B T \{ P_1 \ln P_1 + P_2 \ln \alpha_{12} P_2 + P_3 \ln \alpha_{13} P_3 + P_4 \ln \alpha_{14} P_4 \} \quad (4-105)$$

4.7.4 Steady State Values of the Parameters

If we set all $dP_i/dt = 0$ in (4-100 to 4-103), we can solve for the steady state occupations of the energy levels. However, the full expressions are complicated, so we are encouraged to use the plausible assumption that the hyperfine splitting, $\Delta\epsilon$, is small and so

$$\alpha = e^{\Delta\epsilon/K_B T} \approx 1$$

With this approximation we obtain the results that

$$(P_1^S + P_4^S) = (P_2^S + P_3^S) = 1/2 \quad (4-106)$$

and that

$$P_1^S = [(a_{14}\alpha_{14} + b_{14})(a_{23}\alpha_{23} + a_{23} + 2b_{23}) + C(a_{14}\alpha_{14} + b_{14} + a_{23}\alpha_{23} + b_{23})]/2D \quad (4-107)$$

$$P_2^S = [(a_{23}\alpha_{23} + b_{23})(a_{14}\alpha_{14} + a_{14} + 2b_{14}) + C(a_{14}\alpha_{14} + b_{14} + a_{23}\alpha_{23} + b_{23})]/2D \quad (4-108)$$

with

$$D = (a_{14}\alpha_{14} + a_{14} + 2b_{14})(a_{23}\alpha_{23} + a_{23} + 2b_{23}) + C(a_{14}\alpha_{14} + a_{14} + 2b_{14} + a_{23}\alpha_{23} + a_{23} + 2b_{23})$$

It is interesting to note that in this approximation it is easy to get population inversion between level one and level two. I.e., we obtain $P_2^S > P_1^S$ for the easily satisfied condition

$$\frac{a_{23}}{b_{23}} (\alpha_{23} - 1) > \frac{a_{14}}{b_{14}} (\alpha_{14} - 1) \quad (4-109)$$

This simply means that particles are relaxing into level two faster than they are being removed by thermal or radiative excitation. In the case that transitions between levels one and four are saturated ($b_{14}/a_{14}\alpha_{14}$ large, say) then, condition (4-109) is easily met. Similarly, levels three and four are inverted ($P_4^S > P_3^S$) for the situation in which (4-109) is true. Thus, it is possible to get stimulated emission by irradiating the system with a weak source of radiation of frequency ν such that $h\nu = \Delta\epsilon$. The energy emitted per unit time by weak stimulation of the

transition between level one and level two is given by

$$\begin{aligned} J_A^{12} &= N(\Delta\epsilon) b_{12} (P_2^S - P_1^S) \\ &= N(\Delta\epsilon) b_{12} \left(\frac{1}{2}\right) \left[\frac{a_{23}(\alpha_{23} - 1)}{a_{23}\alpha_{23} + a_{23} + 2b_{23} + C} \right] \end{aligned} \quad (4-110)$$

Under the conditions given above, it can be further demonstrated that

$$P_2^S - P_3^S \approx \frac{a_{23}(\alpha_{23} - 1)}{a_{23}\alpha_{23} + a_{23} + 2b_{23} + C} \quad (4-111)$$

and that if the system is illuminated with a weak source of radiation of frequency ν_{23} , the rate at which the system absorbs energy is given by

$$\begin{aligned} J_A^{23} &= N(\epsilon_{23}) b_{23} (P_2^S - P_3^S) \\ &= N(\epsilon^\circ) b_{23} \left[\frac{a_{23}(\alpha_{23} - 1)}{a_{23}\alpha_{23} + a_{23} + 2b_{23} + C} \right] \end{aligned} \quad (4-112)$$

If the steady state values of the occupation probabilities, calculated from (4-106 to 4-108) are substituted into (4-104), it is readily seen that the steady state rate of entropy production always increases with increasing field strengths (b_{14} , b_{23}).

By substituting (4-106) into (4-105) and rearranging, it is

possible to write the free energy in the form

$$\begin{aligned}
 A^S &= N \{ \epsilon^\circ - (\epsilon^\circ + \Delta\epsilon) P_1^S - (\epsilon^\circ - \Delta\epsilon) P_2^S \} \\
 &+ NK_B T \left\{ \frac{1}{2} \ln \left(\frac{1}{2} - P_1^S \right) + \frac{1}{2} \ln \left(\frac{1}{2} - P_2^S \right) \right. \\
 &\left. + P_1^S \ln \left(\frac{P_1^S}{\frac{1}{2} - P_1^S} \right) + P_2^S \ln \left(\frac{P_2^S}{\frac{1}{2} - P_2^S} \right) \right\} \quad (4-113)
 \end{aligned}$$

The first term in (4-113) is a pure energy term and the second term is a pure entropy term.

In the event that

$$P_1^S < \frac{1}{2} \left[\frac{1}{1 + e^{-(\epsilon^\circ + \Delta\epsilon)/K_B T}} \right] \quad (4-114)$$

and

$$P_2^S < \frac{1}{2} \left[\frac{1}{1 + e^{-(\epsilon^\circ - \Delta\epsilon)/K_B T}} \right] \quad (4-115)$$

the steady free energy A^S is an increasing function of the radiation fields (b_{14} , b_{23}). Thus, increasing the strength of the radiation increases the free energy of the system. To clarify conditions (4-114) and (4-115) further, let us look specifically at (4-114) for the two cases

$$(i) \quad (\epsilon + \Delta\epsilon) \ll K_B T$$

$$(ii) \quad (\epsilon + \Delta\epsilon) \gg K_B T$$

In the first case, we must have $P_1^S < 1/4$ for A to be strictly increasing, a condition which is impossible in our model. I.e., even under saturation, at frequency ν_{14} , P_1 can be no smaller than $1/4$. In the event that case (ii) holds, it is necessary only to have $P_1 < 1/2$, which is easily achieved by applying a radiation field at frequency ν_{14} , such that P_1^S is decreased below $1/2$. Similar reasoning holds for condition (4-115).

We see, therefore, that there exists a critical radiation field* above which increasing either the radiation field (of frequency ν_{23} or ν_{14}) increases both the rate of entropy production and the free energy in the steady state.

4.7.5 Results and Discussion of the Four Level Model

The behaviour of the four level model was examined** for many sets of parameters. Some interesting examples will now be presented.

It is apparent from Table 4-13 that the mini-max principle is still operative in the four level model. It is seen that some terms in the entropy production rate are increasing and that some terms are decreasing as the system evolves in time.

* Alternatively, one could refer to critical populations!

** When time-dependent solutions of (4-100 to 4-103) were required, standard library routines available at the McMaster Computer Centre were used.

Table 4-13

Mini-Max Behaviour of the Four Level Model*

Time (arbitrary)	D1 ^{**} (NK _B)	D2 (NK _B)	D3 (NK _B)	D4 (NK _B)	D5 (NK _B)	A (NK _B T)
0	0.0	0.0	0.0	0.0	.684	-.698
.1	.00554	.0157	.00535	.000181	.351	-.527
.2	.0136	.0563	.0330	.000366	.242	-.349
.3	.0218	.114	.0797	.000537	.178	-.217
.4	.0295	.181	.137	.000691	.136	-.125
.5	.0368	.254	.199	.000827	.106	-.0613
.6	.0434	.330	.264	.000947	.0842	-.0187
.7	.0493	.404	.327	.00105	.0679	-.00224
.8	.0547	.476	.387	.00115	.0555	.0284
.9	.0594	.545	.443	.00123	.0459	.0409
1.0	.0636	.609	.495	.00130	.0384	.0490

* The system was initially in equilibrium and at time $t = 0$ it was illuminated with radiation coupling levels one and four. The system parameters were $a_{12} = .001$; $a_{14} = .001$; $a_{23} = .1$; $\alpha = 1.01$; $\alpha_{23} = 100.$; $b_{14} = .3$; $b_{23} = 0.0$.

**

$$D1 = a_{14}(\alpha_{14}P_4 - P_1) \ln (\alpha_{14}P_4/P_1)$$

$$D2 = a_{12}(\alpha P_2 - P_1) \ln (\alpha P_2/P_1)$$

$$D3 = a_{23}(\alpha_{23}P_3 - P_2) \ln (\alpha_{23}P_3/P_2)$$

$$D4 = a_{34}(\alpha P_4 - P_3) \ln (\alpha P_4/P_3)$$

$$D5 = b_{14}(P_4 - P_1) \ln (P_4/P_1)$$

Fig. 4.19 shows the effect of changing the ratio of b_{14}/a_{14} on the free energy. It is seen that a minimum radiation intensity (b_{14}) is required before the free energy is positive in the steady state. The dashed curves in this figure show that if the system is illuminated simultaneously with radiation coupling levels one and four, and levels two and three, that the steady state free energy is larger than it would have been if only radiation coupling levels one and four had been present. Thus, the system is able to increase its free energy by accepting free energy simultaneously from two radiation fields.

Fig. 4.20 shows the difference in the behaviour of the system when certain parameters are changed during the evolution of the system from its equilibrium state. It is apparent that the larger the steady state rate of entropy production, the larger is the free energy (e.g., curve 2 in Fig. 4.20 (b) is higher in the steady state than curve 1; difficulties of scale prevented this from being more clearly shown). Thus, the system has the largest store of free energy when it is dissipating energy at the largest rate.

At equilibrium, the populations of level one and level two are such that

$$p_1^{\text{eq}} - p_2^{\text{eq}} = \frac{\alpha_{13}(\alpha - 1)}{\alpha_{12}\alpha_{13} + \alpha_{13} + \alpha + 1} \quad (4-116)$$

and we have already seen in (4-110) that in the steady state (with b_{14} large and $\alpha_{12} \approx 1$)

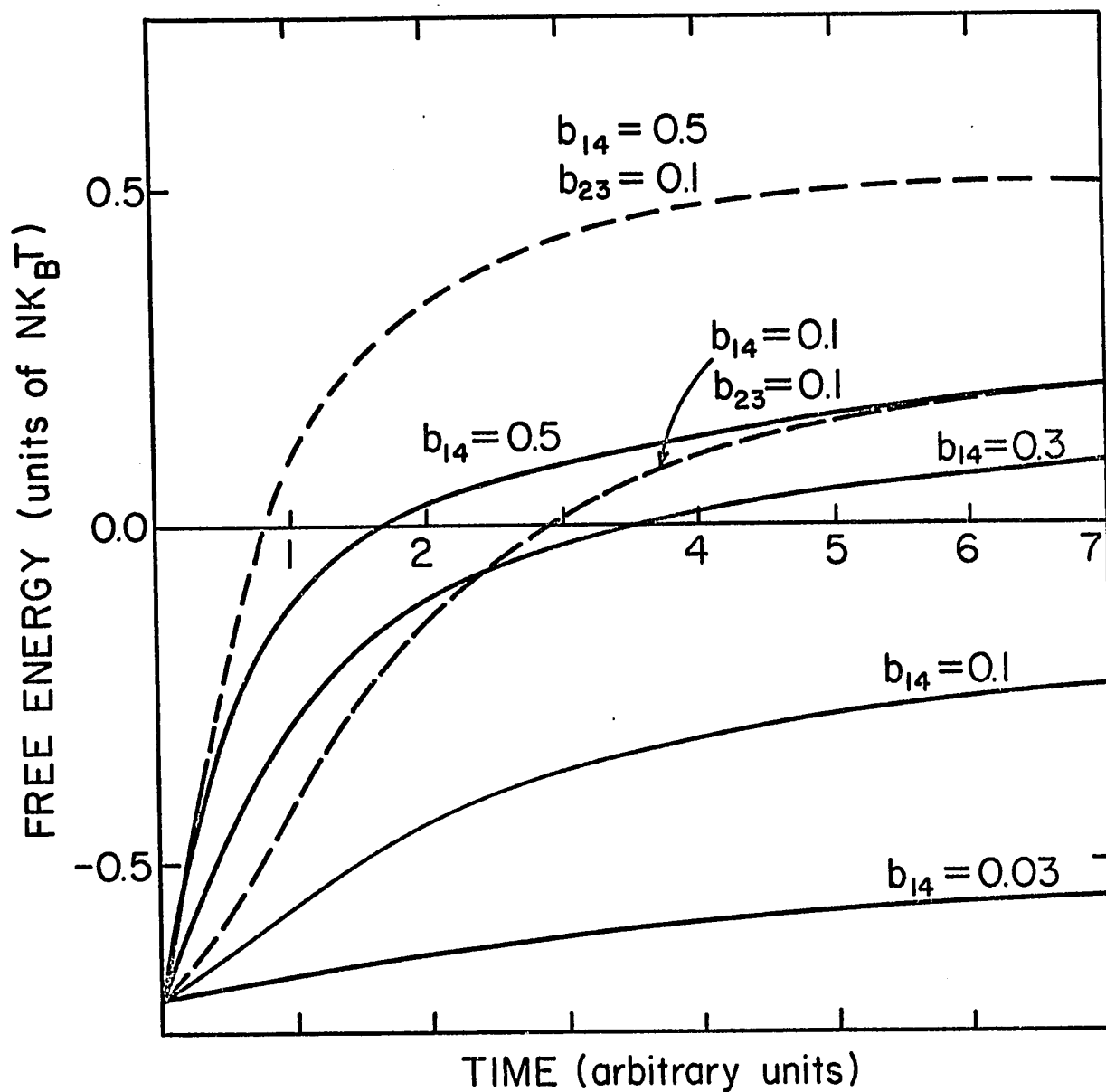


Fig. 4.19 Critical b_{14}/a_{14} . Free energy versus time. The system was initially in equilibrium. The parameters were: $C = .1$, $a_{14} = .001$, $a_{23} = .001$, $\alpha_{12} = \alpha_{34} = 1.01$, $\alpha_{23} = 100$, and $\alpha_{14} = 102.01$. The b values are given on the figure. Notice the marked increase of the free energy when two radiations are present (dashed curves).

Fig. 4.20 (a) Parameter change. Entropy production versus time. The system was initially in equilibrium and the initial parameters were $C = .01$, $a_{14} = .001$, $a_{23} = .001$, $\alpha_{12} = \alpha_{34} = 1.01$, $\alpha_{14} = 102.01$, $\alpha_{23} = 100.$, $b_{14} = .1$, and $b_{23} = 0.0$. At $t = .15$, we have: curve 1, $b_{14} = 1.0$; curve 2, $b_{23} = .1$, and curve 3, $a_{23} = .1$.

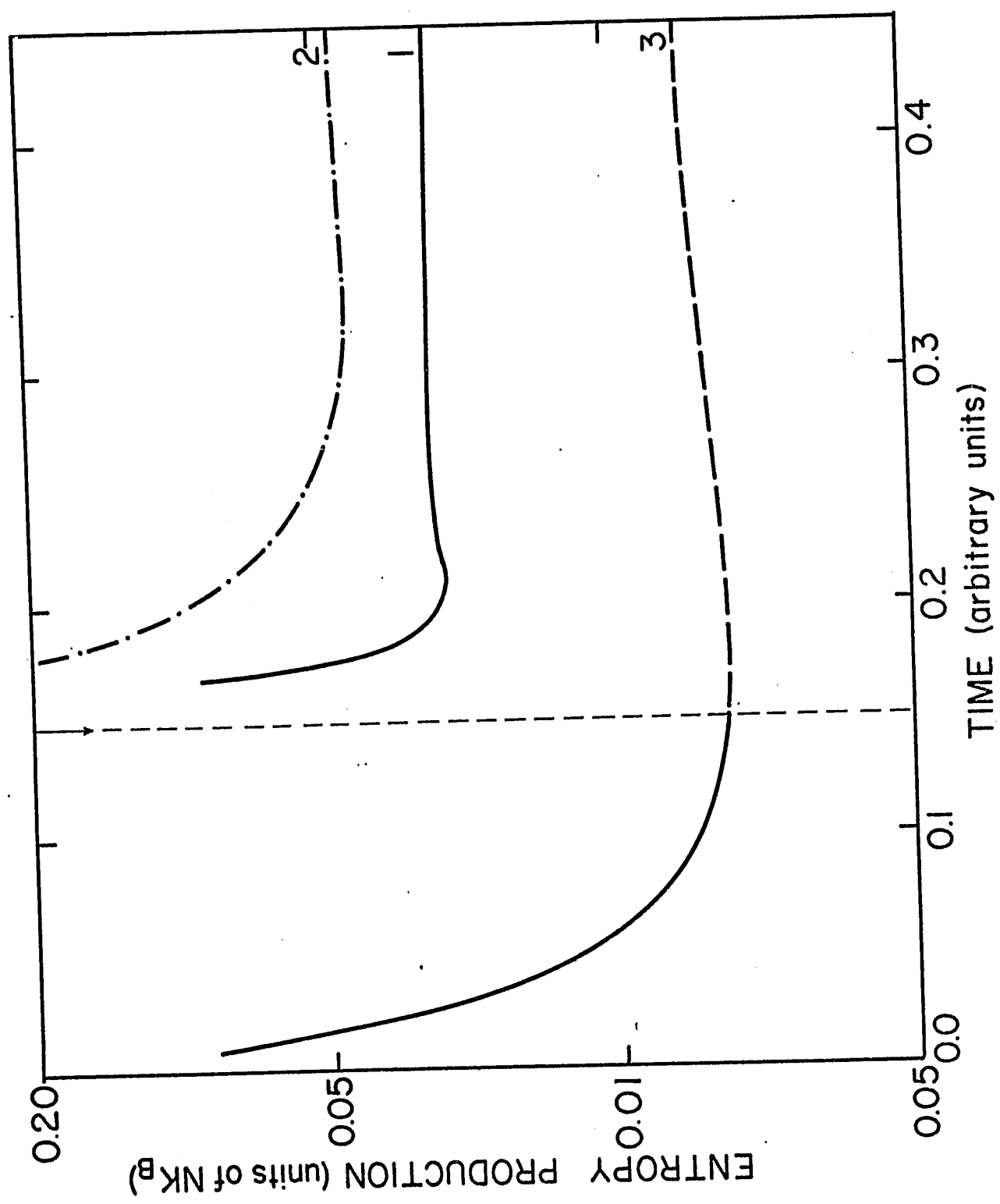


Fig. 4.20 (a)

