

## Molecular Abundances in Stellar Atmospheres. II.

T. Tsuji\*

Observatoire de Paris-Meudon

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**Summary.** Chemical equilibria of 36 elements are solved for the physical conditions of cool stellar atmospheres. It is found that the molecular species formed (monoxide, dioxide, halide etc.) and the degree of molecular association, (i.e. the fraction of atoms locked in molecules) are well correlated with the position of each element (both Group and atomic weight) in the periodic table.

In the atmospheres of carbon-rich stars, molecular formation is generally less important than in oxygen-rich atmospheres except for some carbon compounds. The metal oxides in oxygen-rich atmospheres are

generally replaced by metal carbides, especially by dicarbides, in carbon-rich atmospheres. The formation of carbides in carbon-rich atmospheres, however, is less effective than that of the corresponding metal oxides in oxygen-rich atmospheres. In carbon stars, it is shown that the Si/S ratio plays a critical role just like the C/O ratio.

**Key words:** equilibrium constants — chemical equilibrium — molecular abundance — atmospheres of cool stars

### I. Introduction

The theoretical study of the atmospheres of cool stars began with the study of dissociative equilibria in stars (e.g. Russell, 1934; Fujita, 1939, 1940, 1941; Swings, 1958). The problem of chemical equilibria in stellar atmospheres is still one of the basic obstacles to our understanding the atmospheres of cool stars. In recent years, with the improvements in thermochemical data, the problem has further been studied by many authors from different points of view. In a previous paper, we studied the role of polyatomic molecules in stellar atmospheres for various values of H, C, N, O ratios (Tsuji, 1964; hereafter referred to as Paper I). In that study, however, we mainly discussed the dissociative equilibrium of molecules composed of H, C, N and O, but the theory of compounds including other elements has been limited to the evaluation of some of the equilibrium constants. Though several authors (e.g. Dolan, 1965; Vardya 1966a; Morris and Wyller, 1967) have included other elements in their studies, the elements considered so far have been limited to the relatively abundant ones. For a detailed analysis and interpretation of the spectra of cool stars, it is desirable to have a more thorough analysis of the chemical equilibria of other elements.

The atmospheres of cool stars are complicated systems of chemical equilibria in which about a hundred elements are mixed and there are many possible chemical reactions to form molecules. It is of course

interesting to see what kinds of molecules are formed but the more fundamental problem is to determine the equilibrium partial pressure of the free neutral atom for each element. This partial pressure is usually determined by several species that consume large amounts of the element and these species are referred to as the major species for the element. Such major species can be known by intuition in a simple case, but generally they depend on temperature, gas pressure and chemical composition, and may be determined only by solving the chemical equilibrium, considering all the species which may be important. This analysis is vital since, if any major species is omitted in the equilibrium computation, the resulting equilibrium composition is not correct at all. For this reason, we have made a careful survey of the compounds to be included in the equilibria, in order to obtain a general view of the major species of each element.

Once the equilibrium partial pressure for each element is known, the determination of the abundance of any molecule is straightforward. Also, detailed analysis of the chemical equilibrium for each element is important not only for determining the molecular abundance but also for the analysis of atomic line spectra and the determination of the elemental abundances of cool stars. The degree of molecular association, i.e. the fraction of atoms that are locked in molecules, is determined by the coupled chemical equilibria for many elements. It is expected, however, that the degree of molecular association is related to the chemical prop-

\* On leave of absence from Department of Astronomy, University of Tokyo.

erties of the elements in the periodic table, and one of the purposes of the present study is to clarify this relationship for selected representative elements.

