MOLECULAR EQUILIBRIUM IN STARS

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RESUMEN. Se presenta una revisión de los métodos de estudio del equilibrio molecular en condiciones estelares. Todas las constantes de equilibrio para las moléculas diatómicas y triatómicas se expresan en términos de constantes espectroscópicas, permitiendo tomar en cuenta totalmente la variación isotópica. Delineamos los procedimientos numéricos para la solución de las ecuaciones de las concentraciones en equilibrio de un número arbitrario de elementos (incluyendo iones) y moléculas.

ABSTRACT. A review is given of the methods for the study of molecular equilibrium under stellar conditions. All the equilibrium constants for diatomic and triatomic molecules are given in terms of spectroscopic constants, allowing full account to be taken of isotopic variation. Numerical procedures are outlined for the solution of the equations for the equilibrium concentrations of an arbitrary number of elements (including ions) and molecules.

Key words: EQUATION OF STATE – STARS: ATMOSPHERES

1. INTRODUCTION

Perhaps the earliest recognition of the presence and significance of molecules in stars is that of Secchi who in 1867 classified stellar spectra into four categories: blue-white stars with few metallic lines; yellow (solar type) stars with many metallic lines; orange-red stars with molecular bands shaded to the red; and ruby-red stars with molecular bands shaded to the violet. The shading or degrading of the molecular bands, and used by Secchi as a classification criterion, can be traced to the sign of the coefficient of the quadratic term in the formula

$$\bar{\nu}_m = \bar{\nu}_0 + am + bm^2$$

for the location in wavenumber $\bar{\nu}_m$ of the lines of a diatomic molecular band as a function of the ordinal position m. The coefficient b is given by

$$b = B_u - B_l$$

where B_u and B_l are the rotational constants for the upper (u) and lower (l) electronic levels with

$$B = h/(8\pi^2 cI) \quad and \quad I = \mu r^2$$

where I is the moment of inertia, μ is the reduced mass and r is the internuclear separation which varies with the electronic level. The sign of the coefficient b thus depends on the relative values of B (and therefore r) for the two levels associated with a band. Specifically, for shading to the red $b > 0$ (i.e., $B_u > B_l$ or $r_u < r_l$) and for shading to the violet $b < 0$ (i.e., $B_u < B_l$ or $r_u > r_l$). However, the direction of shading is not the same for all band systems of the same molecule so that it is imprecise as a basis of classification. In the Harvard classification of stellar spectra, molecular bands are recognised in classes G (CH, CN), classes K/M/S (TiO, ZrO) and classes R/N (C_2, CH, CN). A particular feature of the Harvard classification is the branching and

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overlap which occurs for the later spectral classes. Both the Secchi and the Harvard classifications naturally exhibit the strong correlation with stellar temperature.

In parallel with the rapid developments in the theory of molecular structure, spectra and equilibrium, quantitative studies of the abundances of molecules in stars have been made by many workers. Following the earlier studies of Atkinson (1922), Wildt (1929), Russell (1932) and others, a fairly comprehensive account of molecular equilibrium in stars was given by Rosseland (1936). The work of Russell dealt mainly with diatomic molecules but did also include the triatomic molecules H_2O and CO_2. Later work has extended the study of molecular equilibrium in stars to include polyatomic molecules as well as to the influence of molecules in the hydrostatic and radiative structure of the stellar atmospheres. The extensive work of Fujita and Tsuji (see Fujita 1970 for references from 1935) has helped to elucidate the branching of the classification of the spectra of cool stars as primarily a phenomenon relating to the relative abundances of the elements C, N and O. The modelling of the atmospheres and emergent spectra of cool stars has demanded a more detailed knowledge of the thermal and radiative properties of molecules. Monochromatic and mean opacities for stellar atmospheres including molecular absorption have been studied by Gaustad (1963), Auman and Bodenheimer (1967), Tsuji (1966, 1971), Alexander (1975), Alexander *et al.* (1983) and Carson and Sharp (1991). The study of molecular equilibrium is a prerequisite for all aspects of molecular physics involving the equation of state, heat capacity, and radiative transfer.

2. CHEMICAL EQUILIBRIUM

Chemistry relates to the making and breaking of molecular bonds. The simplest case may be represented by the chemical reaction expressed in the form

$$A + B = AB .$$
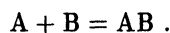
Each such reaction process may proceed in the forward (left to right) or the backward (right to left) directions, in competition for the reagents A, B and AB. If the rate of the forward reaction equals the rate of the backward reaction both reactions will have apparently ceased, and a dynamical balance or chemical equilibrium will have been established.