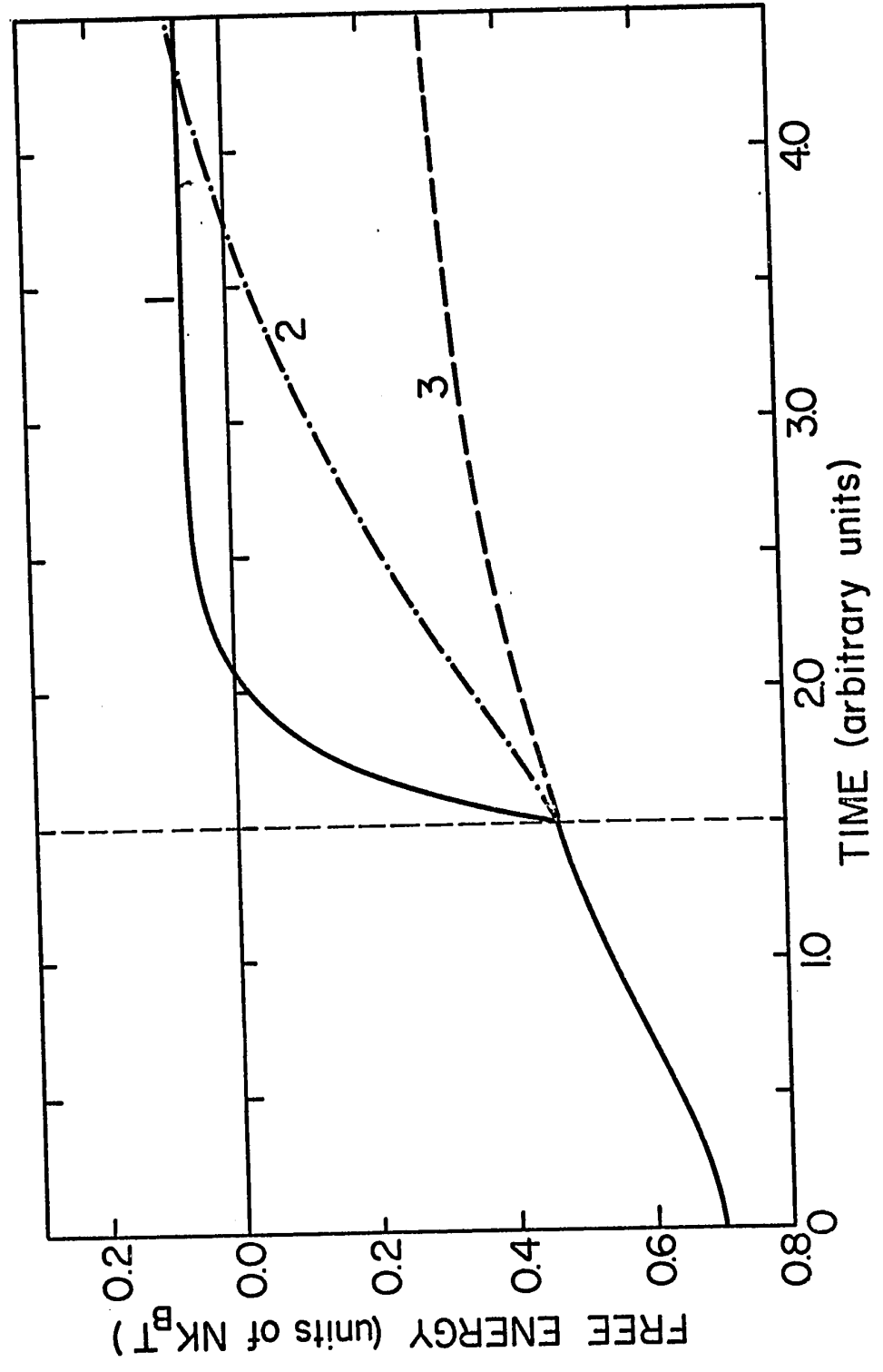


Fig. 4.20 (b) Free energy versus time. The parameters are the same as in Fig. 4.20 (a).

$$P_2^S - P_1^S = \frac{1}{2} \left[\frac{\alpha_{23}(\alpha_{23} - 1)}{\alpha_{23}^2 + a_{23} + 2b_{23} + C} \right] \quad (4-117)$$

It is apparent from (4-117) that if either b_{23} or C are large the populations of levels two and one will be nearly equal. It is also apparent that the "polarization" of levels one and two in the steady state is in the direction opposite to that at equilibrium. Although it is not obvious from a comparison of (4-116) and (4-117) that the degree of polarization is much larger in the steady state (and of opposite sign) than it is in equilibrium, this fact is readily perceived by an examination of Table 4-14. We see that an enhancement of 30 or 40 over the equilibrium polarization is easily achieved. In addition, the "sign" of the polarization is reversed in most instances. It is also apparent that increasing the ratio of b_{14}/a_{14} (i.e., approaching closer to saturation) increases this "dynamic" polarization of levels one and two.

We see in Fig. 4.21 the experimental results for the dynamic polarization of nuclei by the saturation of electronic transitions. The level scheme of the system in Fig. 4.21 is similar to ours but the reader is referred to Abragam (1961); Chapter 8 for more information concerning the details (Fig. 8-10 in Abragam's book). The enhancement of the polarization is experimentally of the order of 50x and of reversed sign. This result is consistent with the data contained in Table 4-14.

Further discussion of this model will be postponed to the discussion at the end of this chapter.

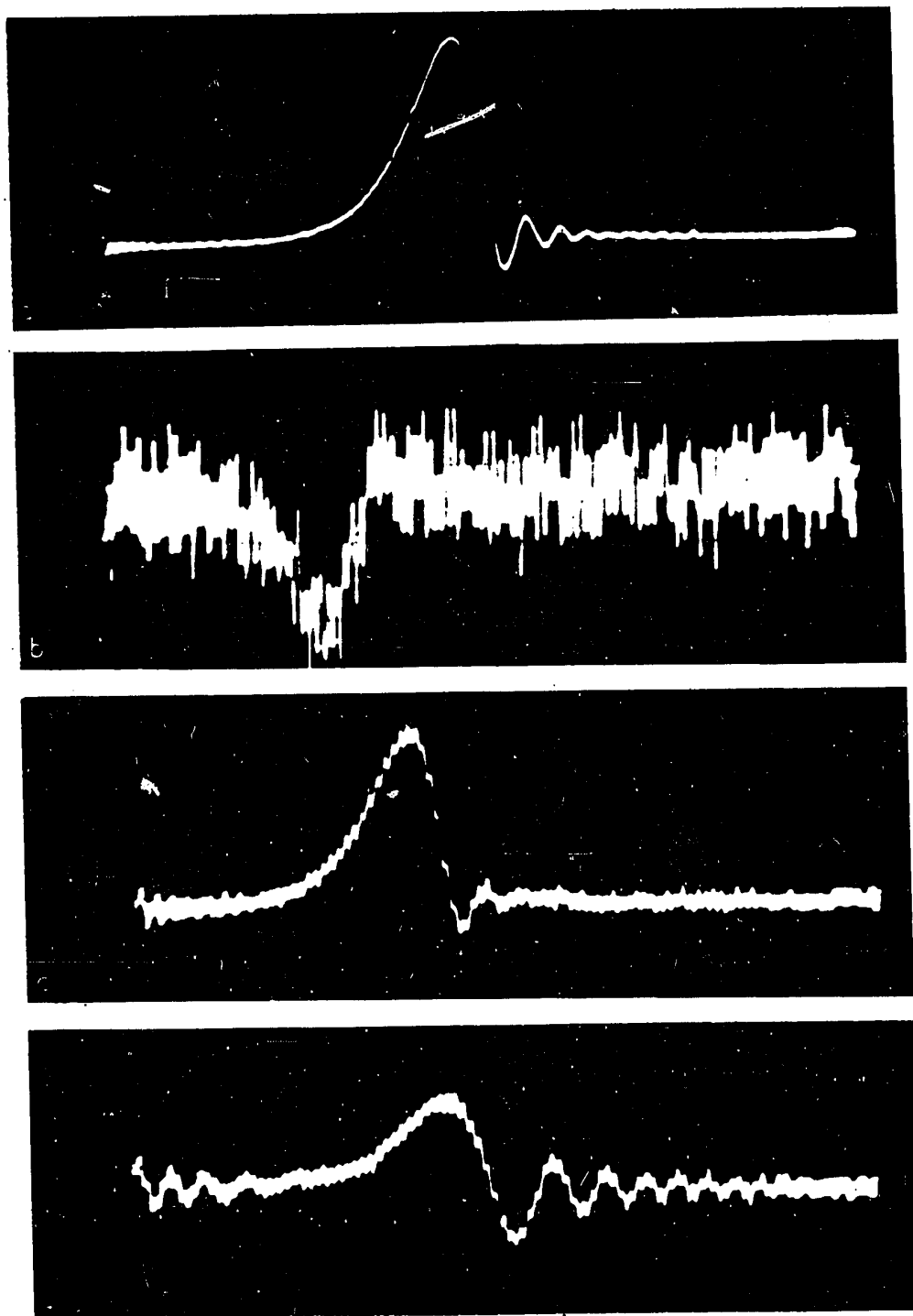


Fig. 4.21 Enhanced Polarization of nuclei in solution. (a) Enhanced proton signal. (b) Normal proton signal, scale 50x (a). Note reversal of signal. (c) Enhanced signal of F^{19} . (d) Enhanced signal of Li^7 (ref., fig. 8.10 of Abragam, 1961).

Table 4-14

Enhancement of Polarization

C	a ₁₄	a ₂₃	α	α_{23}	b ₁₄	b ₂₃	P ₁ - P ₂ (Equilibrium)	P ₁ - P ₂ (Steady State)
.0001	.001	.001	1.01	100	.1	0.0	+ .00493	-.169
.01	.001	.001	1.01	100	.1	0.0	+ .00493	-.148
.01	.001	.001	1.01	100	.1	.001	+ .00493	+ .000666
.1	.001	.001	1.01	100	.1	0.0	+ .00493	-.0699
.1	.001	.001	1.01	100	1.0	0.0	+ .00493	-.133
.0001	.01	.001	1.01	100	.1	0.0	+ .00493	-.0458
.0001	.001	.001	1.01	10	.1	0.0	+ .00453	-.239

* The steady state values are the exact steady state values, calculated with no approximations

4.8 TWO LEVEL MODEL WITH FLOW

4.8.1 Introduction

The model presented in this section is an extension of the two level model discussed in section 5.3. Fig. 4.22 gives a schematic representation of the modified two level system. This represents a collection of n non-interacting particles. The n particles each have two accessible energy states which are coupled by thermal and radiative transitions*. The system is assumed to be maintained at a constant temperature T . In addition, we postulate that the total number of particles n , in the "active" area is not necessarily constant. Specifically, we allow particles to flow in or out of the systems. We assume that particles in state one leave or enter the system at a rate given by $\beta(N - n_1)$ (particles per unit time), and that particles leave or enter the system while in state two at a rate $\gamma_{23}n_2$ or $\gamma_{32}n_3$, respectively. n_3 is the number of particles in an infinitely large storage area memory. It is apparent from the above definition that if $n_1 > N$, the system will lose particles from state one and if $n_1 < N$, the system will gain particles in state one. Thus, level one will equilibrate with the particle bath when the active region has N particles in state one. Using the definitions above we can write the equations** which govern the time evolution of the system

* The a , α , b of Fig. 4.22 are the same as those of Fig. 4.1 of this chapter. There are n_1 particles in state one and n_2 particles in state two.

** The solutions are presented in Appendix 2.

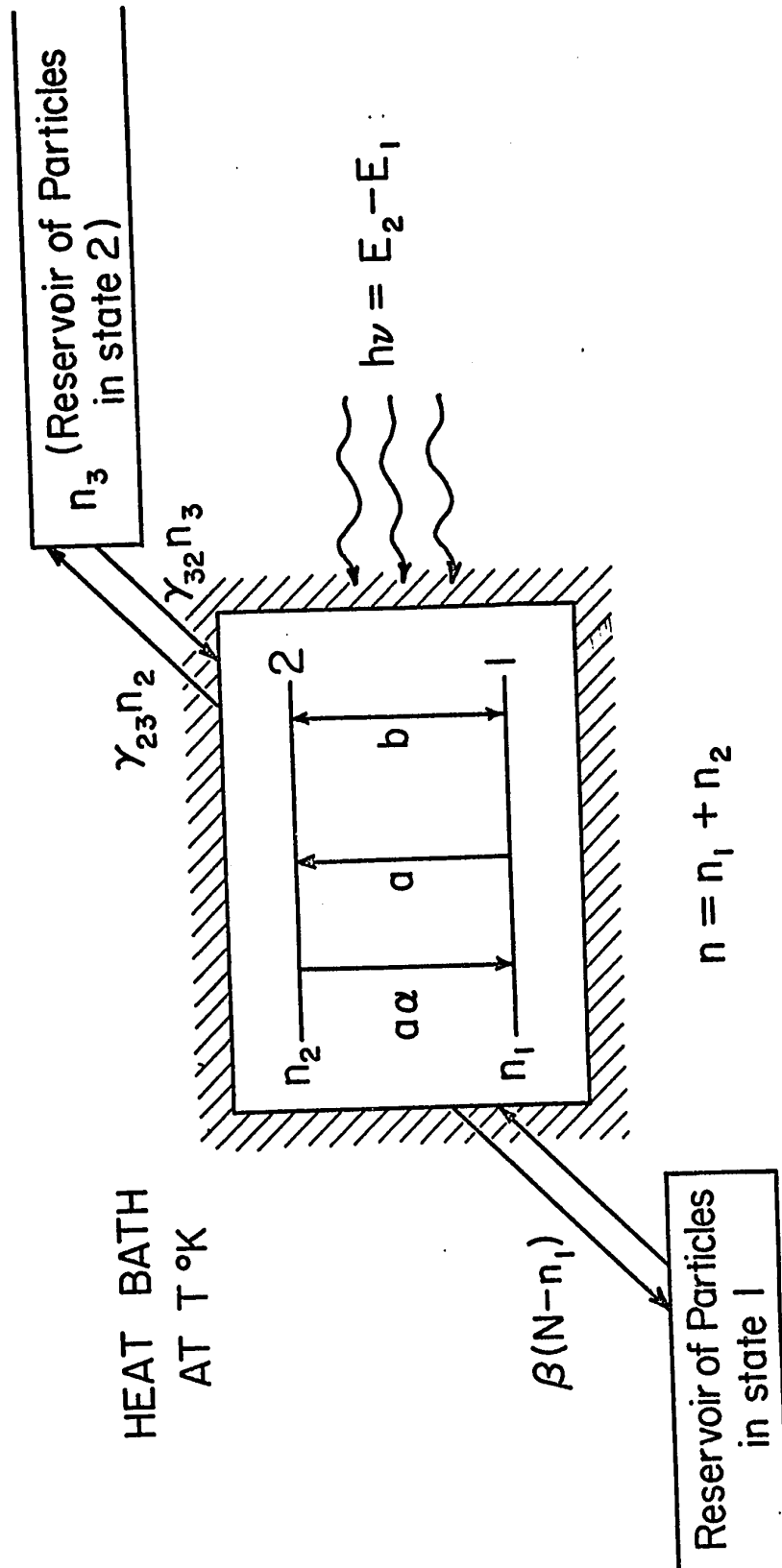


Fig. 4.22 Schematic of two level model with particle flow

$$\frac{dn_1}{dt} = \beta(N - n_1) + (a\alpha + b) n_2 - (a + b) n_1 \quad (4-118)$$

$$\frac{dn_2}{dt} = (a + b) n_1 - (a\alpha + b) n_2 + [\gamma_{32}n_3 - \gamma_{23}n_2] \quad (4-119)$$

$$\frac{dn_3}{dt} = [\gamma_{23}n_2 - \gamma_{32}n_3] \quad (4-120)$$

and

$$n = n_1 + n_2 \quad (4-121)$$

$$\frac{dn}{dt} = \beta(N - n_1) + [\gamma_{32}n_3 - \gamma_{23}n_2] \quad (4-122)$$

We define the occupation probabilities P_i such that

$$P_i = n_i/n. \quad (i = 1, 2) \quad (4-123)$$

4.8.2 Thermodynamic Functions

The rate of entropy production \dot{S}_i is written as the sum of individual contributions, viz.

$$\dot{S}_i = \left(\frac{dS}{dt}\right)_{\text{Bath}} + \left(\frac{dS}{dt}\right)_{\text{configurational}} + \left(\frac{dS}{dt}\right)_{\text{particle flow}} \quad (4-124)$$

If we define the configuration entropy S_c in the normal fashion we obtain

$$\begin{aligned}
 \left(\frac{dS}{dt}\right)_{\text{configurational}} &= \frac{dS_i}{dt} \\
 &= \frac{d}{dt} \left[-nK_B \sum_{i=1}^2 \left(\frac{n_i}{n}\right) \ln \left(\frac{n_i}{n}\right) \right] \\
 &= -K_B \sum_{i=1}^2 n_i \ln \left(\frac{n_i}{n}\right) \quad (4-125)
 \end{aligned}$$

The contribution due to interaction with the heat bath is given (see 4.4 for a derivation) by

$$\left(\frac{dS}{dt}\right)_{\text{Bath}} = K_B (\ln \alpha) (a_2 n_2 - a_1 n_1) \quad (4-126)$$

Defining the chemical potential of level one as zero the rate of entropy production due to particle flow can reasonably be taken as

$$\left(\frac{dS}{dt}\right)_{\text{particle flow}} = \left(\frac{\Delta \epsilon}{T}\right) [\gamma_{23} n_2 - \gamma_{32} n_3] \quad (4-127)$$

where $\Delta \epsilon = E_2 - E_1$ is the energy the system gains or loses for each particle entering or leaving the system.

Adding the terms in (4-124) and simplifying, we obtain the result

that

$$\begin{aligned} \dot{S}_i = nK_B \{ & a(\alpha P_2 - P_1) \ln (\alpha P_2/P_1) \\ & + b(P_2 - P_1) \ln (P_2/P_1) \\ & + (\gamma_{23}P_2 - \gamma_{32}n_3/n) \ln (\alpha P_2) \\ & + \beta(P_1 - N/n) \ln P_1 \} \end{aligned} \quad (4-128)$$

The first two terms in (4-128) are the same as we had for the simple two level model, although, we must remember that the multiplier, n , is not constant as it was in the simpler model. These terms are of course positive definite. The remaining terms, while normally positive, can for certain situations be negative. This is acceptable behaviour provided the sum, \dot{S}_i , remains positive. In any case, the steady state entropy production can easily be shown to be positive definite (anticipating the steady state occupations in (4-130) to (4-132)).

The free energy of the system, A , may be written

$$A = nK_B T \{ P_1 \ln P_1 + P_2 \ln \alpha P_2 \} \quad (4-129)$$

where we again emphasize that n is no longer constant.

4.8.3 The Steady State

Setting $\frac{dn_i}{dt} = 0$ in (4-118) to (4-120) and solving for the steady state occupations, we obtain

$$n_1^S = N \quad (4-130)$$

$$n_2^S = \left(\frac{a+b}{a\alpha+b}\right) N \quad (4-131)$$

$$\begin{aligned} n_3^S &= (\gamma_{23}/\gamma_{32}) n_2^S \\ &= (\gamma_{23}/\gamma_{32}) \left(\frac{a+b}{a\alpha+b}\right) N \end{aligned} \quad (4-132)$$

Furthermore, we have the result that

$$P_2^S/P_1^S = n_2^S/n_1^S = (a+b)/(a\alpha+b) \quad (4-133)$$

which is the same ratio as obtained in the simple two level model. Thus, the results pertaining to the steady state of the simple two level model are also applicable here. For example, in order that the steady state free energy be positive, under saturation, it is necessary that $\alpha > 4$ or $\Delta\epsilon > 2 K_B T \ln 2$.

4.8.4 Calculations and Discussion

The interesting feature of this model is that the active region

(consisting of $n = n_1 + n_2$ particles) can be used as a transducer to convert low energy particles (n_1 of them) into high energy particles (n_2 of them), which can then be removed from the system in a higher energetic state. Thus, in the presence of radiation and a source of particles in state 1, the system will supply particles to a reservoir (n_3 particles).

In Fig. 4.23, we see the effects of different initial conditions. In the event that the initial population of particles in level two is smaller than their steady value, the free energy shows a net increase as the system approaches the steady state. Thus, processes increasing the population of level two increase the free energy of the system (and also its ability to provide high energy particles for the reservoir n_3). Concomitant with the free energy curves we see that the behaviour of the entropy production rate varies from purely maximal (1, a) to purely minimal (2, b).

Fig. 4.24 shows the effect of decreasing the level spacing. The Boltzmann factor has been decreased by a factor of 5 and the free energy has been reduced by roughly the same factor. The entropy production curves no longer show purely maximal behaviour.

In Fig. 4.25 we see the effect of increasing the ratio of b/a . Again, as in Fig. 4.23, the entropy production shows both maximal and minimal behaviour. The ratio of b/a was increased by a factor of 5, over Fig. 4.23, and we see that the free energy and the rate of entropy production have both increased by a factor of about 2. Both the free energy and the entropy production depend strongly on P_2 , and since P_2^S increases one-half as quickly as b , so also do A and \dot{S}_1 .

In Fig. 4.26, we introduce a model of a stirred tank chemical

Fig. 4.23* The system parameters were $a_{12} = .01$, $b_{12} = .1$, $\alpha_{12} = 25$, $\alpha_{23} = 1 \times 10^4$, $\alpha_{32} = 1 \times 10^{-7}$, $\beta = .1$ and $NM = 1 \times 10^3$. With steady values $N_3^S = 3.14 \times 10^5$, $N_2^S = 3.14 \times 10^2$, $N_1^S = 1 \times 10^3$.