## II. The Equilibrium Constant and the Thermochemical Data

We assume that the stellar atmosphere is in local thermodynamical equilibrium, and that the chemical equilibrium at each point in a stellar atmosphere can be treated as that of an ideal gas at constant pressure and temperature. We consider a gaseous reaction in which a molecule  $X_l Y_m Z_n$  is formed from its constituent free atoms  $X$ ,  $Y$  and  $Z$ :



For this reaction, the equilibrium constant  $K_p$  can be defined by

$$K_p = \frac{P_X^l P_Y^m P_Z^n}{P_{X_l Y_m Z_n}}, \quad (2)$$

where  $P_X$ ,  $P_Y$ ,  $P_Z$ , and  $P_{X_l Y_m Z_n}$  are the partial pressures of  $X$ ,  $Y$ ,  $Z$ , and  $X_l Y_m Z_n$  respectively. The equilibrium constant,  $K_p$ , can be calculated from

$$\begin{aligned} \ln K_p = & l \left[ -\frac{F^0 - H_0^0}{RT} \right]_X + m \left[ -\frac{F^0 - H_0^0}{RT} \right]_Y \\ & + n \left[ -\frac{F^0 - H_0^0}{RT} \right]_Z - \left[ -\frac{F^0 - H_0^0}{RT} \right]_{X_l Y_m Z_n} \\ & - \frac{\Delta H_0^0(X_l Y_m Z_n)}{RT}, \end{aligned} \quad (3)$$

where  $\Delta H_0^0(X_l Y_m Z_n)$  is the heat of atomization of  $X_l Y_m Z_n$  and  $[-(F^0 - H_0^0)/RT]$ 's are the free energy functions.

The most important molecular data in calculating the equilibrium constant is the heat of atomization or the dissociation energy. The heats of atomization adopted in the present study are summarized in Table 1. Some of these data were extensively discussed in a monograph by Gaydon (1968) and in compilations by Chao *et al.* (1965–1968). For these species, we refer only to one of these reviews, and in general not to the original literature. When the values adopted in these two sources differ, we adopt the one which seems to be based on well-founded experimental data. Sometimes, it was difficult to judge which was the better, both values being based on Birge-Sponer extrapolation which does not give an unique solution, or being estimated by analogy with a similar bonding. In such cases, we use a mean value, and we refer to both sources. For more recent data and for species not covered by these reviews, we refer to the original literature. Moreover, the heats of atomization of some of the important molecules had to be estimated. We comment on these cases below.

For calculating the free-energy functions, it is also necessary to have structural data of the molecular species. Such data are available in several compilations (e.g. Herzberg, 1945, 1967; McBride *et al.*, 1963; Chao *et al.*, 1965–1968), or in the literature cited in Table 1. If no such data are available, they are estimated: bond distances are estimated by analogy with similar bonding, vibrational frequencies are calculated by the valence force model with force constants estimated by analogy with similar bonding, and electronic multiplicities are assumed to be the same as those of the similar electronic configuration.

*Molecules Composed of H, C, N and O.* The dissociation energies for these species are discussed in Paper I and we rediscuss only CN. The dissociation energy of CN has long been at issue, and values of 7.5, 7.9 and 8.2 eV have been suggested. In paper I, we adopted the highest value. Gaydon (1968) has reviewed the problem in detail and has shown that the situation is still confusing. He was finally led to favour an intermediate value and recommended  $D(C-N) = 7.75 \pm 0.2$  eV (178 kcal/mol). Recently, Dibeler and Liston (1968) have indicated  $D(C-N) = 7.9$  eV (182.5 kcal/mol). They cited several other experimental results that agree with their own and also remarked that any systematic errors in their analysis will lead to their value being a lower limit to the true value. Accordingly, we use the value of  $D(C-N) = 7.9$  eV (182 kcal/mol) in the present study.

Other species for which the heats of atomization should be revised more than 0.05 eV from the values adopted in Paper I are the following:

NH (88 kcal/mol  $\rightarrow$  74 kcal/mol),

C<sub>2</sub>H (273 kcal/mol  $\rightarrow$  278 kcal/mol),

and C<sub>2</sub>N (329 kcal/mol  $\rightarrow$  320 kcal/mol).

For the other species composed of H, C, N and O, the dissociation energies adopted in Paper I are essentially unchanged. Equilibrium constants, however, are all recalculated based on new thermochemical data, if available, and on the new definition of the equilibrium constant given by Eq. (2). In paper I, the equilibrium constant was defined for a binary reaction, whilst, in the present study, it is defined for the formation of molecules from gaseous, neutral atoms. The two definitions give identical values only for diatomic molecules.