2.1. Reaction Rate and Equilibrium Constant

A major key to the understanding of chemical equilibrium is provided by the Law of Mass Action (1864) of Guldberg and Waage, which states that the rate at which a chemical reaction proceeds is directly proportional to the concentrations of all the reagents at the time. Other factors can also affect the rate, e.g., temperature, pressure and physical state. Thus if we express the concentration by number density and denote by n_A, n_B and n_{AB} the number densities of A, B and AB respectively, the forward rate $\mathcal{N}_f$ and the backward rate $\mathcal{N}_b$ may then be written

$$\mathcal{N}_f = k_f n_A n_B \text{ and } \mathcal{N}_b = k_b n_{AB}$$

where k_f and k_b are the constants of proportionality or rate coefficients required by the Law of Mass Action. For equilibrium we then require $\mathcal{N}_f = \mathcal{N}_b$ which yields the condition

$$n_A n_B / n_{AB} = k_b / k_f = K_n$$

where K_n is now the *equilibrium constant*. A more general kind of chemical reaction between the reagents R_i may be expressed in the form

$$\nu_1 R_1 + \nu_2 R_2 + \nu_3 R_3 + \ldots = \sum_i \nu_i R_i = 0$$

wherein the stoichiometric coefficients ν_i are positive or negative integers which are the numbers of each of the reagents taking part. The equilibrium condition is now

$$\prod_i n_i^{\nu_i} = K_n \quad \text{or} \quad \sum_i \nu_i \ln n_i = \ln K_n .$$

If we use the partial pressures p_i instead of the number densities n_i to represent the concentrations, the equilibrium condition takes the form

$$\prod_i p_i^{\nu_i} = K_p \quad \text{or} \quad \sum_i \nu_i \ln p_i = \ln K_p$$

which with the correspondence $p_i = n_i kT$ gives

$$K_p = (kT)^\nu K_n \quad \text{or} \quad \ln K_p = \ln K_n + \nu \ln(kT) \quad \text{with} \quad \nu = \sum_i \nu_i .$$

A further alternative form is obtained by introducing for the concentrations

$$c_i = n_i/n = p_i/p \quad \text{where} \quad n = \sum_i n_i \quad \text{and} \quad p = \sum_i p_i$$

giving

$$\ln K_c = \ln K_n - \nu \ln n = \ln K_p - \nu \ln p .$$

The above relations do not of course serve to determine the rate coefficients k_f and k_b, or indeed the equilibrium constants K_n, K_p and K_c, which all depend on the physical conditions. Furthermore, any change of the physical conditions will alter the forward and backward reaction rate coefficients, but necessarily in different ways. Thus the equilibrium constant will be altered and the equilibrium concentrations will be shifted in that direction in which the rate coefficient is enhanced relative to that in the other direction.

2.2. Thermodynamics

From the point of view of thermodynamics, in a system consisting of a mixture of substances R_i whose amounts are not fixed but may vary (due to addition, removal or chemical reactions), the state of the system cannot be completely specified by two of the state variables T, V, P, E, S but require also the specification of the amounts N_i. Changes in the system, including changes in the N_i, must be subject to the laws of thermodynamics including the relation

$$dQ = TdS = dE + PdV - \sum_i \mu_i dN_i$$

where the chemical potentials μ_i are given by

$$\mu_i = (\partial E/\partial N_i)_{S,V} = -T(\partial S/\partial N_i)_{V,E} = P(\partial V/\partial N_i)_{E,S} .$$

Defining the Helmholtz free energy F and the Gibbs free energy G by the relations

$$F = E - TS \quad \text{with} \quad dF = -PdV - SdT + \sum_i \mu_i dN_i$$

and

$$G = F + PV \quad \text{with} \quad dG = +VdP - SdT + \sum_i \mu_i dN_i$$

thermodynamic equilibrium requires that, at constant T and V, F is a minimum so that

$$dF = \sum_i \mu_i dN_i = 0 \quad \text{and} \quad \mu_i = (\partial F/\partial N_i)_{T,V}$$

while, at constant T and P, G is a minimum so that

$$dG = \sum_i \mu_i dN_i = 0 \text{ and } \mu_i = (\partial G/\partial N_i)_{T,P} .$$

Now the equation representing the reaction, namely,

$$\sum_i \nu_i R_i = 0$$

implies that

$$dN_i/\nu_i = C(\text{constant})$$

and the equilibrium condition becomes

$$\sum_i \nu_i \mu_i = 0 .$$

If F and G and thus the chemical potentials μ_i can be evaluated then the equilibrium condition effectively determines the equilibrium constant. The classical approach used empirical specific heats for the evaluation of E, S, F and G, and thence the equilibrium constants (see, for example, Herzberg, 1945).