The initial conditions were: curve 1(a) $N_1 = .99 NM$, $N_2 = 4/5 N_2^S$, and $N_3 = .1 N_3^S$; curve 1(b) $N_1 = .99 NM$, $N_2 = 6/5 N_2^S$ and $N_3 = .1 N_3^S$; curve 3(a) $N_1 = 1.1 NM$, $N_2 = 4/5 N_2^S$, and $N_3 = .1 N_3^S$; curve 3(b) $N_1 = 1.1 NM$, $N_2 = 6/5 N_2^S$, and $N_3 = .1 N_3^S$.

Fig. 4.24* The system parameters were the same as for Fig. 4.23, except here, $\alpha_{12} = 5$. The steady values were $N_3^S = 7.31 \times 10^5$, $N_2^S = 7.31 \times 10^2$, and $N_1^S = 1 \times 10^3$. The initial conditions were calculated as for Fig. 4.23.

Fig. 4.25* The system parameters were the same as for Fig. 4.23, except here, $b_{12} = .5$. The steady values were $N_3^S = 6.8 \times 10^5$, $N_2^S = 6.8 \times 10^2$, and $N_1^S = 1 \times 10^3$. The initial conditions were calculated as for Fig. 4.23.

* Note that $\Delta A \equiv A(t) - A(t = 0)$ for these figures.

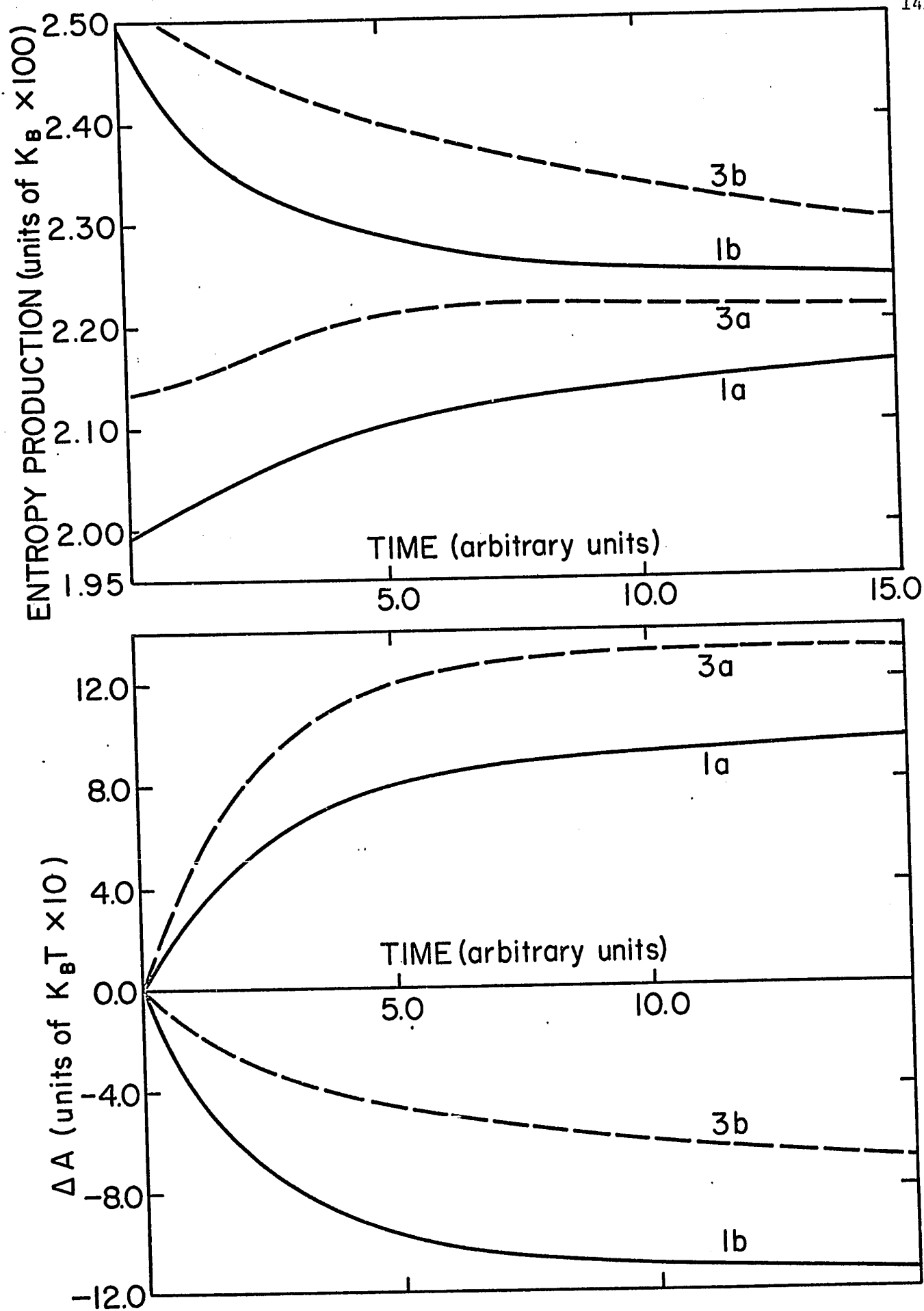


Fig. 4.23

Entropy production and free energy versus time.

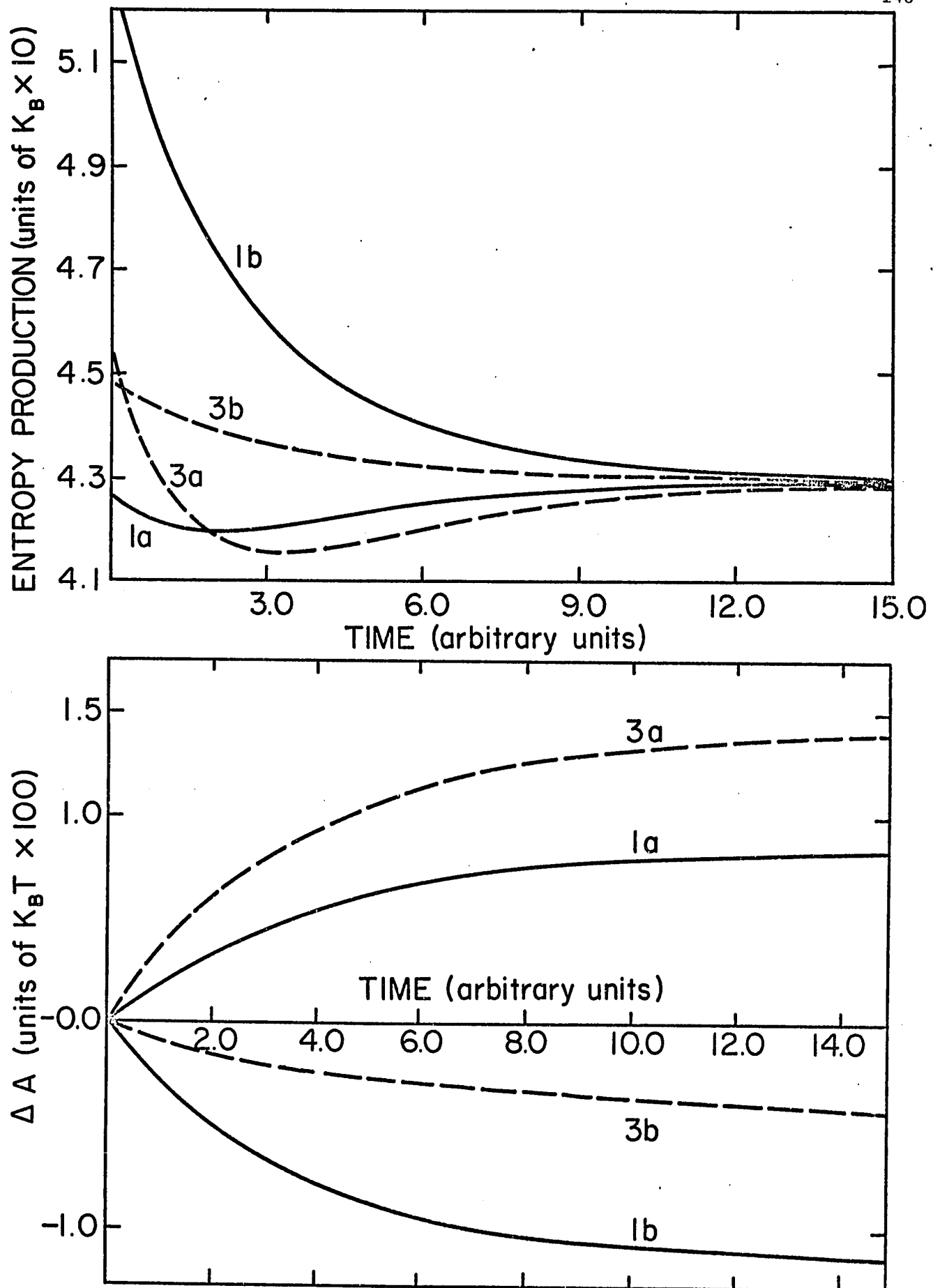


Fig. 4.24 Entropy production and free energy versus time.

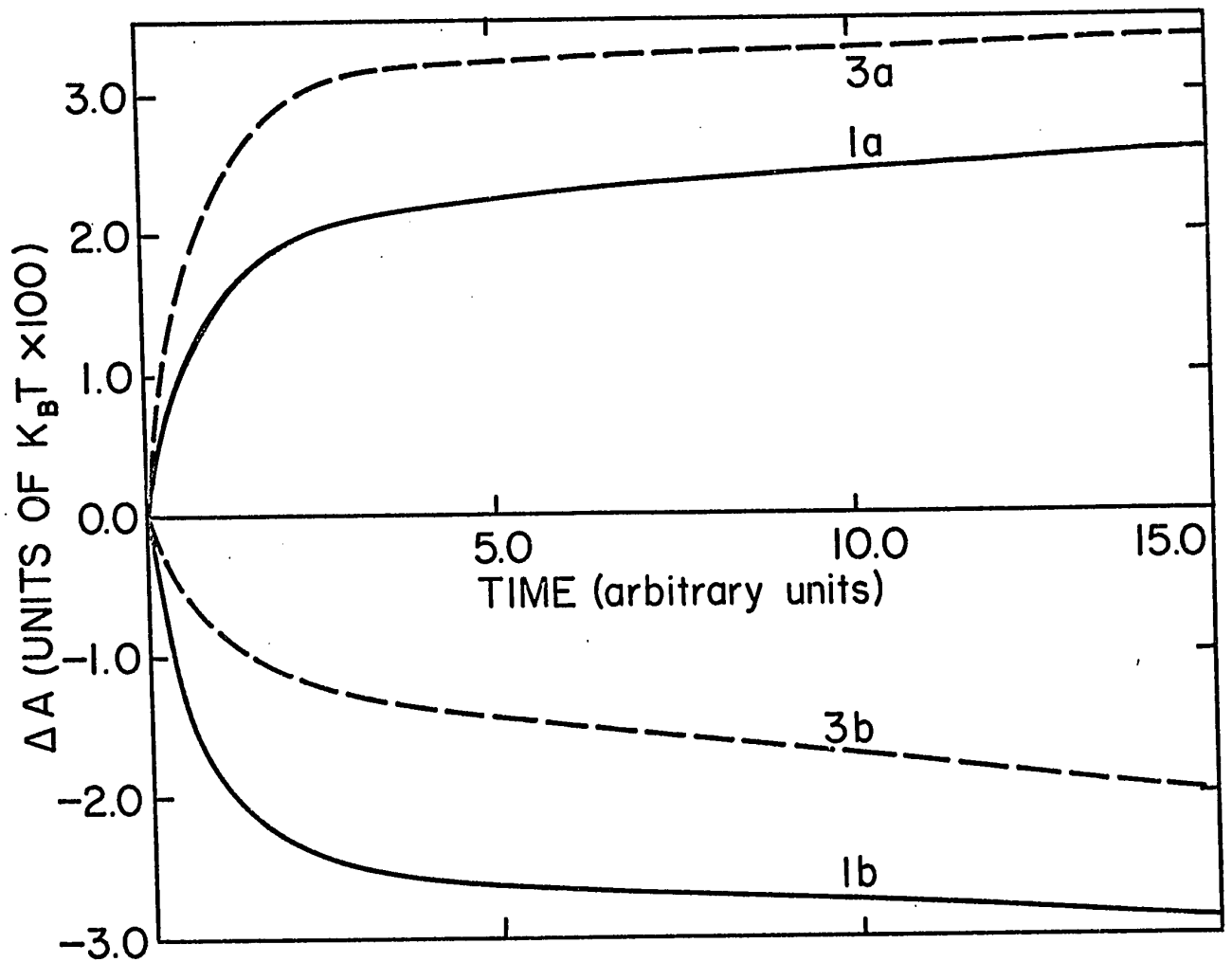
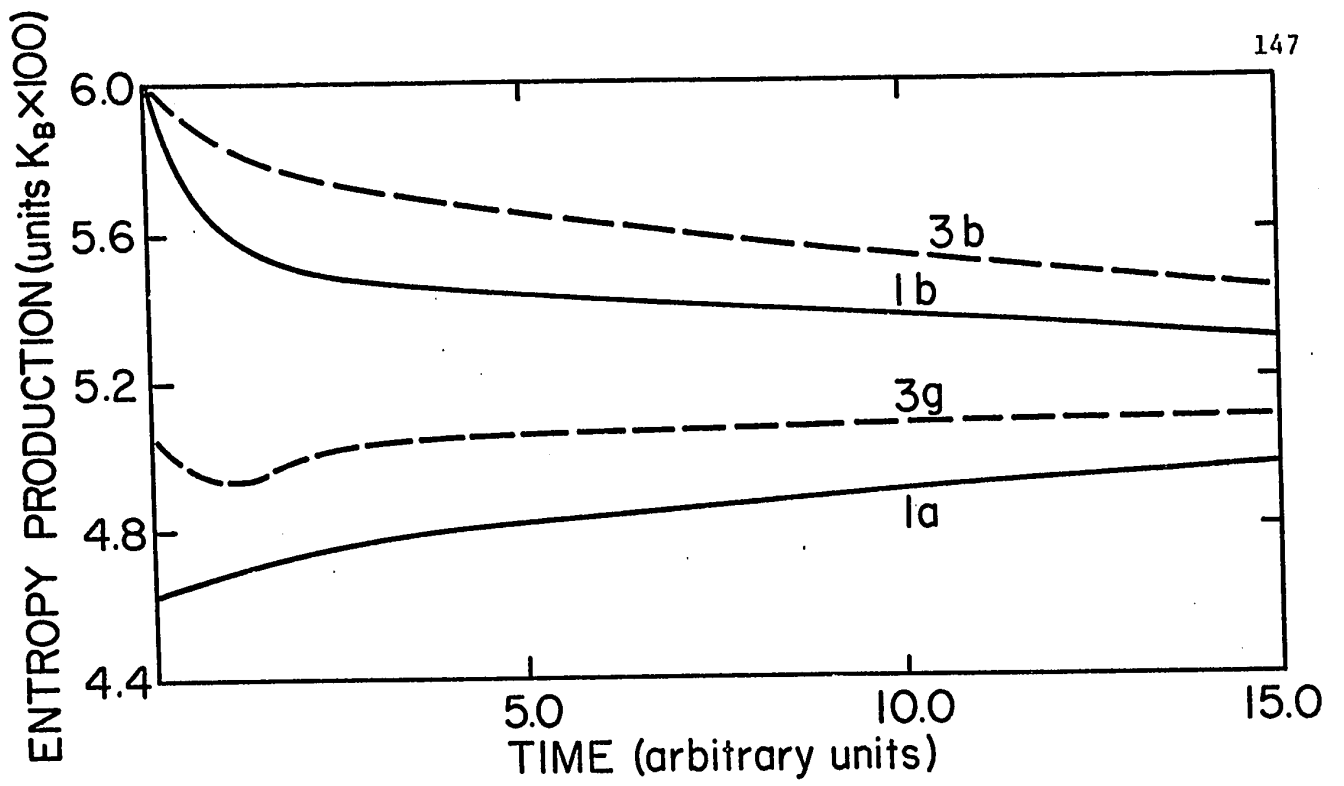


Fig. 4.25 Entropy production and free energy versus time.

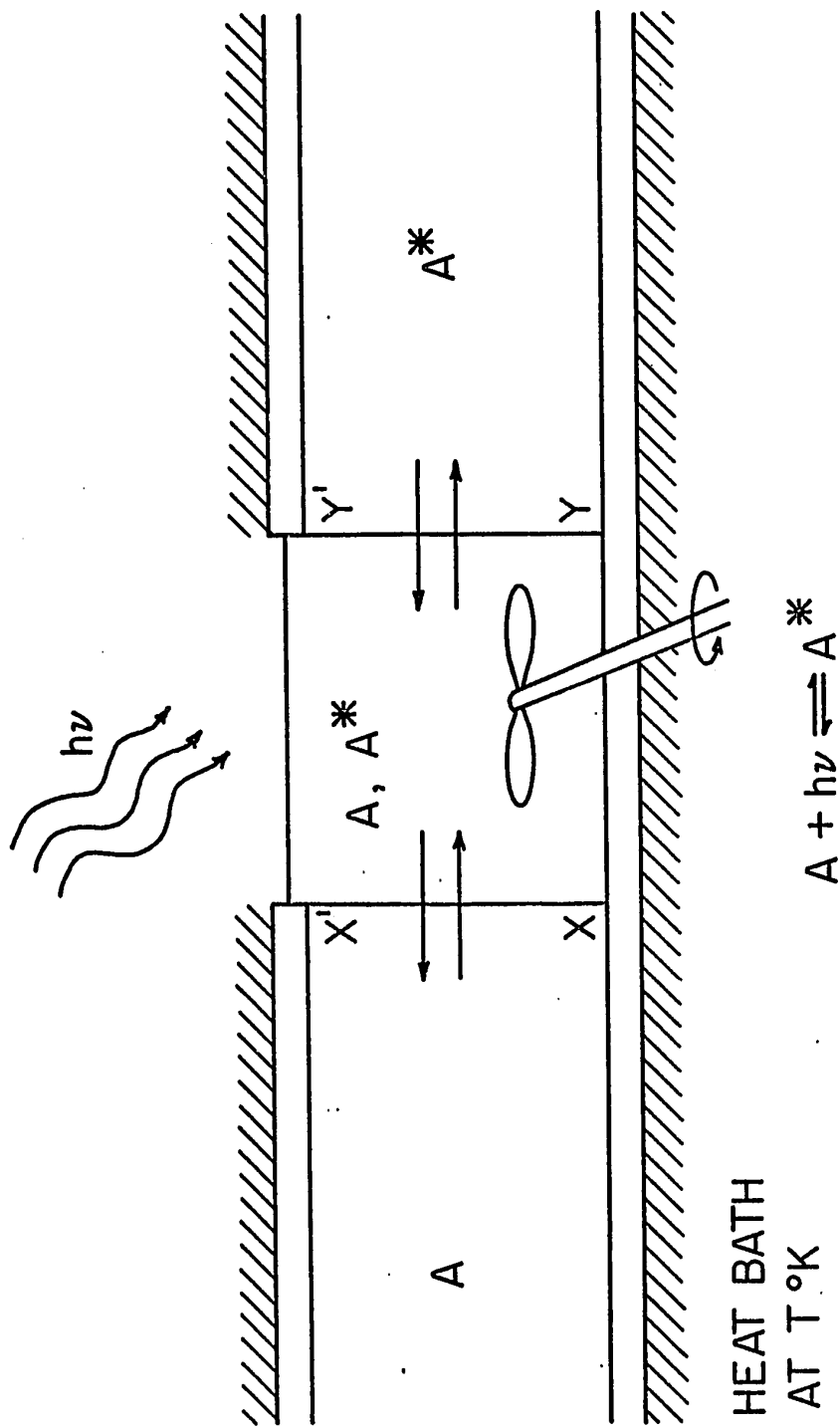


Fig. 4.26 Schematic of hypothetical photo-chemical reaction system. Membrane $x-x'$ is permeable only to species A and membrane $y-y'$ is permeable only to species A^* . The system is assumed to be isothermal.

reactor which may be a practical analogue of our theoretical system. The photochemical reaction



is supposed to be producing high energy particles, A^* , and at the same time material (A, A^*) is entering and leaving the system. If we assume that the membrane xx' is permeable only to species A and that membrane yy' is permeable only to A^* then this chemical reactor is completely analogous to our two level model with particle flow. This system is also a simple model of the primary process of photosynthesis. For example, one proposed scheme of photosynthesis (Calvin, 1959) suggests that a photon of light absorbed by chlorophyll in its ground state excites the chlorophyll molecule into its singlet state (exciton states, our population n_2) where its energy is then able to be carried away as an exciton, and eventually the energy which it carries is utilized in driving some chemical reaction (e.g., the production of carbohydrates or ATP).