*Hydrides.* For most metallic hydrides, dissociation energies were taken from Gaydon (1968). They have mostly been determined by the Birge-Sponer extrapolation and by predissociation.

*Carbides.* From laboratory work, little is known about gaseous metal monocarbides. Gaydon (1968) has cited an upper limit to  $D(\text{Ti}-\text{C})$  of 5.75 eV. This value is based on a mass spectrometric study by Chupka *et al.* (1958) who have pointed out that the intensity peak

corresponding to TiC (mass number of 60) is extremely weak and that no positive identification of TiC could be made. On the contrary, recent studies have revealed that gaseous dicarbides ( $\text{MC}_2$ ) or tetracarbidides ( $\text{MC}_4$ ) are the most stable species in carbon-metal systems (e.g. De Maria *et al.*, 1965; Stearns and Kohl, 1970; other work cited in Table 1). The predominance of dicarbides has been explained by the high electron affinity of the  $\text{C}_2$  radical as compared with either C or  $\text{C}_3$ . Furthermore, it has been shown that  $\text{M}-\text{C}_2$  bond energies are well correlated with  $\text{M}-\text{O}$  bond energies, and, generally,  $D(\text{M}-\text{C}_2)$  is smaller than  $D(\text{M}-\text{O})$  by about 1 eV (De Maria, 1968). This fact can be verified by referring to Table 1 (note that  $D(\text{M}-\text{C}_2) = H_0^0(\text{MC}_2) - H_0^0(\text{C}_2)$ ).

It has also been suggested that correlation between the dissociation energies arises because the  $\text{C}_2$  radical has the character of pseudo-oxygen (Chapka *et al.*, 1958; De Maria, 1968). This correlation has been applied to estimate the dissociation energies of  $\text{AlC}_2$  and  $\text{ZrC}_2$ . After our computations were completed, we learned of the result of a laboratory measurement of  $D(\text{Zr}-\text{C}_2)$  by Stearns and Kohl (1971). Their result is a rather small value of  $D(\text{Zr}-\text{C}_2) = 137 \pm 6$  kcal/mol. This is about 2 eV smaller than the value of  $D(\text{Zr}-\text{O})$ , and hence about 1 eV smaller than the value estimated by the empirical rule noted before. The equilibrium partial pressure of Zr, however, is little affected by the formation of  $\text{ZrC}_2$  even in the atmosphere of carbon stars, as will be shown in section V. The effect of the revised dissociation energy on the calculation of the  $\text{ZrC}_2$  abundance is accounted for by changing the value of the equilibrium constant by  $\Delta \log K_p = -\Delta D/\theta$ , where  $\Delta D = D(\text{revised}) - D(\text{adopted})$ . In addition, the structural parameter of  $\text{ZrC}_2$  is not well established. In the present study, we have assumed a linear asymmetric structure and the ground electronic state of  $\text{ZrO}$ . Stearns and Kohl (1971), however, have pointed out that these assumptions are not necessarily appropriate for  $\text{ZrC}_2$ .

For elements of Groups Ia, IIa, VIIa, VIII, Ib and IIb, the dicarbides may not be important since the dissociation energies of the monoxides and hence of the carbides are relatively small.

**Nitrides.** Experimental studies of the stability of metallic nitrides have been carried out only recently. For example,  $\text{ZrN}$  was studied by Gingerich (1968a) and  $\text{TiN}$  by Stearns and Kohl (1970). The possible presence of stable gaseous nitrides was suggested on the ground that nitrogen is a highly electronegative element and that also many solid metal nitrides are known. The dissociation energies of many gaseous nitrides of Groups III–VI transition metals have been estimated by Gingerich (1968b) on the basis of an empirical correlation. Some of these values are listed in Table 1.