2.3. Statistical Mechanics

In the statistical mechanical formulation of thermodynamics a key role is played by the partition function

$$Z = \sum_n g_n \exp(-E_n/kT)$$

where the g_n and E_n are the statistical weights and the energy levels for the ensemble. As long as the individual members of the ensemble are independent we may write

$$Z = \prod_i Z_i \text{ or } \ln Z = \sum_i \ln Z_i$$

where Z_i is the partition function for the component consisting of N_i members and is given by

$$Z_i = z_i^{N_i}/N_i!$$

in which z_i is the individual member partition function. Using Stirling's approximation ($\ln n! = n \ln n - n$) we then have

$$\ln Z_i = N_i \ln(ez_i/N_i) .$$

In terms of the partition function the Helmholtz free energy is given by

$$F = -kT \ln Z = -kT \sum_i \ln Z_i = -kT \sum_i N_i \ln(ez_i/N_i)$$

so that we now obtain for the chemical potential

$$\mu_i = (\partial F/\partial N_i)_{T,V} = -kT \ln(z_i/N_i)$$

provided the z_i are independent of the N_i. Thus we have

$$\sum_i \nu_i \mu_i = -kT \sum_i \nu_i \ln(z_i/N_i) = 0$$

giving

$$\prod_i N_i^{\nu_i} = \prod_i z_i^{\nu_i} \text{ or } \prod_i n_i^{\nu_i} = K_n = \prod_i (z_i/V)^{\nu_i}$$

as the condition for chemical equilibrium. We may now expand z_i as a product of internal and external partition functions

$$z_i = z_{i,in} z_{i,ex}$$

with

$$z_{i,in} = \sum_j g_{ij} \exp(-E_{ij}/kT)$$

where now the g_{ij} and E_{ij} refer to the internal energy levels of the member and

$$z_{i,ex} = V(2\pi m_i kT/\hbar^2)^{3/2} = V G_i$$

where m_i is the mass. We now obtain

$$K_n = \prod_i n_i^{\nu_i} = \prod_i (G_i z_{i,in})^{\nu_i} .$$

Finally, referring all the E_{ij} to their respective ground levels E_{i1} and introducing the heat of reaction H defined by

$$H = \sum_i \nu_i E_{i1}$$

the equilibrium constant takes its more familiar form

$$K_n = \prod_i (G_i z_{i,in})^{\nu_i} \exp(-H/kT) .$$

3. DISSOCIATION AND IONIZATION EQUILIBRIUM

The theory outlined above applies equally well to the dissociation of molecules and to the ionization of atoms (or ions). For the diatomic process A + B = AB the equilibrium condition is $\mu_{AB} = \mu_A + \mu_B$ or

$$K_n(AB) = n_A n_B / n_{AB} = (z_A z_B / z_{AB})(2\pi m kT/\hbar^2)^{3/2} \exp(-D_{AB}/kT)$$

where now z denotes only the internal partition function, D_{AB} is the dissociation energy, and m is the reduced mass

$$m = m_A m_B / m_{AB} = m_A m_B / (m_A + m_B) .$$

Similarly, for the triatomic process A + B + C = ABC the equilibrium condition is $\mu_{ABC} = \mu_A + \mu_B + \mu_C$ or

$$K_n(ABC) = n_A n_B n_C / n_{ABC} = (z_A z_B z_C / z_{ABC})(2\pi m kT/\hbar^2)^3 \exp(-D_{ABC}/kT)$$

where now D_{ABC} is the dissociation energy, and m is the reduced mass given by

$$m^2 = m_A m_B m_C / m_{ABC} = m_A m_B m_C / (m_A + m_B + m_C) .$$

Likewise for the ionization process A = A$^+$ + e$^-$ the equilibrium condition is $\mu_A = \mu_{A^+} + \mu_{e^-}$ or

$$K_n(A) = n_{A^+} n_{e^-} / n_A = (z_{A^+} z_{e^-} / z_A)(2\pi m kT/\hbar^2)^{3/2} \exp(-I/kT)$$

where I is the ionization energy and m is the reduced mass

$$m = m_{A^+} m_{e^-} / m_A = m_{A^+} m_{e^-} / (m_{A^+} + m_{e^-}) \approx m_{e^-} .$$

The latter form of the ionization equilibrium equation is usually referred to as the Saha formula. For a more general discussion including electron degeneracy see Carson (1985).