4.9 SUMMARY OF IMPORTANT CHARACTERISTICS OF THE MODELS

In view of the fact that certain specific properties of the models have been discussed previously, they will not be repeated; however, in conclusion we list a few general features of these models:

- (1) they all follow the mini-max principle of entropy production
- (2) to have a positive free energy (self-organisation) in the steady state, the system must tend to a state far from equilibrium (i.e., $b/a > \text{critical value}$)

- (3) the models, although very simple, are qualitatively representative of a wide class of physical and biological systems which undergo an evolution involving a change in their free energy content (organisation).

CHAPTER 5

RADIATION ABSORBING MODELS WITH NON-LINEAR EQUATIONS

5.1 INTRODUCTION

In this chapter we extend the models previously discussed to include the possibility of particle-particle interactions. In the dilute limit, it is reasonable to assume that such particle-particle interactions (e.g., binary collisions, spin-spin interaction, etc.) are very weak compared to the interaction between the particles and the environment (thermal or radiative transitions). However, as the concentration of the particles increases the likelihood of particle-particle interactions increases.

When two particles interact it is possible that the energy state of each particle will change, one particle gaining energy at the expense of the second. It is therefore reasonable to talk about competition between particles for the energy which is available in the system.

Here we consider a collection of two (or more) types of particles which, in the most general case, are allowed to interact with each other and with the environment. We begin the discussion with a derivation of a set of equations governing the time evolution of the system, and a set of thermodynamic functions which characterize the system. We then examine a model system for the Overhauser class of interactions which serves to illustrate certain interesting features of the general discussion.

5.2 DERIVATION OF THE SYSTEM EQUATIONS

The equations will be derived for a system of two interacting species. Generalizations to an arbitrary number of interacting species will not be given explicitly but are apparent from the form of the equations.

Let us assume that each of the two kinds of particles have two accessible energy states and they are distributed homogeneously throughout some kind of diluent. The mixture (diluent plus particles) is in good thermal contact with a heat bath which is maintained at temperature T . The entire system is irradiated with radiation of frequencies ν , such that

$$h\nu^\beta = E_2^\beta - E_1^\beta = \Delta\epsilon^\beta \quad \beta = 1, 2 \quad (5-1)$$

where the superscript β refers to the type of particle and the subscripts refer to the upper (2) or lower lying energy levels (1), respectively.

If the number of particles N^1, N^{2*} are small then it is reasonable to assume that species interact very seldom. We can therefore write linear equations for the time evolution of the very dilute system as

* As usual, we assume $N^1 = n_1^1 + n_2^1$ where n_1^1 is the number of particles of species 1 in state 1, and n_2^1 is the number of particles of species 1 in state 2. We then define occupation probabilities $P_1^1 = n_1^1/N^1$, $P_2^1 = n_2^1/N^1$, and similarly for species 2.

$$\begin{aligned} \frac{dP_i^\beta}{dt} &= \sum_j (\Lambda_{ji}^\beta P_j^\beta - \Lambda_{ij}^\beta P_i^\beta) \\ &= \sum_j (\lambda_{ji}^\beta + \Gamma^\beta) P_j^\beta - (\lambda_{ij}^\beta + \Gamma^\beta) P_i^\beta \end{aligned} \quad (5-2)$$

where the transition probabilities are defined as in section 4.2.

Now if we increase the density of each kind of particle, the probability of a collision between particles increases and at some point the probability of binary collisions* will be sufficiently large that equation (5-2) must be modified.

Let us assume that binary interactions between particles of two different species can only occur following one of the two schemes indicated in Fig. 5.1**. In scheme (i) of Fig. 5.1, a particle of type 1 gains energy at the expense of a particle of type 2. If the energy differences between the allowed levels of each particle system are not the same, the extra energy (Q) can be surrendered to the heat bath (e.g., in a solid solution, phonon creation). In scheme (ii) of Fig. 5.1, a particle of type 1 loses energy to a particle of type 2. If the energy level differences for the two species is not the same, then at the time of collision the

* We use this term as inclusive of a large class of interactions which lead to the same phenomenology.

** According to these schemes, interactions between particles of the same species leaves the populations of that species unchanged and, are thus, not detectable.

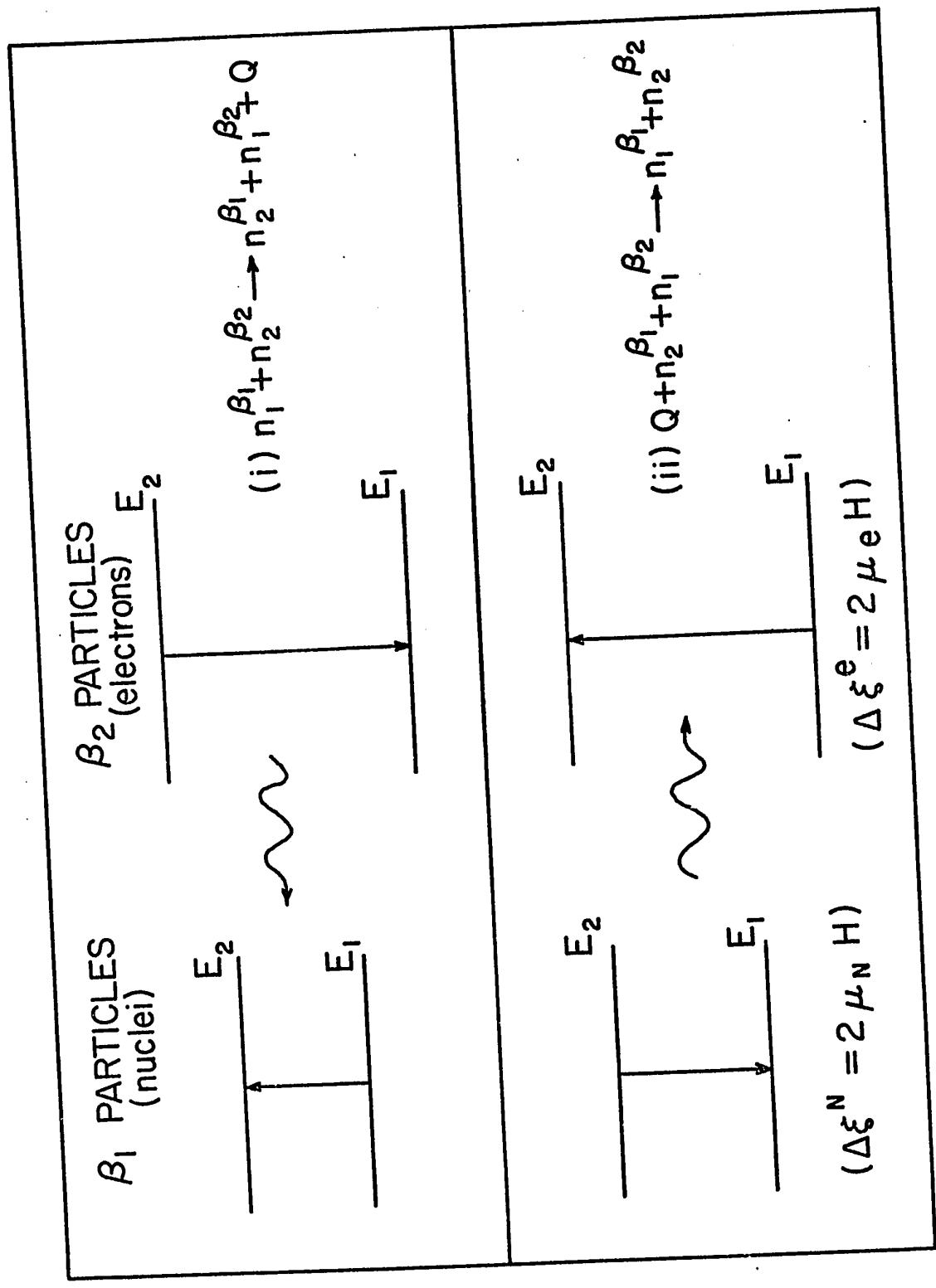


FIG. 5.1 Schematic representation of binary interaction.

interacting pair must be able to absorb the shortfall in energy from the heat bath. In some general way such a collision is a type of three particle event which requires that both types of particles and a quantum of energy are at the same position in time and space before the reaction can occur.

It is apparent that such events would be unlikely if $\Delta\epsilon^2 - \Delta\epsilon^1$ is large and thus such reactions would only occur slowly.

Defining $w_{12}^{(1)} P_1^1 P_2^2$ as the number of transitions per unit time of type (i) and $w_{21}^{(1)} P_2^1 P_1^2$ as the number of transitions per unit time of type (ii), we can write for species 1

$$\left. \frac{\partial P_1^1}{\partial t} \right|_{\text{collision}} \equiv w_{21}^{(1)} P_2^1 P_1^2 - w_{12}^{(1)} P_1^1 P_2^2 \quad (5-3)$$

and similarly for species 2 with the collision term reversed in sign, i.e.,

$$\left. \frac{\partial P_1^1}{\partial t} \right|_{\text{collision}} = - \left. \frac{\partial P_1^2}{\partial t} \right|_{\text{collision}}$$

Thus, the equations governing the time evolution of the system can be written

$$\frac{dP_1^1}{dt} = (\Lambda_{21}^1 P_2^1 - \Lambda_{12}^1 P_1^1) + \left. \frac{\partial P_1^1}{\partial t} \right|_{\text{collision}}$$

$$= (\Lambda_{21}^1 P_2^1 - \Lambda_{12}^1 P_1^1) + [w_{(2\ 1)}^1 P_2^1 P_1^2$$

$$- w_{(1\ 2)}^1 P_1^1 P_2^2] \quad (5-4)$$

and similarly for dP_1^2/dt .

The generalization to more than two species of two level particles is evident from the form of (5-4). For each type of binary interaction a new term of the form (5-3) is added to (5-4). This generalization will not be discussed further.

In the steady state, if it exists, we have $dP_i^j/dt = 0$ for all i, j . From (5-4), we obtain for the steady state

$$\frac{P_2^1}{P_1^1} = \frac{[\Lambda_{12}^1 + w_{(1\ 2)}^1 P_2^2]}{[\Lambda_{21}^1 + w_{(2\ 1)}^1 P_1^2]} \quad (5-5)$$

In the event that particles of type 1 interact only with particles of type 2, and not significantly with the environment, then we have the further condition that

$$\Lambda_{12}^1 = \Lambda_{21}^1 \approx 0 \quad (5-6)$$

and the polarization of species 1 (i.e., the relative populations of the two allowed states) reduces to

$$\frac{P_2^1}{P_1^1} = \frac{w_{12}^{(12)}}{w_{21}^{(12)}} \frac{P_2^2}{P_1^2} \quad (5-7)$$

This implies that the polarization of species 1 is strictly proportional to the polarization of species 2. We will return to this point later.

With reference to Fig. 5.1, we see that the transition probabilities for the interaction are related through the Boltzmann factors such that

$$\alpha w_{12}^{(12)} = \theta w_{21}^{(12)} \quad (5-8)$$

or defining

$$w \equiv w_{21}^{(12)} \quad (5-9)$$

we can simplify our notation to

$$w_{12}^{(12)} = \frac{\theta}{\alpha} w \quad (5-10)$$

where

$$\alpha^1 = \exp(\Delta \epsilon^1 / K_B T) \equiv \alpha \quad (5-11)$$

and

$$\alpha^2 = \exp(\Delta\epsilon^2/k_B T) \equiv \theta \quad (5-12)$$

with these definitions we then obtain from (5-4)

$$\frac{dP_1^1}{dt} = (\Lambda_{21}^1 P_2^1 - \Lambda_{12}^1 P_1^1) + w[P_2^1 P_1^2 - \frac{\theta}{\alpha} P_1^1 P_2^2] \quad (5-13)$$

5.3 THERMODYNAMIC FUNCTIONS

5.3.1 Free Energy

Provided that the energy level structure of the particles is left unchanged by the effect of binary collisions (this assumption was implicit in our previous derivations) and the system is in good contact with a heat bath (at $T^\circ K$), we can write (see section 4.2.6)

$$\begin{aligned} A = & N^1 k_B T \{P_1^1 \ln P_1^1 + P_2^1 \ln \alpha P_2^1\} \\ & + N^2 k_B T \{P_1^2 \ln P_1^2 + P_2^2 \ln \theta P_2^2\} \end{aligned} \quad (5-14)$$

Henceforth, (with no loss of generality) we shall normally assume that the number of particles of each species is the same, thus.

$$N^1 = N^2 \equiv N \quad (5-15)$$

and

$$A = NK_B T \{ P_1^1 \ln P_1^1 + P_2^1 \ln \alpha P_2^1 + P_1^2 \ln P_1^2 + P_2^2 \ln \theta P_2^2 \} \quad (5-16)$$

5.3.2 Entropy Production

The expression for the entropy production rate in a system with particle-particle interactions is slightly more complicated than the expression given in 4.2.6. Neglecting the entropy exchanged between the particles and the monochromatic radiation fields, we can write the entropy production rate, \dot{S}_i , as the sum

$$\dot{S}_i = \left(\frac{dS}{dt} \right)_{\text{Bath}} + \left(\frac{dS^1}{dt} \right)_c + \left(\frac{dS^2}{dt} \right)_c \quad (5-17)$$

where $(dS/dt)_{\text{Bath}}$ is the entropy produced by the exchange of energy (at $T^\circ\text{K}$) between the system and the heat bath. The terms $(dS^1/dt)_c$, $(dS^2/dt)_c$ represents the change in entropy of 1 or 2 type particles due to configurational changes (i.e., in level populations).

In the usual way we can write the configurational entropy of particles of species β as

$$(S^\beta)_c = -NK_B \sum_i P_i^\beta \ln P_i^\beta \quad (5-18)$$

so

$$\left(\frac{dS}{dt}\right)_c^\beta = -NK_B \dot{P}_2^\beta \ln(P_2^\beta/P_1^\beta) \quad (5-19)$$

where $\dot{P}_2^\beta \equiv dP_2^\beta/dt$ and where we have used the fact that $\sum_i P_i^\beta = 1$.

The contribution due to exchange of energy with the heat bath can be written in the form

$$\left(\frac{dS}{dt}\right)_{\text{Bath}} = -\frac{1}{T} \left(\frac{dU^1}{dt} + \frac{dU^2}{dt} \right) \quad (5-20)$$

where dU^1/dt and dU^2/dt are the rates of change of the thermal energies of system 1 and 2 respectively. After substitution and rearrangement, we obtain

$$\left(\frac{dS}{dt}\right)_{\text{Bath}} = NK_B \{ (\ln\alpha)(P_2^1) + (\ln\theta)(P_2^2) \} \quad (5-21)$$

After substitution in (5-17) and simplification we finally obtain

$$\begin{aligned} \dot{S}_i = & NK_B \{ (\lambda_{21}^1 P_2^1 - \lambda_{12}^1 P_1^1) \ln(\alpha P_2^1/P_1^1) \\ & + \Gamma^1 (P_2^1 - P_1^1) \ln(P_2^1/P_1^1) + (\lambda_{21}^2 P_2^2 - \lambda_{12}^2 P_1^2) \ln(\theta P_2^2/P_1^2) \\ & + \Gamma^2 (P_2^2 - P_1^2) \ln(P_2^2/P_1^2) \\ & + w [P_2^1 P_1^2 - \frac{\theta}{\alpha} P_1^1 P_2^2] \ln [(\alpha P_2^1/P_1^1)(P_2^2/\theta P_1^2)] \} \quad (5-22) \end{aligned}$$

It is to be noted that since each term in (5-22) is of the form $(x - 1) \ln x$, that \dot{S}_1 as given by (5-22) is positive definite as required. The first four terms in the entropy production rate are the same as though the system were composed of independent particles of two types, each type coupling to the heat bath and the radiation field. The remaining term is due to the interaction, and is to be interpreted as the entropy indirectly surrendered to the heat bath when inter-species transitions occur.

5.4 OVERHAUSER TYPE INTERACTIONS

5.4.1 Introduction

Overhauser (1953) proposed that the population distribution of nuclear spins will under certain conditions be determined by the electronic magnetic moment rather than by the nuclear magnetic moment. Since the magnitude of the electronic magnetic moment is several hundred times the magnitude of the nuclear magnetic moment, we can anticipate situations leading to a large enhancement of the nuclear polarization. This polarization may either be positive or negative, depending upon the precise mechanisms of the interaction. (An early experimental example of negative polarization in a liquid was reported by Bennett and Torrey (1957).)

Overhauser stated that such an effect is most likely in metals when the electron spin resonance is saturated and when the principle relaxation mechanism of the nuclear spins is the $\underline{I} \cdot \underline{S}$ hyperfine coupling with the electronic spins. This effect has been observed experimentally

(Carver and Schlichter, 1953; and 1956) and the phenomenon of "dynamic polarization" is well represented in the literature (Webb, 1961).

5.4.2 Coupling of Electron and Nuclear Spins

The model discussed in this section is similar to Klein's (1955) model for the Overhauser effect. In this contribution, however, we emphasize the importance of an evaluation of the free energy for a complete characterization of the spin system. Furthermore, our particular model generates enhanced negative polarizations, so, is not the classical Overhauser effect but a related phenomenon, the "Underhauser Effect" (e.g., Pake, 1962).

Let us consider a collection (still reasonably dilute) of N nuclear spins (with magnetic moment, μ_N) and N electronic spins (with magnetic moment, μ_e). All "particles" have spin $\frac{1}{2}$ and when the system is placed in a magnetic field (H), the energy level structure of the system may be represented by the scheme shown in Fig. 5.1. The nuclear Zeeman levels are $\pm\mu_N H$ and the electronic Zeeman levels are $\pm\mu_e H$.

We now assume that the nuclei undergo transitions due to their interaction with the electronic spins, only. The effect of this interaction is therefore properly represented by schemes (i) and (ii) of Fig. 5.1. The electronic spins also couple to the heat bath and to a source of microwave radiation of frequency ν such that

$$\nu = 2\mu_e H/h$$

(5-23)

5.4.3 The Rate Equations

The electronic transition probabilities a , $a\alpha^*$ (for transitions due to interaction with the heat bath) and b (for transitions due to interaction with the radiation field) are defined as in Chapter 4.

If w is the probability of a transition per unit time for a type (ii) interaction between the nuclear spins and the electronic spins, we can write the equations governing the time evolution of the systems from (5-13) as

$$\begin{aligned} \frac{dP_1^e}{dt} \equiv \dot{P}_1^e = & [(\alpha a + b) P_2^e - (a + b) P_1^e] \\ & + w[P_2^e P_1^N - (\theta/\alpha) P_1^e P_2^N] \end{aligned} \quad (5-24)$$

and

$$\frac{dP_1^N}{dt} \equiv \dot{P}_1^N = w[(\theta/\alpha) P_1^e P_2^N - P_2^e P_1^N] \quad (5-25)$$

where P_1^e represents the probability that an electronic spin is in state one and P_1^N represents the probability that a nuclear spin is in state one, and similarly for P_2^e and P_2^N .