**Oxides.** Gaseous metal oxides have been relatively well studied in the laboratory, and dissociation energies are available for almost all the monoxides listed in Table 1. The dissociation energies of some of the astrophysically interesting molecules, however, are still controversial. For example the dissociation energy of  $\text{TiO}$  has long been believed to be about 6.8 eV, but recently Wahlbeck and Gilles (1967) have suggested that  $D(\text{Ti}-\text{O}) = 7.26 \pm 0.10$  eV ( $167.38 \pm 2.30$  kcal/mol). This high value is now generally accepted (Chao *et al.*, 1965–1968; Gaydon, 1968) and we have also used this value.

Atomization energies of some of the metal dioxides have been reviewed by Brewer and Rosenblatt (1961). No direct experimental determinations are available for metal dioxides of Group IIIa metals and lanthanides. The existence of some of the metal dioxides, however, has been predicted on the basis of the stability of the corresponding metal tetracarbidides. The atomization energies for  $\text{YO}_2$  (De Maria *et al.*, 1965; Kohl and Stearns, 1970b),  $\text{CeO}_2$  (Balducci *et al.*, 1965) and  $\text{NdO}_2$  (Balducci *et al.*, 1968) have been estimated from those for  $\text{YC}_4$ ,  $\text{CeC}_4$ , and  $\text{NdC}_4$ , respectively, on the basis of the pseudo oxygen hypothesis for  $\text{C}_2$ . The atomization energies for  $\text{ScO}_2$  and  $\text{LaO}_2$  are estimated from  $D(\text{MO}-\text{O})/D(\text{M}-\text{O})$  ratios for Y, Ce and Nd with the known values of  $D(\text{Sc}-\text{O})$  and  $D(\text{La}-\text{O})$ .

**Sulphides.** A summary of presently available data on the dissociation energies of metal sulphides is given by Coppens *et al.* (1967). The available data on the dissociation energies of metal sulphides and metal nitrides show close agreement and we may assume  $D(\text{M}-\text{S}) \approx D(\text{M}-\text{N})$  to estimate the one if the other is known. This assumption has been applied to estimate  $D(\text{Zr}-\text{S})$  from the known  $D(\text{Zr}-\text{N})$ . Little is known about metal disulphides, though they might be of importance since some of the metal dioxides are quite stable.

The thermochemical data for non-metallic sulphur compounds are relatively well known and have been taken mostly from Chao *et al.* (1965–1968).

**Halides.** There are many kinds of gaseous metal halides such as  $\text{MX}$  (monohalide),  $\text{MX}_2$  (dihalide),  $\text{MX}_3$  (trihalide),  $\text{MX}_4$  (tetrahalide),  $\text{M}_2\text{X}_2$  (dimer) etc., where M stands for a metal and X for a halogen. In stellar atmospheres, it is generally sufficient to consider monohalides and dihalides, though sometimes trihalides are relatively more abundant. The thermochemical data for monohalides are well known, and those for dihalides have been reviewed by Brewer *et al.* (1963).

**Other compounds.** For alkali metals, alkaline earth metals and Group IIIb elements, hydroxyl compounds are quite stable. The thermochemical data for them are mostly found in Chao *et al.* (1965–1968), and some new determinations are given by Cotton and Jenkins (1968). The importance of considerable number of

Table 1. Heats of atomization of simple molecules (in kcal/mol)