3.1. Partition Functions

3.1.1. Particles

For particles such as electrons or protons, or atomic nuclei which can be treated as particles, the internal partition function is simply the spin degeneracy

$$z_{in} = g_s = 2s + 1$$

where s is the spin quantum number.

3.1.2. Atoms and Ions

At the stellar temperatures and densities where molecules are abundant, negative atomic ions, for example, H^-, are also formed, although their abundances are limited by their low electron affinities coupled with a usually low free-electron density. For such ions the number of bound electronic levels is finite and small, so that the partition function sum can be readily evaluated (in the case of only one bound level the sum reduces to the statistical weight of the level). For isolated neutral atoms (and where appropriate positive ions), because of the Coulomb nature of the field at large distances, the number of bound levels is infinite. For such systems the partition function has to be evaluated with due regard to the presence of other systems in a real physical situation. All the techniques for accomplishing this are equivalent to the introduction of a convergence factor $P(n)$ multiplying each term of the partition function sum

$$z = \sum_n g_n P(n) \exp(-E_n/kT) \; .$$

The simplest choice of $P(n)$ is a step function

$$P(n) = 1 \text{ for } n \le n_{max} \text{ and } P(n) = 0 \text{ for } n > n_{max}$$

which applies a cut-off at some $n = n_{max}$ determined by, for example, the requirement that orbital radius is limited by the nearest neighbour distance. A disadvantage of this procedure is that it results in a partition function which is a discontinuous function of the physical variables. An alternative, and more satisfactory, choice for $P(n)$ is a continuous function which represents a probability that the level n contributes a term to the sum. Two, only apparently different, ways of viewing this procedure consider $P(n)$ as a factor modifying *either* the level degeneracy (Carson and Hollingsworth, 1968) *or* the occupation probability first introduced by Claas (1949) and recently re-used by Hummer and Mihalas (1988). If n is the principal quantum number so that g_n is proportional to n^2, then for convergence P_n must decrease more rapidly than n^{-3}. Assuming that the orbital radius r_n is also proportional to n^2, the nearest neighbour probability gives

$$P(n) = \exp(-an^6)$$

where a is a constant related to the nearest neighbour distance. Numerical experiments show that the discontinuous and the continuous probability procedures, when used consistently, do lead to very similar results, at high temperature and low density.

3.1.3. Molecules

The determination of molecular partition functions is conditioned by the complexity of molecular energy levels, and we will here only outline the essential features. Assuming that the molecular energy levels—electronic,

vibrational and rotational—are independent and therefore additive, the internal molecular partition function can be written as a product of electronic, vibrational and rotational factors

$$z = z_e z_v z_r .$$

For stable molecules the number of bound electronic levels is finite and the electronic partition function can be easily evaluated given the energy levels E_n and the statistical weights

$$g_n = 2(2S_n + 1)/(1 + \delta_0^{\Lambda_n})$$

for levels characterized by the spin and electronic quantum numbers S and Λ. The potential well of each bound electronic level only supports a finite number of vibrational energy levels. The energies are given by

$$E_v(v)/hc = \omega_e(v + 1/2) - \omega_e x_e(v + 1/2)^2 + \omega_e y_e(v + 1/2)^3 + \dots$$

where v is the vibrational quantum number and ω_e, x_e, and y_e are constants. In the harmonic approximation the vibrational partition function is

$$z_v(\omega_e) = \sum_v g_v \exp(-E_v/kT) \approx \{1 - \exp(-hc\omega_e/kT)\}^{-1}$$

with modifications when anharmonic terms are included. For a triatomic molecule with three normal modes with wavenumbers ω_i and degeneracies d_i, to the same approximation the vibrational partition function is

$$z_v(\{\omega_i\}) = \prod_i \{z_v(\omega_i)\}^{d_i} = \prod_i \{1 - \exp(-hc\omega_i/kT)\}^{-d_i} .$$