In addition, we have the constraint that

* We assume that the electronic Boltzmann factor $\alpha = \exp(2\mu_e/K_B T)$ and the nuclear Boltzmann factor $\theta = \exp(2\mu_N/K_B T)$.

$$(P_1^e + P_2^e) = 1 = (P_1^N + P_2^N) \quad (5-26)$$

The steady state values are found by setting $dP_1^e/dt = dP_1^N/dt = 0$, and solving equations (5-24) and (5-25), simultaneously. We obtain the results

$$\left. \begin{aligned} (P_1^e)^S &= (\alpha a + b) / (\alpha a + a + 2b) \\ (P_2^e)^S &= (a + b) / (\alpha a + a + 2b) \end{aligned} \right\} \quad (5-27)$$

and

$$\left. \begin{aligned} (P_1^N)^S &= \theta(\alpha a + b) / [\alpha(a + b) + \theta(\alpha a + b)] \\ (P_2^N)^S &= \alpha(a + b) / [\alpha(a + b) + \theta(\alpha a + b)] \end{aligned} \right\} \quad (5-28)$$

In the event that the electron spins are saturated ($b \gg \alpha a$), the steady state nuclear polarization is given by

$$(P_2^N/P_1^N)^S \approx \alpha/\theta \quad (5-29)$$

where

$$\begin{aligned} \alpha/\theta &= e^{2\mu_e H/K_B T} e^{-2\mu_N H/K_B T} \\ &= e^{2(\mu_e - \mu_N)H/K_B T} \end{aligned} \quad (5-30)$$

Since $\mu_e \approx 1000 \mu_N$, we see that the nuclear polarization is strongly determined by the electronic Boltzmann factor and thus the polarization is greatly enhanced. We re-emphasize that for this particular choice of interaction, we obtain an inverse Overhauser effect, i.e., large negative polarization.

5.4.4 Thermodynamic Functions and Discussion

Utilizing (5-22), we write the rate of entropy production, \dot{S}_i , as

$$\begin{aligned} \dot{S}_i &= NK_B \{ a(\alpha P_2^e - P_1^e) \ln (\alpha P_2^e / P_1^e) \\ &+ b(P_2^e - P_1^e) \ln (P_2^e / P_1^e) \\ &+ w[(\theta/\alpha) P_1^e P_2^N - P_2^e P_1^N] \ln [(\theta P_2^N / P_1^N) (P_1^e / \alpha P_2^e)] \} \end{aligned} \quad (5-31)$$

which in the saturated steady state reduces to

$$\begin{aligned} \dot{S}_i|_{\text{sat}} &= \frac{NK_B}{2} \{ a(\alpha - 1) \ln \alpha \} \\ &= \left(\frac{\mu_e H}{T} \right) [Na(\alpha - 1)] \end{aligned} \quad (5-32)$$

With reference to (5-16) we write the free energy as

$$A = NK_B T \{ P_1^e \ln P_1^e + P_2^e \ln \alpha P_2^e + P_1^N \ln P_1^N + P_2^N \ln \theta P_2^N \} \quad (5-33)$$

If we substitute (5-27) and (5-28) into (5-33) it can be shown that the steady state free energy A^S is a monotonically increasing function of b . I.e., the stored free energy increases as the system approaches saturation. A is clearly larger here than it would be for the electronic system alone.

It can be seen from (5-32) that the saturated steady state rate of entropy production is the same as it would be if there was no coupling to the nuclear system. However, as long as the system is out of the steady state, the entropy production rate can be shown to be greater for the system coupling electronic and nuclear spins than it is for the electronic system alone.

To illustrate the thermodynamic significance of these calculations, let us consider Fig. 5.1. This describes the behaviour of the nuclear spin system when the electronic system is maintained at saturation. For every case examined, the "excess" rate of entropy production (the electronic system always dissipates at a constant rate) due to the internal relaxation of the nuclear spins decreases to zero as the system approaches the steady state. Simultaneously, the nuclear free energy increases and, for a sufficiently large separation of the nuclear energy levels, becomes positive. The nuclear free energy can only become positive for the negative polarization effect (i.e., large P_2). This property of the free energy is further illustrated in Table 5-1 where for equilibrium with the heat bath (in this case, via the coupling to the electronic system) the free energy is a negative minimum. For enhanced polarizations in the positive sense (larger P_1) the free energy can approach zero but it is only for large P_2 (tendency to negative polarization) that the free energy becomes positive.

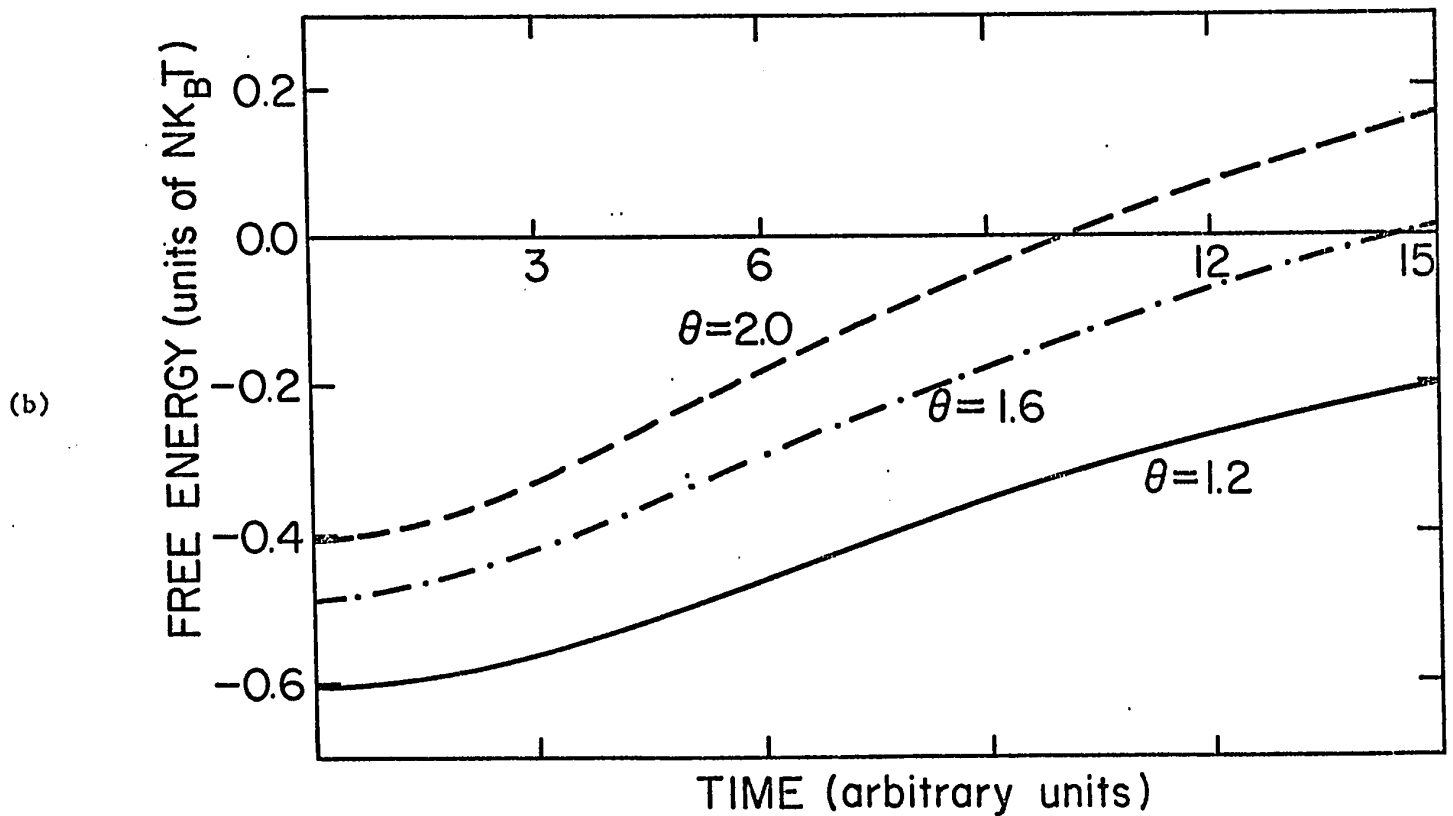
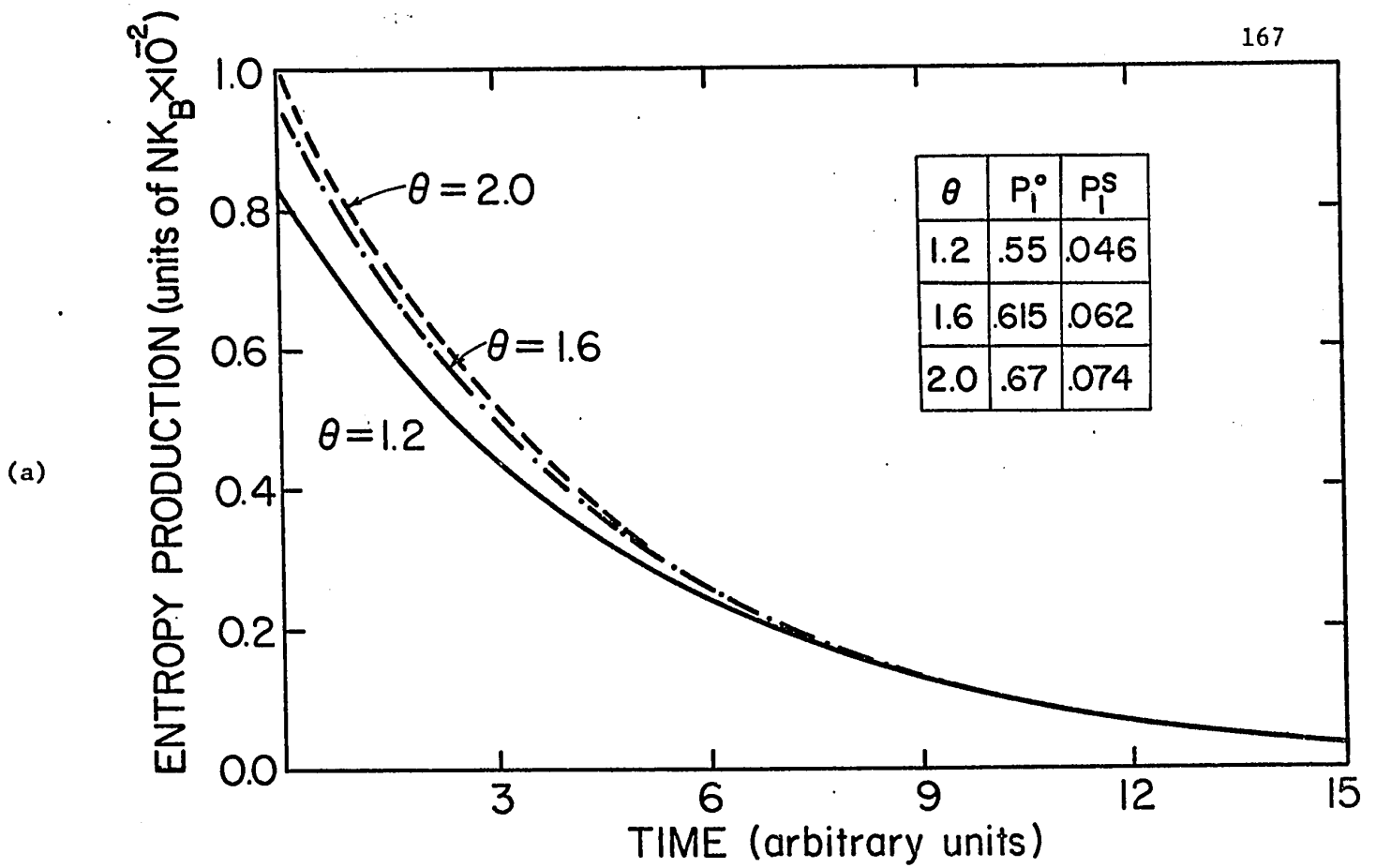


Fig. 5.2 Dynamic polarization in the model. (a) Entropy production in nuclear system versus time. (b) Free energy of nuclear system versus time.

Table 5-1

Values of Free Energy for Various Values of P_1

P_1 (= $1. - P_2$)	A^* (Units of $NK_B T$)
.999	- .0063
.99	- .130
.9	- .164
.833+	- .182
.8	- .178
.7	- .127
.6	- .029
.5	+ .111
.4	+ .297
.3	+ .516
.2	+ .787
.1	+1.12
.01	+1.54
.001	+1.60

* The free energy was calculated for the two level model using

$$A = NK_B T \{ P_1 \ln P_1 + P_2 \ln \theta P_2 \} \text{ where } \theta = 5.$$

+ This is the occupation probability for equilibrium with the heat bath. Note that the free energy assumes its minimum value at this point.

In the context of self-organising systems, we can say that a system which is able to utilize constrained internal degrees of freedom (here the extra degree of freedom involves the electron spin-nuclear spin interaction which is supposed to be zero before some time t and non-zero later) can spontaneously increase its store of free energy. During the approach to the steady state, the system has an "excess" dissipation, but the steady state itself is maintained by the same energy flow from the surroundings that existed before the degree of freedom was removed (i.e., before the interaction was turned on). It is worth remarking that the internal system goes to "equilibrium" in the sense of zero dissipation but not in the sense of minimum free energy. If the system has a degree of freedom which is removed by an external constraint (coupling) then it is possible that the dissipation rate will be enhanced at all times. In that event, the free energy can be larger or smaller than it was prior to removing the degree of freedom.

CHAPTER 6

APPLICATIONS AND DISCUSSION OF THE THERMODYNAMIC FORMALISM

6.1 INTRODUCTION

The literature in applied physics and chemistry abounds with problems concerning the stability of steady state irreversible systems which have been characterized as analytically indeterminate. Such problems bear a close resemblance to the problems of morphogenesis and differentiation in living systems, whose apparent indeterminacy has led repeated generations of life scientists to espouse the various forms of vitalism. Physical scientists have long dealt with their particular problems by invoking "ad hoc" thermokinetic principles which have by-and-large led to good predictions. However, the absence of fundamental justifications for the principles used has left most workers with a strong feeling of uneasiness.

The reason for the apparent indeterminacy in these problems is now becoming clear. The path up to the stable steady state is invariably one which involves discrete symmetry changes which cannot be incorporated uniquely into the initial conditions nor the partial differential equations which describe the process. Furthermore, the observed path up to the stable steady state is, as often as not, non-analytic, involving nucleation steps (corresponding to a change in symmetry) which require large fluctuations for initiation. Interestingly enough, digital computer solutions of the appropriate differential equations in fluid mechanics often achieve a

correct description of the final steady state vortex structure even though the equations themselves contain no detailed information about the outcome (Kirkaldy, 1972). The reason for this is that the mesh error associated with the difference equations injects a stochastic element into the calculations which allows the computer to search a fluctuating phase space which is denied to the differential equations. We are forced to conclude, therefore, that the computer solution represents a physical path more realistically than does the analytic solution of a partial differential equation.

In the foregoing sections we investigated the kinetic phase space of a selection of simple, but generalizable quantum models to a thermodynamic depth which is unmatched in previous work. This has indicated clearly that the potential surface(s) which describe the environs of the steady state has a mini-max character rather than a simple minimum as proposed by numerous workers to date. There is a hint as to this mini-max character in Onsager's (1931) original papers, but this aspect was not explored further by him. On the other hand, Prigogine's school (e.g., Glansdorff and Prigogine, 1954) has exclusively emphasized the minimal character of appropriate potential functions.

For the past decade, Kirkaldy has argued on both empirical and theoretical grounds that a kinetic potential which can deal with problems of morphogenesis, if such a potential exists, must have the mini-max character, and our calculations strongly support this conjecture. In this section we plan to draw on the close analogies between our models and a series of physio-chemical systems examined earlier by Kirkaldy in published and unpublished manuscripts in an attempt to improve the plausibility of his general conjecture. Furthermore, we undertake the

thermodynamic analysis of a class of population and growth problems, introduced to mathematical biology by Volterra (1928) and Lotka (1956) on the basis of general perceptions which may be derived from our model calculations.

6.2 A CAMPFIRE

Consider the kinetic characteristics of the physio-chemical process that occurs following the ignition of a campfire in still air and reasonably assume that the integrated brightness is monotonic with the dissipation and that the flame area is monotonic with the free energy. (Note that the fuel is not a part of the system but rather a source of free energy inflow, complemented by the oxygen inflow.) Such a configuration usually rises rapidly to a quasi-steady state of maximum dissipation and free energy and remains there for an appreciable time since the area of the ignited wood surface is quasi-constant. Now let us briefly perturb the fire, first by blowing on it, and secondly by dampening it. In the first case the steady state returns to a minimum in the dissipation rate and the free energy following the perturbation, and in the second case it returns to a maximum in the dissipation rate and the free energy. The steady state is therefore (approximately) characterized by a mini-max behaviour in the dissipation rate.

The two level model discussed in section (4.5) has an identical general character. Consider a steady state at a fixed radiation intensity b (which corresponds to the steady state inflow of oxygen and fuel to the fire). If we briefly perturb b upward, the system returns to a minimum and if we perturb b downward it returns to a maximum in the

dissipation and the free energy. A campfire is, in our view, an excellent thermodynamic prototype for the life history of biological individuals. From a nuclear beginning it proceeds to spontaneously increase its mastery over the free energy sources in the environment (by expanding the reaction area and draft) until maximum dissipation and free energy are attained. This is precisely the property of biological individuals which was designated by Bertrand Russell (1927) as "chemical imperialism". Furthermore, the fire "dies" when its free energy sources are exhausted. The minimal character of the growth evolution, as with biological growth, is more subtle. It has to do with the continuous relaxation of all reaction, diffusion and viscous flow processes into the heat sink. For biological systems, Prigogine and Wiame (1946) described this as a decrease in the metabolic rate per unit volume.

6.3 THE BÉNARD INSTABILITY

Hydrodynamicists and astrophysicists have long shared an interest in a particular instability known as the Bénard problem. This instability arises when a mass density gradient and a temperature gradient are counterpoised. The Bénard problem is associated with the simplest possible boundary condition, viz., two plane parallel isothermal surfaces, at temperatures T_1 and T_2 , which are separated by a fluid, the whole system being in a gravitational field. The lower temperature T_1 is at the higher gravitational potential. This models the thermal configuration in stars, which explains the strong astrophysical interest (Chandrasekhar, 1961). The instability is initiated at a critical value of the temperature gradient when the denser liquid at the top begins to fall, leading to a

vortex-like configuration of the fluid (a change of symmetry) between the surfaces.

The marginal state of this instability has been accurately characterized theoretically through linear perturbation theory (Chandrasekhar, 1961) and via the local potential method of Prigogine (Shechter and Himmelbau, 1965). Some progress has been made in the description of the transient, non-linear regime (e.g., Segel, 1965). However, the relaxed state in the non-linear vortex regime continues to evade precise theoretical description.

It has been proposed (Kirkaldy, 1972), and we agree with the proposal, that the evolution up to the steady vortex-like state can be characterized as an approximate maximum in the dissipation rate. A similar proposition, applicable to the problem of boiling heat transfer, has been presented by Hammel and Baumeister (1966). As far as the heat transfer is concerned this is clear enough for the dissipation rate is proportional to $(T_2 - T_1)^2/R$ where R is the thermal resistance and $T_2 - T_1$ is a constant. R necessarily tends to a minimum as the circulation builds up to its steady value. The concomitant minimal character which we are conjecturing for all processes of this class is probably the determinant in the morphological uniformity which is observed, as the following example suggests. The interactive morphology is therefore uniquely determined by a mini-max principle.