Group in periodic table	Atomic number	Element	MH	MC	MC <sub>2</sub>	MN	MO	MO <sub>2</sub>	MS
Ia	1	H	103 [1]	80 [1]	278 [1]	74 [2]	101 [1]	164 [1]	83 [1]
	3	Li	56 [2]	—	—	71 [1]	81 [2]	—	—
	11	Na	47 [2]	—	—	—	65 [1]	—	—
	19	K	44 [1]	—	—	—	63 [1]	—	—
	37	Rb	39 [2]	—	—	—	—	—	—
IIa	4	Be	53 [2]	—	—	89 [1]	106 [2]	—	88 [2]
	12	Mg	46 [2]	—	—	79 [1]	94 [2]	—	68 [1]
	20	Ca	39 [2]	—	—	—	100 [2]	—	74 [2]
	38	Sr	38 [2]	—	—	—	97 [2]	—	74 [2]
	56	Ba	41 [2]	—	—	—	121 [9]	—	95 [2]
IIIa	21	Sc	—	—	—	112:[10]	165 [11]	336:[12]	113 [13]
	39	Y	—	—	295 [14]	124:[10]	172 [11]	350:[14]	126 [13]
	57	La	—	—	297 [16]	133:[10]	194 [11]	370:[12]	138 [13]
	58	Ce	—	—	303 [17]	—	194 [11]	370:[18]	136 [13]
	60	Nd	—	—	289 [19]	—	173 [11]	360:[20]	—
IVa	22	Ti	—	127:[2]	277 [22]	110 [23]	168 [1]	292 [1]	110 [13]
	40	Zr	76 [1]	—	302 [12]	134 [24]	193 [1]	334 [1]	134:[12]
Va	23	V	—	—	277 [26]	116:[10]	149 [2]	296 [27]	—
VIa	24	Cr	66 [2]	—	248 [26]	96:[10]	101 [2]	228 [27]	—
VIIa	25	Mn	55 [2]	—	—	—	96 [2]	218 [27]	69 [2]
VIII	26	Fe	—	—	—	—	98 [1]	—	76:[30]
	28	Ni	60 [2]	—	—	—	97:[2]	—	—
Ib	29	Cu	66 [2]	—	—	—	82 [1]	—	71 [2]
IIb	30	Zn	20 [2]	—	—	—	65 [2]	—	48 [2]
IIIb	5	B	78 [2]	—	293 [31]	112 [1, 2]	191 [1]	318 [1]	118 [2]
	13	Al	67 [2]	83 [1]	229:[12]	78 [1, 2]	106 [2]	192 [1]	88 [1, 2]
IVb	6	C	80 [1]	141 [1]	321 [1]	182 [32]	256 [1]	382 [1]	181 [1]
	14	Si	71 [2]	105 [1]	300 [1]	117 [1, 2]	190 [1]	297 [1]	147 [2]
Vb	7	N	74 [2]	182 [32]	320 [1]	225 [1]	150 [1]	222 [1]	120 [33]
	15	P	81 [2]	138 [2]	—	166 [1]	148 [2]	268 [27]	130 [1, 2]
VIb	8	O	101 [1]	256 [1]	331 [1]	150 [1]	118 [1]	142 [1]	124 [2]
	16	S	83 [1]	181 [1]	—	120 [33]	124 [2]	254 [1]	102 [1]
VIIb	9	F	135 [1]	130 [1]	—	71 [1]	51 [1]	136 [1]	65 [2]
	17	Cl	102 [1]	88 [2]	—	92 [2]	63 [1]	122 [1]	63 [3]
	35	Br	89 [1]	75 [1]	—	67 [1]	55 [2]	—	—
	53	I	70 [1]	—	—	—	46 [2]	—	—

1. Chao *et al.* (1965 – 1968). 2. Gaydon (1968). 3. McBride *et al.* (1963). 4. Brewer *et al.* (1963). 5. Hildenbrand (1968). 6. Bautista and Margrave (1963). 7. Cotton and Jenkins (1968). 8. Novikov and Gurvich (1966). 9. Kalf and Alkemade (1970). 10. Gingerich (1968b). 11. Ames *et al.* (1967). 12. Estimated, see the text. 13. Coppens *et al.* (1967). 14. De Maria *et al.* (1965) and Kohl and Stearns (1970a). 15. Shenyavskaya *et al.* (1966). 16. Chupka *et al.* (1958). 17. Balducci *et al.* (1969). 18. Balducci *et al.* (1965). 19. De Maria *et al.* (1967). 20. Balducci *et al.* (1968). 21. Zambov and Margrave (1966). 22. Stearns and Kohl (1970). 23. Stearns and Kohl (1969). 24. Gingerich (1968a). 25. Zambov and Margrave (1967). 26. Kohl and Stearns (1970b). 27. Brewer and Rosenblatt (1961). 28. Kent and Margrave (1965). 29. Kent *et al.* (1964). 30. Marquert and Berkowitz (1963). 31. Verhaegen *et al.* (1964). 32. Dibeler and Liston (1968). 33. O'Hara (1970).

compounds not covered in Table 1 or in Paper I were also checked by applying the thermochemical data given by Chao *et al.* (1965 – 1968). Most of them were found to be unimportant at temperatures above 1000 °K for a normal chemical composition.