The rotational levels may be represented by the formula

$$E_r(J)/hc = BJ(J + 1) - D\{J(J + 1)\}^2 + \dots$$

where J is the rotational quantum number and B and D are the rotational constants. The rotational partition function, in the rigid rotator approximation, is given by

$$z_r(B) = \sum_J g_J \exp(-E_J/kT) \approx \int (2J + 1) \exp(-E_J/kT) dJ \approx kT/hcB$$

which is accurate to quite low temperatures. Asymptotic expansions, including also the non-rigid terms in the energy, have been developed for greater accuracy. For a triatomic molecule with three principal moments of inertia I_A, I_B, I_C and corresponding rotational constants A, B, C the rotational partition function, in the rigid rotator approximation, is

$$z_r(A, B, C) \approx \{\pi(kT/hc)^3/(ABC)\}^{1/2} \exp\{-Bhc/(4kT)\}$$

with suitable substitutions for the asymmetric top, symmetric top and spherical top cases. When account is taken of the possible identity of nuclei in symmetric locations, the rotational partition function must be divided by the symmetry number σ which depends on the symmetry group of the molecule. For two such identical nuclei in diatomic molecules and triatomic molecules $\sigma = 2$. For the rare case of three identical nuclei in a triatomic molecule in an equilateral configuration (for example, H_3^+) $\sigma = 6$.

3.1.4. Isotopes

The above theory is readily generalized to include the possibility that each atom may be present in the form of more than one isotope. Atomic energy levels and partition functions are subject to a very small nuclear

mass effect which may be ignored in the ionization equilibrium. However, since molecular energy levels, particularly the vibrational and rotational levels, are functions of the masses of the atoms involved, these and the associated partition functions and equilibrium constants must be calculated separately for each isotopic molecule. To sufficient approximation it may be assumed that all molecular internuclear separations and force constants are invariant under isotopic substitution. Thus, if the spectroscopic constants are available for only one isotopic variant, they may be calculated for all other isotopic variants. One particular aspect of isotopic substitution in molecules is the change in the dissociation energy, as measured from the lowest vibrational level, which has the consequence of energetically favouring the equilibrium abundance of heavier isotopic molecules.

3.1.5. Interactions

Interactions between the members of an assembly may be included through additional terms in the partition functions. In the general case, the internal partition functions now become functions of the number densities, thus effectively introducing additional terms in the free energies (Graboske *et al.* 1969, 1971; Fontaine *et al.* 1977; Carson, 1985; Hummer and Mihalas, 1988).

3.2. Solution of the Equilibrium Equations

For each ionization or dissociation reaction there corresponds an equation of equilibrium, each equation linking the concentrations of one or more compounds with their constituent elements. In the context of ionization equilibrium the terms 'compounds' and 'elements' pertain equally well to the various ions considered as compounds of nuclei and electrons considered as elements. To fully determine the equilibrium concentrations of $\mathcal{N}_e$ elements and $\mathcal{N}_c$ compounds requires a total of $(\mathcal{N}_e + \mathcal{N}_c)$ relations. Of these $\mathcal{N}_e$ relations are provided by the conservation of the number of each element, leaving $\mathcal{N}_c$ relations to be specified from exactly $\mathcal{N}_c$ equilibrium conditions involving the $\mathcal{N}_c$ compounds. When account is taken of isotopes, each is treated as a distinct 'element' or 'compound' with its own conservation or equilibrium condition. Note that there may be more than one compound involved in any given equilibrium relation, provided that overall each compound appears at least once. Redefining n_i as the number density of each element i which is free (not in a compound), and N_i as the total number density of the same element (i) (both bound in compounds and free), the conservation of the element requires

$$N_i = n_i + \sum_c \nu_{ic} n_c$$

where n_c is the number density of the compound (c), ν_{ic} is the number of times the element (i) appears in the compound (c), and the sum is taken over all compounds. Using the $\mathcal{N}_c$ equilibrium relations to eliminate the n_c from each of the $\mathcal{N}_e$ conservation equations then gives $\mathcal{N}_e$ relations between the $\mathcal{N}_e$ concentrations n_i. The resulting simultaneous non-linear equations may be solved by iterated substitution or linearization from a trial solution. Thus by specifying the temperature T and the composition by the N_i, the equilibrium concentrations of all elements and compounds can be determined.

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