6.4 THE EUTECTIC (EUTECTOID) REACTION

Physical chemists and metallurgists have long been intrigued by the condensed state process whereby a supersaturated phase γ (solid or liquid)

is transformed co-operatively into a two phase lamellar α (solid) + β (solid) structure. The growth configuration observed under controlled velocity conditions is shown in Fig. 6.1 (after Jackson and Hunt, 1966). The purely solid state reaction can be carried out isothermally (due to the small latent heat evolution) and it is this reaction which we will focus on here.

The isothermal reaction is initiated by a quench from a stable γ solution range into an unstable two phase $\alpha + \beta$ range as indicated schematically in Fig. 6.2 (a). Following the nucleation of α and β at grain boundaries, co-operative cellular fronts are soon established. These local fronts are represented schematically in Fig. 6.2 (b). The initiation and progress of this reaction is therefore chemically analogous to that of the campfire described above.

Given the mean lamellar spacing, S , the thermodynamic and diffusion parameters and the surface energies $\sigma^{\alpha\beta}$, $\sigma^{\gamma\beta}$ and $\sigma^{\gamma\alpha}$, it has been found possible to obtain an accurate relation between the steady state velocity, V , the undercooling, ΔT , and the spacing, S , and to calculate the precise shapes of the interface as a function of S (e.g., Fig. 6.1) (Zener, 1946; Hillert, 1957; and Puls and Kirkaldy, 1972). The approximate $V(S, \Delta T)$ relation is

$$\begin{aligned}
 v &\sim \frac{\Delta T}{S} \left[1 - \left(\frac{2\sigma^{\alpha\beta} T_E}{\Delta H \Delta T} \right) \frac{1}{S} \right] \\
 &= \frac{\Delta T}{S} (1 - S_C/S)
 \end{aligned} \tag{6-1}$$

where T_E is the eutectoid temperature, ΔH is the latent heat per unit

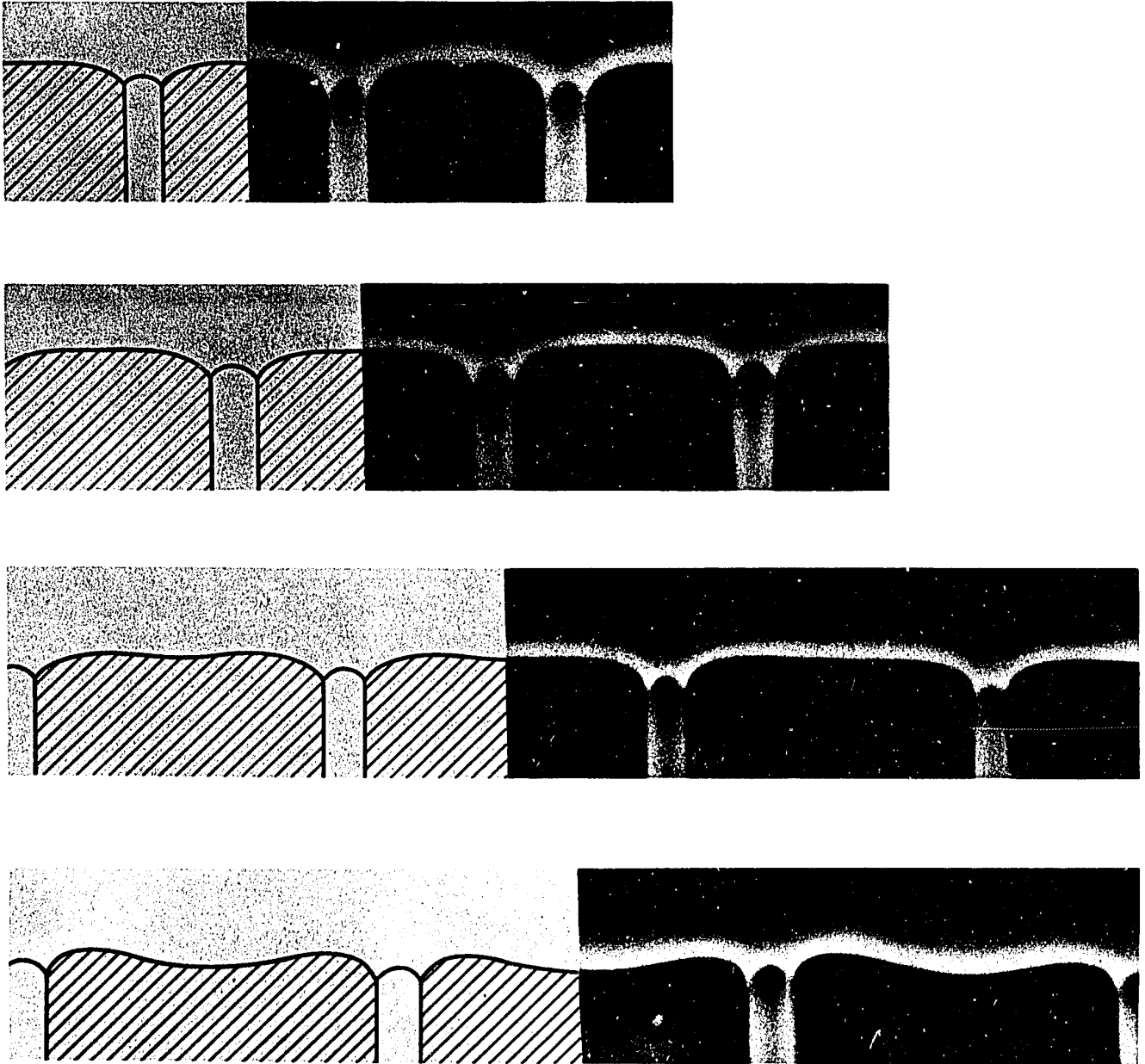


Fig. 6.1 Calculated and observed interface shapes for the carbon tetrabromide-hexachloroethane eutectic (after Jackson (1966) Fig. 13).

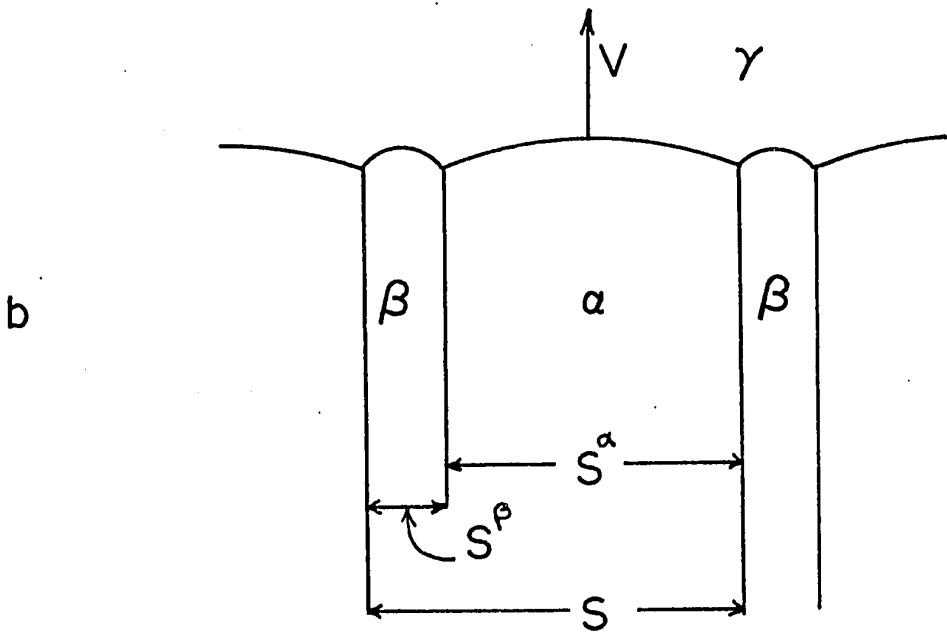
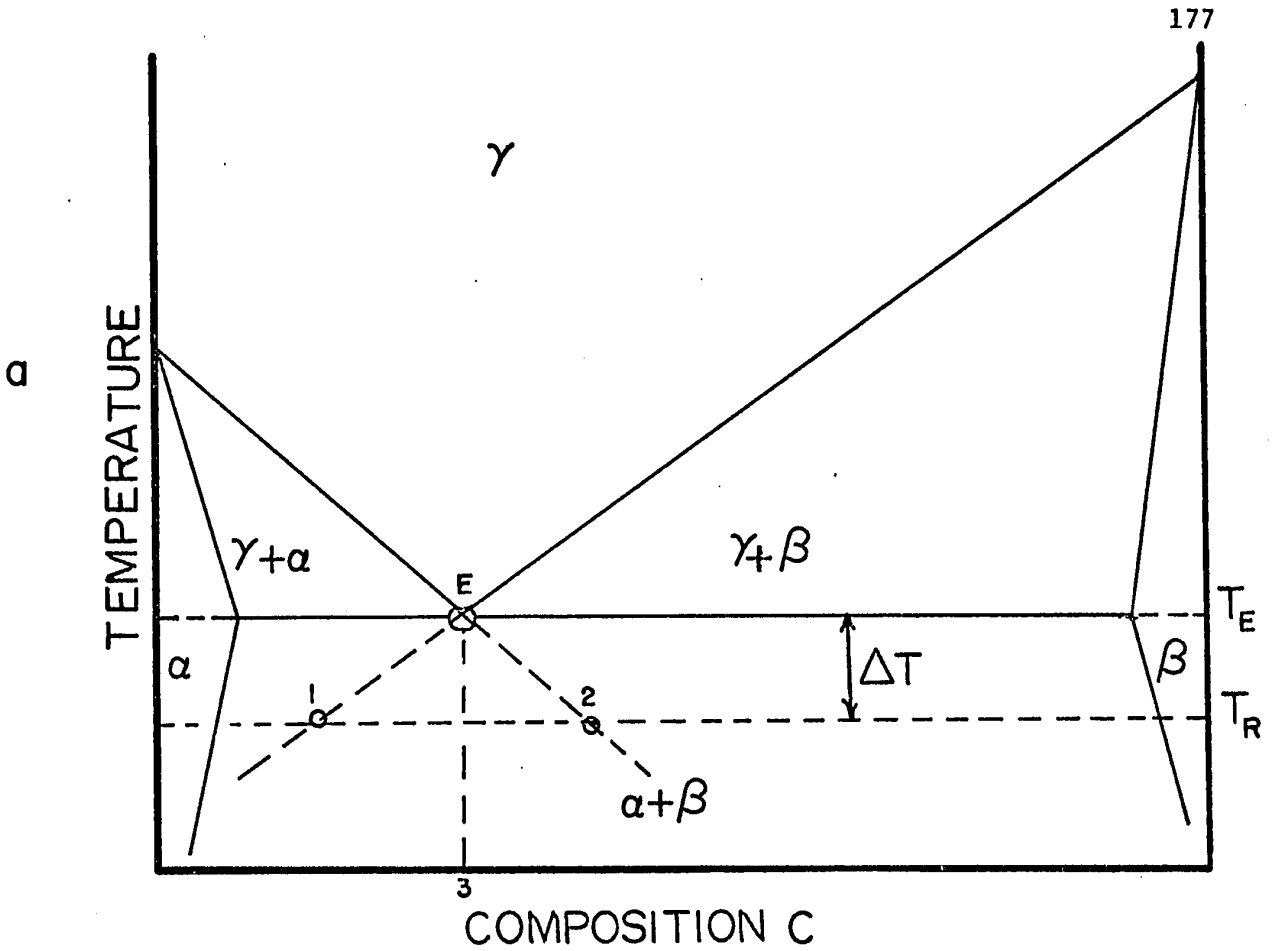


Fig. 6.2 (a) Schematic eutectic phase diagram. Compositions at 1, 2, 3 are $C_0^{\gamma\beta}$, $C_0^{\gamma\alpha}$ and C_∞^γ , respectively. (b) Model lamellar eutectic interface.

volume transformed and $S_C = 2\sigma^{\alpha\beta} T_E / \Delta H \Delta T$ is that spacing where all the free energy available to drive the reaction is stored in the interlamellar surfaces. I.e., V is necessarily zero when $S = S_C$. Since in this experiment ΔT is fixed and known, (6-1) represents a single relation between V and S . The configuration, which experimentally is found to correspond to a unique V and S , is therefore not specified by the steady state theory. Zener conjectured in 1946 that nature chooses the state of maximum velocity ($dV/dS = 0$) and the inferences from this were not too far from the observations. Later workers pointed out on the basis of perturbation arguments (e.g., Cahn (in Hunt and Jackson), 1966; Kirkaldy, 1968) that this spacing ($S = 2S_C$) is unstable and that the stable spacing must be larger. Puls and Kirkaldy (1972) argued that the steady state must be near the maximum in the dissipation rate and in particular, since

$$\frac{dV}{dt} \sim \frac{1}{S} \left(1 - \frac{S_C}{S}\right)^2 \quad (6-2)$$

the optimum must be at $S = 3S_C$. They presented as part of the argument a Le Chatelier type perturbation calculation which generates the same stability point. They also noted that the stability point had a minimal character as well since perturbations of the local spacing with the mean spacing S fixed would necessarily be followed by linear relaxation processes with a normal minimal character. The stability point was therefore averred to be a minimax configuration.

We propose to demonstrate in the following that the eutectoid

reaction is a generalization of the two-level model with particle flow presented in section 4.8 and therefore that the thermodynamic character of the latter represents a partial theoretical justification for the thermodynamic principles conjectured by Kirkaldy (ibid) for the eutectoid reaction.

We first point out that the isothermal eutectoid reaction has a well-defined heat bath (the crystal lattice), as required by the quantum models. We further note that the quantum states of the surface atoms (~ 0.5 e.V.) will be about kT (~ 0.1 e.V.) and the chemical states in the γ diffusion field will be kT (~ 0.1 e.V.). We can accordingly focus our attention on the surface states as designated by the surface energies ($\sigma^{\alpha\beta}$, $\sigma^{\gamma\beta}$ and $\sigma^{\gamma\alpha}$) in establishing a positive monotonic mapping into the quantum model.

The eutectoid system is taken as a box of unit cross-sectional area A , containing the interface and diffusion zone, and ending at the interface cusps which move at a uniform velocity, V .

The radiation flow, $N\Delta\epsilon(P_1 - P_2)b$ into the quantum system is recognized to map uniformly into the chemical free energy flow into the eutectoid system ($V\Delta F_0$, where ΔF_0 represents the free energy per unit volume stored in a supersaturated solution) provided that the initial condition of the quantum system corresponds to all states empty and the initial condition of the eutectoid system is a supersaturated solution with no surfaces. Following the turning on of the radiation and the nucleation of the eutectoid precursor (an α - β combination nucleus) the two kinetic and thermodynamic paths are parallel if we let P_2 represent the frontal surface states ($\sigma^{\gamma\alpha}$ and $\sigma^{\gamma\beta}$) and P_3 represents the trailing

surfaces ($\sigma^{\alpha\beta}$) which flow out of the system at the cusps. For the quantum system, the steady state is always a precise maximum in the entropy production and the free energy (Fig. 4.23) suggesting a similar steady state for the eutectoid system. If the population P_2 is momentarily perturbed upward (by increasing b) the quantum system relaxes back to a minimum in the dissipation and the free energy. The analogous perturbation of the eutectoid system involves a local change in the spacing, S , with the average fixed. This necessarily results in a perturbation (lengthening) of the frontal surface. This too is expected by analogy and in agreement with Kirkaldy's conjecture to relax back to uniform spacing and a minimum in the dissipation and surface free energy.

It should be pointed out that Kirkaldy's conjecture concerning the quasi-steady maximal eutectoid evolution path as a function of the average S , described by equation 6-1, does not necessarily follow from the quantum model behaviour since in the latter case the path is spontaneous and smooth, while in the latter case it was defined as quasi-steady. It therefore remains as a matter of faith that spontaneous paths are reasonable thermodynamic representations of associated quasi-steady paths. Since the quasi-steady path is by definition a non-analytic (involving discontinuous symmetry (spacing) changes) it was probably wishful on our part to think that a continuum model on the real axis could be found to justify the thermodynamic behaviour of a naturally discontinuous process. We suspect now that the only appropriate macroscopic theoretical models will be described in the complex plane in such a way that singularities on the real axis will represent the discontinuous symmetry changes which are involved in the quasi-steady process paths (e.g., see section 2.5).

6.5 THE MINI-MAX PRINCIPLE AND THE THEORY OF GAMES

6.5.1 Introduction

There exists an interesting connection between the mini-max principle of irreversible thermodynamics and Von Neumann's mini-max principle in "The Theory of Games and Economic Behaviour" (Von Neumann and Morgenstern, 1967). We will show that a simple stochastic electrical model (a dissipative system) which evolves in accord with the mini-max principle of thermodynamics leads to natural thermodynamic definitions of the concepts of utility and coalition and correct solutions to a particular three person game.

The theory of games (Von Neumann and Morgenstern, *ibid*; Davis, 1970; and McKinsey, 1952, etc.) is a mathematical description of competition between rational players. The players, who are allowed alternating moves, attempt to maximize their earnings or to minimize their losses, if losses are unavoidable, by a careful choice of strategies. In the electrical model to be discussed the rational play of the competitors is replaced by the switching of electrical elements in a manner consistent with the mini-max principle of thermodynamics.

6.5.2 A Stochastic Electrical Model of a Self-Organising System

Before proceeding to the model of a three person game, let us briefly consider a simple stochastic electrical model of a self-organising system suggested by Kirkaldy (1972).

Consider the electrical system shown in Fig. 6.3. There are dead shorts across the top and the bottom of the network and a fixed voltage,

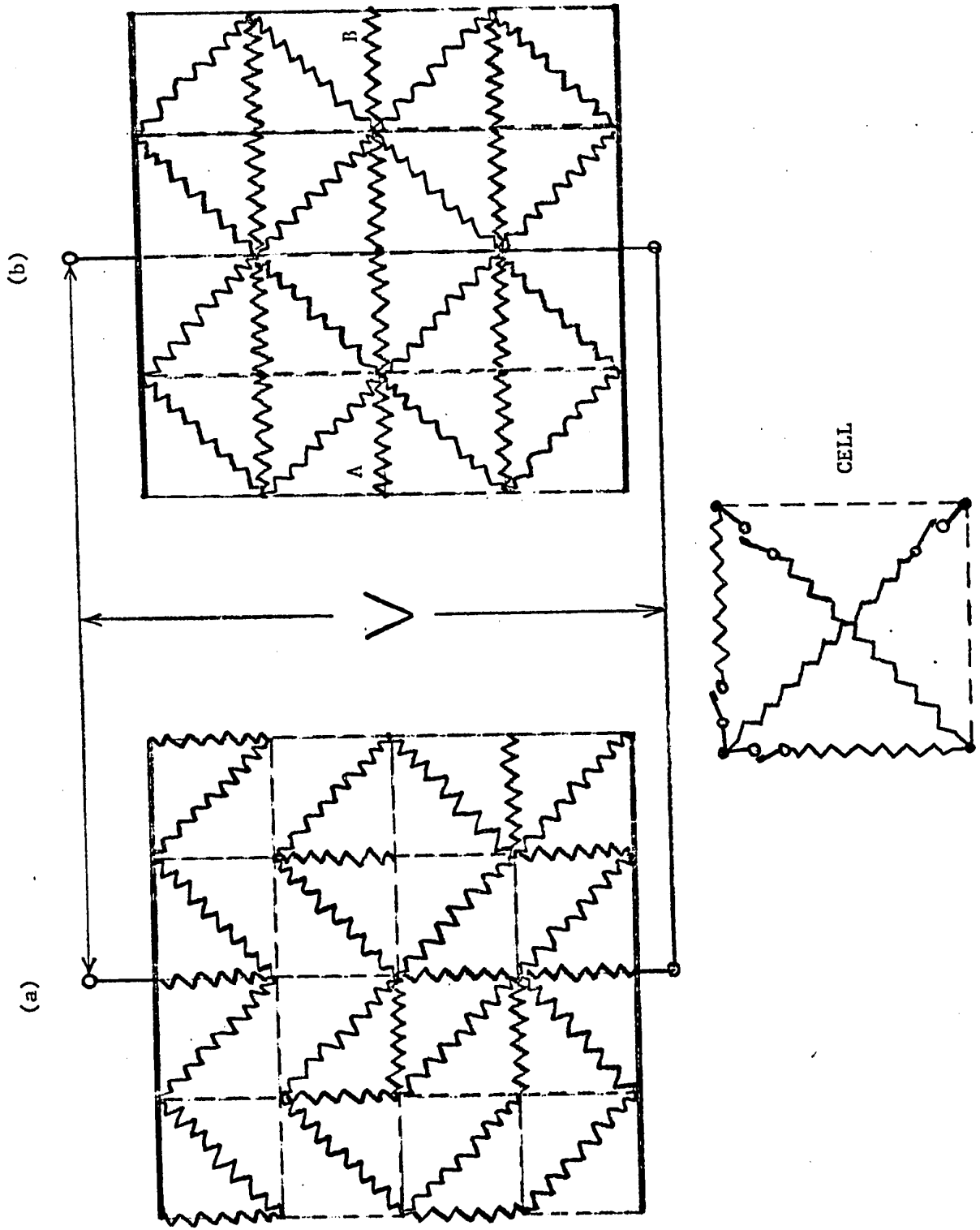


Fig. 6.3 Model of self-organising system.