**Negative Ions.** Electron affinities of negative ions of both atoms and molecules were taken from a recent review by Berry (1969).

### III. Method of Computation

In solving the chemical equilibria in stellar atmospheres, it is not always necessary to incorporate all species at once. For example, the chemical equilibria between H, C, N and O are determined independently of other elements, since the addition of other elements, which are far less abundant than H, C, N and O, does not in



MF	MF <sub>2</sub>	MCl	MCl <sub>2</sub>	MBr	MBr <sub>2</sub>	MI	MI <sub>2</sub>	MOH
135 [1]	—	102 [1]	—	87 [1]	—	70 [1]	—	219 [1]
137 [2]	—	113 [2]	—	101 [1]	—	85 [1]	—	205 [3]
114 [2]	—	97 [1]	—	83 [1]	—	70 [2]	—	186 [1]
117 [2]	—	101 [1]	—	91 [1]	—	76 [1]	—	186 [1]
120 [2]	—	102 [2]	—	92 [2]	—	80 [2]	—	—
146 [1]	—	92 [1]	221 [1]	95 [1]	188 [1]	78 [1]	149 [1]	213 [1]
106 [2]	247 [1]	81 [2]	188 [1]	74 [1]	162 [1]	55 [2]	126 [4]	197 [1]
126 [5]	266 [5]	81 [6]	213 [6]	90 [2]	191 [4]	69 [2]	156 [4]	205 [7]
129 [5]	262 [5]	88 [8]	224 [4]	80 [2]	194 [4]	80 [2]	196 [4]	204 [7]
140 [5]	273 [5]	115 [2]	236 [4]	—	205 [4]	88 [2]	172 [4]	215 [7]
115 [2]	260 [12]	—	—	—	—	—	—	—
118 [15]	291 [12]	81 [2]	—	—	—	—	—	—
141 [15]	302 [12]	—	—	—	—	—	—	—
140 [12]	—	—	—	—	—	—	—	—
130 [21]	273 [21]	—	—	—	—	—	—	—
147 [1]	321 [1]	104 [1]	237 [1]	88 [1]	208 [1]	72 [1]	177 [1]	—
148 [25]	321 [25]	113 [12]	259 [12]	105 [12]	248 [1]	87 [12]	215 [1]	—
—	296 [12]	—	228 [4]	—	196 [4]	—	167 [4]	—
106 [28]	229 [4]	87 [2]	183 [4]	78 [2]	155 [4]	68 [2]	122 [4]	—
101 [29]	220 [4]	85 [2]	186 [4]	74 [2]	159 [4]	67 [2]	128 [4]	—
106 [1]	229 [1]	67 [1]	192 [1]	—	162 [1]	—	129 [1]	—
88 [2]	220 [4]	88 [2]	175 [4]	85 [2]	152 [4]	69 [2]	123 [4]	—
87 [1]	180 [1]	83 [2]	141 [4]	78 [2]	123 [4]	46 [2]	—	—
—	184 [4]	49 [2]	157 [4]	—	132 [4]	32 [1]	100 [4]	—
178 [1]	—	127 [1]	—	103 [1]	—	85 [1]	—	—
158 [2]	279 [1]	117 [2]	209 [1]	100 [1]	—	88 [1]	—	230 [1]
130 [1]	247 [1]	88 [2]	152 [1]	74 [1]	—	50 [2]	—	—
120 [1, 2]	292 [1]	97 [1, 2]	201 [1]	81 [2]	—	—	—	—
71 [1]	139 [1]	92 [2]	—	67 [1]	—	—	—	—
108 [1, 2]	221 [1]	71 [1, 2]	—	—	—	—	—	108 [1, 2]
51 [1]	100 [1]	63 [1]	95 [1]	—	—	—	—	164 [1]
65 [2]	154 [3]	63 [3]	128 [3]	—	—	—	—	—
37 [2]	—	59 [2]	—	55 [2]	—	67 [2]	—	159 [1]
59 [2]	—	57 [2]	—	51 [2]	—	50 [2]	—	160 [1]
55 [2]	—	51 [2]	—	45 [2]	—	42 [2]	—	—
66 [2]	—	50 [2]	—	42 [2]	—	36 [2]	—	—