V , is applied across the shorts. There are two values of resistors in the system. One size of resistor is only allowed to lie on mesh diagonals and the second size of resistor is allowed to lie along vertical or horizontal lines of the mesh. These are the internal structural or "genetic" constraints for the system. The large resistors (those which lie on cell diagonals) are fixed one per cell but may, of course, change their orientation within the cell. The short resistors (those which lie along vertical or horizontal lines) are assumed to be free to diffuse within the system while passing through adjacent sites. The remaining straight lines of the mesh are non-conducting.

The system described above is now prepared in some initial disordered state and is allowed to evolve under the guidance of the mini-max principle of thermodynamics. This process could be performed by using a random number generator to stochastically choose an element of the system (i.e., a resistor) and then randomly choose an allowable neighbouring site. Then some mechanism could be used to exchange the contents of the above selected sites. (Kirkaldy (1972) has in fact designed such a mechanism). In the case of the short resistors, the exchange is only allowed if there is a decrease or no change in the rate of entropy production (proportional to the joule heat). If there is an increase in the entropy production rate, then the system must be returned to its previous configuration. In the case of the large resistors, their change of position (two positions are possible for each resistor) is allowed only if the entropy production increases or remains constant.

In position (a) of Fig. 6.3, the system may be considered as being dead since there is no current flow and hence no dissipation. The system

will only be activated when a short is formed and dissipation begins.

Fig. 6.3 (b) shows one of the very few configurations which is a possible end point of the evolution of the system. The configuration is not absolutely unique and stable since resistors A and B have three electrically equivalent configurations. It is clear, however, that all end points will exhibit a high symmetry and that the system has gained in morphological organisation by seeking a stable configuration which will be at or near a saddle point in the entropy production rate (Kirkaldy, 1965 a, b).

The system could be enriched by including LR^* , CR^* , and LCR^* networks as elements and a modulated AC input. It would then be able to store electrical free energy and we would be able to talk about information storage in the system. It would also be possible to allow active elements to diffuse throughout the network which would create many local saddle points and accord a creative capacity to the model.

6.5.3 A Thermodynamic Model of a Three Person Game

Let us next consider the network shown in Fig. 6.4. This has been designed to represent a three person, zero sum game with pure strategies. One player (at $V = 0$) is non-committal and is intended to represent the environment. Assume, for simplicity, that all resistors are of equal value (i.e., take all $R = 1\Omega$). Further assume that Player A (i.e., the player at V_A) controls resistors 1 and 2 and that Player B (i.e., the player at V_B) controls resistors 3 and 4. This is a realistic economic situation, since if both players are at negative voltages

* L, C, R stand for inductance, capacitance and resistance as usual.

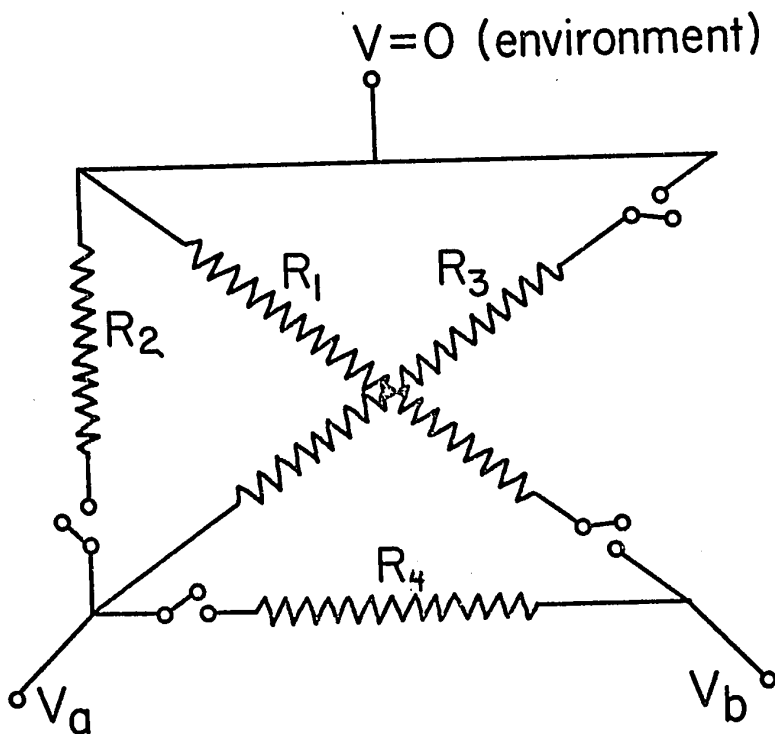


Fig. 6.4 Model network representing a three person zero sum game.

$R_1 = R_2 = R_3 = R_4 = 1\Omega$. V_a and V_b are negative with respect to V .

($V_A, V_B < 0$) they can both expect to gain from the environment. As "rational" players* (at potentials V_A and V_B) they will, of course, both attempt to gain as much commodity (current) as possible. We demonstrate now that similar solutions are obtained whether resistors are switched in or out of the system by rational players or in accordance with the mini-max criterion of thermodynamics. In the thermodynamic representation, the diagonal resistors can only be inter-switched if the entropy production (joule heat) increases or shows no change through the switching action. The short resistors can only be interswitched if the entropy production decreases or shows no change due to the switching action.

According to the rules of the game there are four possible configurations. Player A may choose to have resistor 1 in the circuit and resistor 2 open-circuited or to have resistor 1 open-circuited and resistor 2 in the circuit. Player B has a similar two-fold strategy in which he controls resistors 3 and 4.

The dissipation matrix, whose entries are the values of the dissipation for the various strategies, is given in Table 6-1. The current matrices for each player are given in Table 6-2, the entries being the currents which flow into the players position. By inspection, the sum of the currents is seen to be zero, which of course is necessary for this to be a zero-sum game.

* Rational in the sense defined by Von Neumann and Morgenstern (1967) implies the maximization of earnings or minimization of losses as measured in quantity of a commodity (here, current).

Table 6-1

Entropy Production Matrix T_{σ} . Divide all Entries by $R = 1\Omega$.

		Strategies for (Player at) V_b	
		3	4
Strategies for (Player at) V_a	1	$(V_a - V_b)^2 + V_a^2$ $= 2V_a^2 + V_b^2 - 2V_a V_b$	$(V_a - V_b)^2 + V_b^2$ $= V_a^2 + 2V_b^2 - 2V_a V_b$
	2	$2 V_a^2$	$V_a^2 + V_b^2$

Table 6-2
 Current Matrices for Each Player. Divide all Entries By $R = 1$ to Obtain Current Input.

Strategies for V_b

	3	4
1	$V_b - V_a$	$2V_b - V_a$
2	0	V_b

	3	4
1	$2V_a - V_b$	$V_a - V_b$
2	$2V_a$	V_a

	3	4
1	$-V_a$	$-V_b$
2	$-2V_a$	$-V_a - V_b$

Strategies for V_a

Payoff Matrix For:

(ii) V_a

(iii) V_b

(i) Environment

The properties of these matrices will now be examined as the relative values of V_A and V_B are varied. If we set $\alpha V_A = V_B$, we may write, in terms of α^* , the general game matrix with its four submatrices, as shown in Table 6-3. The five game matrices for (i) $0 < \alpha = 1/2 < 1$; (ii) $\alpha = 1$; (iii) $1 < \alpha = 3/2 < 2$; (iv) $\alpha = 2$; and (v) $2 < \alpha = 3$ are given in Table 6-4, along with the thermodynamic and Game Theory solutions. We see that the two solutions only agree for the last case, $\alpha > 2$. For clarification of the differences, let us examine the matrices in Table 6-4 more closely.

In case (i) where $\alpha = 1/2$, the thermodynamically stable configuration is (1, 3). We might interpret this by saying with reference to Fig. 6.4 that thermodynamics has forced Player A into a coalition with Player B, the coalition being realized by the direct circuit connection (R_1) between V_A and V_B (which lies at the lowest potential). Since we have not at this point admitted coalitions into the Game Theory process, it is not surprising that the Game Theory solution (2, 4) is different than the thermodynamic one.

In the case $\alpha = 1$, there is no unique thermodynamic saddle point, as the solution may fluctuate between (1, 3) and (1, 4). This state is the analogue of a critical point for a kinetic phase transition (change of symmetry). The Game Theory solution remains stable at (2, 4).

Case (iii) ($1 < \alpha < 2$) is similar to case (i). The only difference

* Do not confuse this α with the α previously used to represent the Boltzmann factor.

Table 6-3

Game Matrices with $\alpha V_a = V_b$. For Correct Units: (1) Multiply Entropy Production Matrix by V_a^2/R , (ii) Multiply Current Matrices by $|V_a|/R$.

		Strategies for V_b			
		3	4	3	4
1		$(1 - \alpha)^2 + 1$ $= 2 + \alpha^2 - 2\alpha$	$(1 - \alpha)^2 + \alpha^2$ $= 1 + 2\alpha^2 - 2\alpha$	-1	$-\alpha$
	2	2	$1 + \alpha^2$	-2	$-(1 + \alpha)$
		Dissipation Matrix		Current Matrix for Environment	
1		$2 - \alpha$	$1 - \alpha$	$\alpha - 1$	$2\alpha - 1$
2		2	1	0	α
		Current Matrix for Player 1 (a)		Current Matrix for Player 2 (b)	

Strategies for V_a

Game Matrices for Various α . Use Table 6-3 as the Key. The Boxes Designate Thermodynamic Stability Points. The Circles are Game Theory Saddle Points.

$1 \frac{1}{4}$	$\frac{1}{2}$	- 1	$-\frac{1}{2}$
2	$1 \frac{1}{4}$	- 2	$-\frac{3}{2}$
$\frac{3}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	0
2	1	0	$\frac{1}{2}$

(i) $0 < \alpha = \frac{1}{2} < 1$

1	1	- 1	- 1
2	2	- 2	- 2
1	0	0	1
2	1	0	1

(ii) $\alpha = 1$

$1 \frac{1}{4}$	$2 \frac{1}{2}$	- 1	$-\frac{3}{2}$
2	$3 \frac{1}{4}$	- 2	$-2\frac{1}{2}$
$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	2
2	1	0	$\frac{3}{2}$

(iii) $1 < \alpha = 1.5 < 2$

2	5	- 1	- 2
2	5	- 2	- 3
0	- 1	1	3
2	1	0	2

(iv) $\alpha = 2$

Table 6-4 (cont'd)

5	13'	- 1	- 3
2	10	- 2	- 4
- 1	-2	2	5
2	1	0	3

(v) $\alpha = 3$ (and for all
 $\alpha > 2$)

is that the thermodynamic stability point has moved to (1, 4). The coalition linkage (R_1) has, however, remained in force.

Case (iv) represents another branch, or critical point, in the dissipation matrix which bridges the thermodynamic solutions at states (1, 4) and (2, 4). Finally, with case (v) ($\alpha > 2$) the thermodynamic and Game Theory solutions coincide (at 2, 4), and the coalition (through linkage R_1) has disappeared.

The question arises: Can we modify Game Theory so as to bring its solutions into coincidence with thermodynamic solutions for all cases? The root of the present disagreement is clear enough; the dissipative system is discriminating on the basis of a flow of power (voltage times current) at its terminals whereas the game players concern themselves only with commodity (current) flow.

Let us introduce into Game Theory a utility function which is analogous to the electrical power (delivered) and which for each player is represented by the product of a value (acquisitiveness measure) and a quantity (or current out) and let us conjecture that the total utility of the system must be at a stable mini-max configuration.

Now returning to our example, let utility \equiv power, value \equiv negative of the voltage (the more negative the voltage the more acquisitive is the player) and quantity (or amount of commodity) \equiv current out. Note that by our choice $V = 0$ for the environment its contribution to the total utility function is zero, (that is to say, it is a non-committal player) which is reasonable, if not essential. The total utility matrices are demonstrated in all five cases to be equal to the corresponding dissipation matrices, therefore having the same stable

saddle points. This equality arises from the well-known theorem of circuit theory to the effect that the joule heat (dissipation) is equal to the total power delivered to a system (Tellegen, 1952). Note that in case (v), Player B receives the most commodity from the system and he delivers the most power to the system. He is, therefore, the most "powerful" entrepreneur.

This analogy suggests that for games in which players have different values (acquisitive measures) and which are properly structured, coalitions will be spontaneously generated as in the thermodynamic model. Since elementary Game Theory does not adequately deal with either coalitions or utility, our analogy could serve as an embarkation point for major improvements in the economic discipline.

It is important to note the close connection between the two "critical points" (points of indecision) in the thermodynamic model of a three person game and the two "critical points" of a three level double lasing model, described in sections 4.6 and Fig. 4.17. This matter will be discussed further in section 6.8.

While we may be impressed by the foregoing analogies we still have to ask: Have they any physical significance? To the extent that our model is sufficiently inclusive of the properties of general dissipative processes, and we will assume that it is, then the answer is yes. We grant, of course, that both the thermodynamic electrical model and the Game Theory model of interacting systems have limitations. The resistive model dissipates essentially all of the available energy delivered from the environment, conserving only a small amount as organization of the network at the saddle point. In other words, it does not have sufficient

capacity for available energy storage (capital accumulation) within the system. The Game Theory model errs, on the other hand, by ignoring dissipation altogether, neglecting to note that "rational" thought, playing the game, extraction of available energy from the environment, formation of coalitions, the general turmoil of the market place and simple nourishment of the players contribute to dissipation and must be accounted for in a realistic economic model.

In forcing the Game Theory system into the thermodynamic framework through a particular definition of utility, we have corrected this limitation. We have also implicitly drawn attention to the fact that the "locus vivendi" of the game in the market place and the bodies and minds of the players need not, with the exception of a small organizational contribution or capital accumulation, be a storage place for available energy. What must be stored is the accumulation of commodities at the boundaries of the active system at the same potential at which they were gained in the games (see model with flow, section 4.8). This accumulation only becomes available energy if there are other entrepreneurs at more negative potentials (values) who are prepared to compete for energy from this source. Thus, the entrepreneur who has the "power" to accumulate commodities also has the power to deal them out.

Rational play in Game Theory is based on the utilization of available information. The deep connections between thermodynamics and the theory of games may not seem so surprising when we recall the views of Von Neumann (1966) on the development of a new theory of information:

"Thermodynamical concepts will probably enter into this new theory of information. There are strong indications that

information is similar to entropy and that degenerative processes of entropy are paralleled by degenerative processes in the processing of information. It is unlikely that you can define the function of an automaton, or its efficiency, without characterizing the milieu in which it works by means of statistical traits like the ones used to characterize a milieu in thermodynamics. The statistical variables of the automaton's milieu will, of course, be somewhat more involved than the standard thermodynamical variable of temperature, but they will probably be similar in character."

6.6 ECOLOGICAL COMPETITION AND THE RATE EQUATIONS FOR THE QUANTUM MODELS

It is widely recognized (Lotka, 1956; Samuelson, 1971; Goel et al, 1971; Volterra, 1928; etc.) that chemical rate equations of the form

$$\frac{dN_i}{dt} = \sum k_j N_j + \sum \gamma_{ij} N_i N_j \quad (6-3)$$

can be used to describe inter and (intra) species competition for biological populations. In these equations the N_i are the number of members of species i and the k_j and γ_{ij} are taken as constants. The k_j represent, for example, the birthrate or deathrates of a given competitive species and the γ_{ij} represent the rates at which species i feeds (positive) or is fed upon (negative) by the competing species j .

In ecology, species are grouped into trophic levels where the members of each level feed upon members of lower levels and in turn are fed upon by members of higher levels. The gross ecological efficiency between trophic levels has been determined to be of the order of 10 (Kormondy, 1969). Thus, if there is 100 calories of net plant production, we can expect 10 calories net production at each herbivore level and 1 calorie production at each carnivore level. Thus, the transfer of biomass from one trophic level to a higher trophic level is very inefficient. They are therefore significantly comparable to our quantum-models. For example, let us consider a generalization of the interacting system represented by Fig. 5.1. In this instance we see that one two level system feeds directly upon the radiant free energy and in turn surrenders a portion of its free energy to a secondary system. If we assume that

there is a third two level system, then we can draw the analogy that the primary system of the quantum model corresponds to the lowest level of an ecosystem, the photosynthetic primary producer; the second two level system represents the herbivore level and the third two level system represents the carnivore level. It follows from the character of the model discussed in Chapter 5 that under the biological requirement, where each interacting system couples strongly to the heat bath (such processes correspond to birth and death processes and decay processes), that for a significant population in level two of the third two level system a very large population in level two of the primary system is required (e.g., see equation 5-5). This is analogous to the pyramid effect in biological ecologies wherein a large primary population is required to support a much smaller secondary (or tertiary) population. It is therefore no coincidence that the Volterra-Lotka equations are of the same form as the quantum-based equations for population growth (e.g., equation 5-4).

In mathematical biology (Goel et al, 1971) it is conventional to represent the dissipation due to inter-species coupling by a quantity called the productivity ρ where

$$\rho = \frac{1}{2} \sum |\gamma_{ij}| N_i N_j \quad (6-4)$$

and the N_i are the number of members of each species. For present purposes we redefine these as biomass units, absorbing the constant factors into the γ 's.

This form suggests that the productivity can be associated with the interaction terms in the entropy production for the interacting

particle quantum models. We suggest (since we can associate the N_i with the P_i , the sum of both being conserved) from a further analogy with our model that a complete bio-thermal accounting would include the terms corresponding to self-organisation or relaxation into the heat bath as well as the above terms connected with the transfer of biomass (here, energy) between species.

We presume that the γ_{ij} and the k_j can be related uniquely to the transition probabilities in the quantum models and thus the correspondence can be made unique. Similarly, we can establish a relationship between the free energy of the model system and the biomass of the ecological system.

6.7 COMPARISON OF THE QUANTUM MODEL EVOLUTION WITH PRIGOGINE'S EVOLUTION CRITERION

Prigogine and his collaborators (e.g., section 2.4) have shown that for a large class of systems the time variation of the rate of change of that part of the entropy production which is due to changes in the forces alone is negative definite, becoming zero in the steady state. That is

$$\frac{d_X \sigma}{dt} = \sum_k J_k \frac{dX_k}{dt} \leq 0 \quad (6-5)$$

where the entropy production rate, σ , is the usual bilinear product of independent forces and fluxes. However, this result (6-5) depends upon the assumption that the Gibb's equation exists at each point in the system.

We establish in the following that a result of the form (6-5) is

valid for each of our level models independent of the values of the system variables.

Let us first consider the two and three level models which were discussed in section 4.5 and 4.6. For the two level model of Klein (1958), we can write the entropy production rate as

$$\dot{S}_i \equiv \sigma = NK_B \{ a(\alpha P_2 - P_1) \ln \alpha P_2 / P_1 + b(P_2 - P_1) \ln P_2 / P_1 \} \quad (6-6)$$

where we have identified the relaxation flux as $J_R = NK_B [a(\alpha P_2 - P_1)]$, the radiative diffusion flux as $J_D = NK_B [b(P_2 - P_1)]$ and the conjugate forces as $X_R = \ln(\alpha P_2 / P_1)$ and $X_J = \ln(P_2 / P_1)$. Evaluating (6-6) we obtain

$$\begin{aligned} (1/N) \frac{d_X \sigma}{dt} &= J_R \frac{dX_R}{dt} + J_D \frac{dX_D}{dt} \\ &= K_B \{ a(\alpha P_2 - P_1) \frac{d}{dt} [\ln(\alpha P_2 / P_1)] \\ &\quad + b(P_2 - P_1) \frac{d}{dt} [\ln(P_2 / P_1)] \} \quad (6-7) \end{aligned}$$

After simplification, using the equations of motion (equation 4-42), we obtain the result

$$(1/N) \frac{d_X \sigma}{dt} = - K_B \left\{ \frac{(\dot{P}_1)^2}{P_1} + \frac{(\dot{P}_2)^2}{P_2} \right\} \leq 0 \quad (6-8)$$

which is in precise agreement with Prigogine's result. An equivalent result for Klein's model has already been recognized by Li (1962 b).

If we repeat the analysis for the three level model we again obtain the result that

$$(1/N) \frac{d_X \sigma}{dt} = - K_B \left\{ \frac{(\dot{P}_1)^2}{P_1} + \frac{(\dot{P}_2)^2}{P_2} + \frac{(\dot{P}_3)^2}{P_3} \right\} \leq 0 \quad (6-9)$$

From a comparison of (6-8) and (6-9), generalization to multi-level models is trivial. It is important to realize that no additional assumptions have been used to calculate (6-8) and (6-9).

Similar results are also true for the non-linear Overhauser type models presented in section 5.4. In these instances, we have

$$(1/N) \frac{d_X \sigma}{dt} = - K_B \left\{ \frac{(P_1^N)^2}{P_1^N P_2^N} + \frac{(P_1^e)^2}{P_1^e P_2^e} - \frac{P_1^e P_1^N}{P_1^e P_2^e} \right\} \leq 0 \quad (6-10)$$

where the quantity in the brackets can be easily shown to be positive definite.

While initially it was a surprise to us that our highly non-linear models generated a behaviour which was identical to those based on strict adherence to the generalized Gibbs' equation (e.g., see section 2.4), we have now rationalized this on the basis that the Gibbs' relation for continuum systems (Prigogine, 1955) requires a local Gaussian distribution function for all fluctuation variables which is equivalent to a Maxwell-Boltzmann distribution among energy levels, or equivalently a good system

contact with the local heat bath. In the Prigogine continuum description this allows the thermodynamic forces (not the fluxes) to be expressed uniquely as a gradient of a local state variable, and the relaxation theorem follows directly therefrom. Clearly, our models are based on the same physical conditions.

6.8 THE QUANTUM MODELS AND SYMMETRY CHANGE

The fact that both of our three level quantum model and the Game Theory model undergo a type of phase transition has already been indicated. In this section we attempt to demonstrate that the transitions identified are kinetically equivalent.

Let us briefly recall the character of each type of phase transition. In the Game Theory model we saw that for particular relative values of the potentials V_a and V_b (i.e., of α^*) that the thermodynamic mini-max criterion does not produce a unique game strategy. In fact, when the system is at a critical point, or point of indecision, there are two equivalent strategies. Alternatively stated, a slight change in the values of the resistances or voltages forces the system to a unique stability point. Let us next consider the points of population inversion in the three level model (section 4.6). For the sake of argument, consider the point of population inversion occurring between levels 1 and 2. Here we can write the entropy production due to radiation induced diffusion, σ_R , as

* This is the α of section 6.5, not a Boltzmann factor.

$$\sigma_R = NK_B \{b(P_2 - P_1) \ln (P_2/P_1)\} \quad (6-11)$$

It is seen that

$$\frac{\partial \sigma_R}{\partial P_2} < 0 \quad \text{for} \quad P_2/P_1 < 1$$

and that

$$\frac{\partial \sigma_R}{\partial P_2} > 0 \quad \text{for} \quad P_2/P_1 > 1$$

(6-12)

and thus the behaviour of σ_R changes from minimal to maximal behaviour as the system passes through the inversion point ($P_2 = P_1$) which, therefore, represents a symmetry change in the systems performance. This is analogous to the shift in the stability point which occurs on the game matrix with its corresponding symmetry change. Naturally, similar results are true at the inversion point between levels 3 and 2.

Alternatively, we can view the population inversions in the three level model as optimal strategy changes for the overall system if we associate the free energies radiated to or from the three level pairs (P_1, P_3), (P_1, P_2) and (P_2, P_3) (i.e., $J_A = N\Delta\epsilon_{12}(P_1 - P_2) b_{12}$, etc.) with the utility functions (or powers) of the environment and the two players, respectively.

There is no point in carrying the analogies further because the two "games" actually have a different basic thermodynamic "graininess" and different constraints. We are confident, however, that a three person

game (or electrical model) could be invented which has a thermodynamic character identical with that of the quantum model, or vice-versa.

The main distinction between the two models has to do with the fact that one is continuous (fine-grained) while the other is discrete (coarse-grained). We conjecture that this distinction may be taken as the indicator for designating kinetic transitions as first and second order in close analogy with the phase transition designations of equilibrium thermodynamics. The coarse-grained or first order kinetic transitions are probably those identified by Prigogine and co-workers (1972) and by Kirkaldy (1965 a, b) involving a discrete branching of the kinetic paths and requiring a large fluctuation for transition between paths.

6.9 SOME FURTHER BIOLOGICAL RELATIONSHIPS

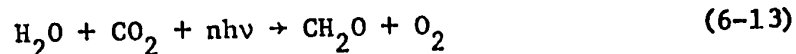
The foregoing demonstrated clearly that highly organised entities are completely consistent with the principles of thermodynamics. In our models we saw that self-organisation has to do with the ability of a system to absorb free energy from its surroundings (i.e., a radiation field), to store a proportion of this and deliver a further fraction to a reservoir (this energy can then be used later to drive other processes). In the absence of an external radiation field, all our systems would relax to thermal equilibrium and their minimum state of organisation, the free energy stored in the system being surrendered to the heat bath and lost. We saw that the free energy content of our systems and the entropy production normally increase with an increasing external radiation field.

Our most informative model of this behaviour is the two level model with flow (section 4.8) in the form applied to the eutectic reaction (section 6.4). In the spontaneous evolution up to the steady state, from an initially un-populated state, this system showed a simultaneous maximization of the free energy inflow, the free energy storage and the rate of entropy production. Indeed it has the precise character designated by Bertrand Russell (1927) as "chemical imperialism". It is therefore appropriate as a basis of discussion of biological systems. Consider, for example the growth of a tree from the seed. It extends its roots, branches and leaf systems to maximize the intake of free energy from the environment, thereby also increasing the reaction rate and dissipation, while at the same time increasing the stored free energy in its woody parts. Along some reaction paths involving fluid flow, chemical reaction and diffusion, it also succeeds in minimizing the entropy production by achieving dynamic efficiency (Prigogine and Wiame, 1946) of fluid transfer, etc. Clearly, its morphogenesis is strongly predicated upon the achievement of the mini-max stability point. Such behaviour is, of course, completely consistent with the free energy balance (equation 3-3) discussed in Chapter 3.

The ultimate source of biological free energy is the sun, the plants* being free energy transducers which fix the solar free energy. Through a photosynthetic process they utilize the free energy of the solar radiation to drive an uphill reaction which in simplified form

* e.g., green plants but there are also other kinds of energy fixers like bacteria.

(Blum, 1951) is



where the radiation (n quanta of energy $h\nu$) must supply an overall free energy of about 115 kg-cal/mole which is then stored as carbohydrate. (There is some current concensus that the physical process of radiation absorption gives rise to a free electron in an excited state which is then utilized later in chemical events.) The remainder of the biological system or ecosystem then feeds on the stored free energy.

If we apply equation (3-3) to the plant system, we interpret the inward flow of free energy as the solar radiation, the outward flow of free energy is that stored in the leaves and trunks and the dissipation is due to the fact that some energy is lost to the heat sink during the different physical and chemical phases of photosynthesis and plant growth, including, for example, the incorporation of the carbohydrates into the macroscopic storage structure.

It was also apparent from the models that a minimum radiation intensity was required before the system could gain a positive free energy*. This is due to the fact that the system is always trying to equilibrate with both the source of free energy (the radiation field) and the free energy

* Relative to our standard state with all particles in level 1 ($U = S = 0$). For biological systems which are analogous to the particular two level system being considered, the standard state is exactly equivalent.

sink (the heat bath). This competition between the two directions of relaxation gives rise to a system free energy which lies intermediate between a minimum value (equilibration with the heat sink) and a maximum value (equilibration with the radiation). Thus, for the free energy to exceed some positive value, the strength of the coupling to the energy source must be larger than some minimum value.

The competition between the two directions of relaxation processes also gives rise to the mini-max behaviour of the entropy production rate. For example, if we examine the two level model (section 4.5) we see that equilibration with the heat bath gives rise to a large entropy production due to the diffusion term (i.e., large $P_1 - P_2$) and a zero thermal relaxation term. However, for equilibration with the radiation source (i.e., large $P_1 - \alpha P_2$), the diffusion term is zero and the term due to thermal relaxation is a maximum. Naturally, an actual system has an intermediate stability state and for arbitrary initial conditions the rate of entropy production can increase or decrease as the system approaches the steady state.

6.10 CONCLUSIONS

We have noted that most modern workers in the thermodynamics of irreversible processes have regarded the tendency of the dissipation rate to maximize as a characteristic of no real significance, and have therefore tried to find an evolutionary criterion in which a related function exhibits purely minimal behaviour. In this contribution we have demonstrated that the maximal part of the general dissipation theorem, with its mini-max character, cannot be neglected and indeed that the maximal character of the dissipation rate is an essential determinant in the evolution of self-organisation in kinetic systems. Furthermore, we have identified boundary conditions for the three level, four level and two level model with flow where the evolutionary path was monotone increasing towards a maximum in the dissipation rate.

The mini-max character arises from an attempt by all kinetic systems to equilibrate simultaneously with the free energy source and the free energy sink. The ultimate steady states of such kinetic or viable systems lie intermediate between complete equilibration with the source or with the sink.

We have demonstrated that the mini-max principle for the entropy production rate is a useful tool for the description and elucidation of the behaviour of both animate and inanimate systems. In all cases, the maximal part of the dissipation rate plays a more significant part in the evolution of self-organisation than does the minimal part.

In the text we have summarized the detailed characteristics of our quantum models so we will not repeat them here. Rather, we record only the most important results:

(1) Both the rate of entropy production and the free energy show a mini-max character, the type of optimum for a given path depending on the precise initial state of the model system. This character can be attributed to the relative strengths of the competing relaxation processes.

(2) The evolutionary character of the force-dependent part of the entropy production rate for the models agrees with the earlier prescriptions of Prigogine and Li, namely

$$\frac{d \dot{X}_i}{dt} \leq 0.$$

(3) The multi-level models exhibit a "second order" kinetic transition which is exemplified by a population inversion, a reversal of one of the free energy flows and a simultaneous change in the symmetry of one of the terms in the system dissipation rate.

(4) Where systems have an internal degree of freedom, they can evolve within this degree of freedom so as to increase the store of free energy. This is often accompanied by an increase in the rate of entropy production.

(5) The two level model with flow, which is our best model of a biological system, is strongly imperialistic in the sense that the inflow of free energy, the organisation and the dissipation all increase in the spontaneous approach to the steady state and along a quasi-steady path which is defined by a monotone increase in the strength of the radiation field.

(6) All models are capable of acting as energy transducers creating high energy particles from low energy particles and incident radiation. In the presence of storage mechanisms they sustain a reservoir of high energy particles for use in a secondary system.

APPENDIX 1

SOLUTIONS FOR THE THREE LEVEL MODEL

The solutions for the general three level model (and thus also the restricted three level model) were found to be

$$P_1 = P_1^S + C_1^1 e^{\lambda+t} + C_1^2 e^{\lambda-t} \quad (1)$$

$$P_2 = P_2^S + C_2^1 e^{\lambda+t} + C_2^2 e^{\lambda-t} \quad (2)$$

and

$$P_3 = 1 - P_1 - P_2 \quad (3)$$

with

$$\lambda_{\pm} = \frac{-K_1 \pm \sqrt{K_1^2 - 4K_2}}{2} \quad (4)$$

where

$$K_1 = [(a_{12}\alpha_{12} + a_{12} + 2b_{12}) + (a_{23}\alpha_{23} + a_{23} + 2b_{23})$$

$$+ (a_{13}\alpha_{13} + a_{13} + 2b_{13})$$

$$\begin{aligned}
K_2 = & [(a_{12} + b_{12}) + (a_{13}\alpha_{13} + a_{13} + 2b_{13})][(a_{12}\alpha_{12} + b_{12}) \\
& + (a_{23}\alpha_{23} + a_{23} + 2b_{23})] - [(a_{12}\alpha_{12} + b_{12} - a_{13}\alpha_{13} - b_{13}) \\
& (a_{12} + b_{12} - a_{23}\alpha_{23} - b_{23})]
\end{aligned}$$

For this model the λ are real and negative and thus all solutions approach their steady values asymptotically.

We also have

$$\begin{aligned}
P_1^S = & [(a_{12}\alpha_{12} + b_{12})(a_{23}\alpha_{23} + b_{23}) \\
& + (a_{13}\alpha_{13} + b_{13})(a_{12}\alpha_{12} + b_{12} + a_{23} + b_{23})]/D \quad (5)
\end{aligned}$$

$$\begin{aligned}
P_2^S = & [(a_{12} + b_{12})(a_{13}\alpha_{13} + b_{13}) + (a_{23}\alpha_{23} + b_{23}) \\
& (a_{12} + b_{12} + a_{13} + b_{13})]/D \quad (6)
\end{aligned}$$

with

$$\begin{aligned}
D = & (a_{12} + b_{12} + a_{13} + b_{13})(a_{23}\alpha_{23} + a_{23} + 2b_{23}) \\
& + (a_{13}\alpha_{13} + a_{13} + 2b_{13} + a_{23}\alpha_{23} + b_{23})(a_{12}\alpha_{12} + b_{12}) \\
& + (a_{13}\alpha_{13} + b_{13})(a_{12} + b_{12} + a_{23} + b_{23})
\end{aligned}$$

where all the symbols a_{ij} , α_{ij} , b_{ij} were defined in Chapter 4.

The coefficients C_i^k are given by

$$C_1^1 = [y(P_1^0 - P_1^S) - (P_2^0 - P_2^S)]/(y - x) \quad (7)$$

$$C_1^2 = [-x(P_1^0 - P_1^S) + (P_2^0 - P_2^S)]/(y - x) \quad (8)$$

where P_1^0 , P_2^0 are the initial values of P_1 and P_2 , and

$$x = \frac{\lambda_+ - (a_{12} + b_{12} + a_{13}\alpha_{13} + a_{13} + 2b_{13})}{(a_{12}\alpha_{12} + b_{12} - a_{13}\alpha_{13} - b_{13})} \quad (9)$$

and

$$y = \frac{\lambda_- - (a_{12} + b_{12} + a_{13}\alpha_{13} + a_{13} + 2b_{13})}{(a_{12}\alpha_{12} + b_{12} - a_{13}\alpha_{13} - b_{13})} \quad (10)$$

The remaining coefficients are

$$C_2^1 = x C_1^1$$

(11)

and

$$C_2^2 = y C_1^2$$

APPENDIX 2

SOLUTIONS FOR THE TWO LEVEL MODEL WITH PARTICLE FLOW

The solutions for the equations governing the time evolution of the two level model with particle flow may be written in the form

$$n_1 = n_1^S + C_1^1 e^{\lambda_1 t} + C_1^2 e^{\lambda_2 t} + C_1^3 e^{\lambda_3 t} \quad (1)$$

$$n_2 = n_2^S + C_2^1 e^{\lambda_1 t} + C_2^2 e^{\lambda_2 t} + C_2^3 e^{\lambda_3 t} \quad (2)$$

$$n_3 = n_3^S + C_3^1 e^{\lambda_1 t} + C_3^2 e^{\lambda_2 t} + C_3^3 e^{\lambda_3 t} \quad (3)$$

where n_1^S , n_2^S , n_3^S are the steady state occupations presented in Chapter 4, the C_i^k are constants, the λ 's are the roots of the equation

$$\lambda^3 + K_1 \lambda^2 + K_2 \lambda + K_3 = 0 \quad (4)$$

with

$$K_1 = (a + b + \beta) + (a\alpha + b + \gamma_{23}) + (\gamma_{32})$$

$$\begin{aligned}
K_2 &= (a + b + \beta)(a\alpha + b + \gamma_{23}) + (a + b + \beta)(\gamma_{32}) \\
&+ (a\alpha + b + \gamma_{23})(\gamma_{32}) - (a\alpha + b)(a + b) \\
&- (\gamma_{23})(\gamma_{32})
\end{aligned}$$

and

$$\begin{aligned}
K_3 &= (a + b + \beta)(a\alpha + b + \gamma_{23})(\gamma_{32}) \\
&- (a\alpha + b)(a + b)(\gamma_{32}) - (a + b + \beta)(\gamma_{23}\gamma_{32})
\end{aligned}$$

The constants C_1^k can all be expressed in terms of C_1^k in the following fashion

$$\begin{aligned}
C_2^1 &= C_1^1 \left[+ \frac{\lambda_1 + (a + b + \beta)}{a\alpha + b} \right] \equiv C_1^1 W_1 \\
C_2^2 &= C_1^2 \left[\frac{\lambda_2 + (a + b + \beta)}{a\alpha + b} \right] \equiv C_1^2 W_2 \\
C_2^3 &= C_1^3 \left[\frac{\lambda_3 + (a + b + \beta)}{a\alpha + b} \right] \equiv C_1^3 W_3
\end{aligned} \tag{5}$$

and

$$c_3^1 = c_2^1 \left[\frac{\gamma_{23}}{\lambda_1 + \gamma_{32}} \right] \equiv c_2^1 z_1$$

$$c_3^2 = c_2^2 \left[\frac{\gamma_{23}}{\lambda_2 + \gamma_{32}} \right] \equiv c_2^2 z_2 \quad (6)$$

$$c_3^3 = c_2^3 \left[\frac{\gamma_{23}}{\lambda_3 + \gamma_{32}} \right] \equiv c_2^3 z_3$$

The C_1^k may in turn be expressed in terms of the steady state occupations n_i^S and the initial occupations n_i^0 as

$$\begin{aligned} c_1^1 = & [(n_1^0 - n_1^S) W_2 W_3 (Z_3 - Z_2) + (n_2^0 - n_2^S) (Z_2 W_2 - Z_3 W_3) \\ & + (n_3^0 - n_3^S) (W_3 - W_2)] / D \end{aligned} \quad (7)$$

$$\begin{aligned} c_1^2 = & [(n_1^0 - n_1^S) W_1 W_3 (Z_1 - Z_3) + (n_2^0 - n_2^S) (Z_3 W_3 - Z_1 W_1) \\ & + (n_3^0 - n_3^S) (W_1 - W_3)] / D \end{aligned} \quad (8)$$

$$\begin{aligned} c_1^3 = & [(n_1^0 - n_1^S) W_1 W_2 (Z_2 - Z_1) + (n_2^0 - n_2^S) (Z_1 W_1 - Z_2 W_2) \\ & + (n_3^0 - n_3^S) (W_2 - W_1)] / D \end{aligned} \quad (9)$$

with

$$D = Z_1 (W_1 W_3 - W_1 W_3) + Z_2 (W_1 W_2 - W_2 W_3) + Z_3 (W_2 W_3 - W_1 W_3)$$

It should be mentioned that all the λ are real and negative and thus the solutions approach the final steady state asymptotically.

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