general change essentially the equilibria between H-, C-, N- and O-compounds. Only Si has some effect, especially when the C/O ratio is very close to unity. For this reason, the chemical equilibria of relatively abundant elements have been discussed rather well in previous studies. On the other hand, to solve the chemical equilibria of a trace element, it seems to be necessary to examine the effects of all the elements that are more abundant. For metallic elements, however, it is generally sufficient to consider associations with non-metallic elements of high electronegativity. Even then, the chemical equilibria of trace elements may be quite complicated in general, since the partial pressures of non-metallic elements are, in turn, determined by the equilibrium with metallic elements of higher abundance. Because of such a complicated coupling effect, it seems

necessary to solve the equilibria of many elements simultaneously.

For the reason noted above, we have selected 36 elements in the present study and the chemical equilibrium of them is solved simultaneously. The chemical abundances adopted in the present study are given in Table 2 in order of decreasing concentration. This composition is based on recent studies of abundances in the sun and in the solar system. These elements are chosen because (1) they are of considerable astrophysical importance, (2) they have an important effect on the chemical equilibria of other elements, and/or (3) thermochemical data of molecular species composed of them are relatively well known.

The computation of the chemical equilibria has been carried out on the basis of Russell's equations (Russell,

Table 2. The standard chemical composition

Element	log $N$	Element	log $N$	Element	log $N$
H	12.00	Cl	5.50: [6]	Sc	3.04 [7]
He	11.21:	Cr	5.47 [7]	Sr	2.82 [4]
O	8.77 [1]	P	5.43 [5]	Br	2.68: [6]
C	8.55 [1]	Ni	5.08 [7]	Zr	2.65 [9]
N	7.93 [1]	K	5.05 [5]	Rb	2.63 [10]
Fe	7.62 [2]	Mn	4.88 [7]	La	2.03 [9]
Si	7.55 [3]	F	4.75: [6]	Nd	1.93 [9]
Mg	7.48 [4]	Ti	4.50 [7]	Ba	1.90 [4]
S	7.21 [5]	V	3.92 [7]	Ce	1.78 [9]
Al	6.40 [5]	B	3.6: [8]	I	1.45: [6]
Ca	6.33 [4]	Cu	3.50 [9]	Be	1.1 [11]
Na	6.18 [5]	Y	3.20: [9]	Li	0.68: [12]

1. Lambert (1968). 2. Baschek *et al.* (1970); Garz *et al.* (1970). 3. Lambert and Warner (1968b). 4. Lambert and Warner (1968c). 5. Lambert and Warner (1968a). 6. Suess and Urey (1956). 7. Warner (1968). 8. Lambert *et al.* (1966). 9. Goldberg *et al.* (1960). 10. Lambert and Mallia (1968). 11. Grevesse (1968); Hauge and Engvold (1969). 12. Peach (1968); Wiehr *et al.* (1968).

1934) which made use of equilibrium constants to express the mass balance constraint for all the elements in terms of the partial pressures of free neutral atoms. This method is simple enough to allow a general treatment of the complicated problem mentioned above. The computer program has been written in such a way that any species and any element can be included in the equilibrium by just adding a data card specifying the molecular formula and equilibrium constant. The chemical equilibrium in a complicated system can also be solved by the minimization of the total free-energy of the system (White *et al.*, 1958). It is, however, unlikely that this method has any marked advantage over that based on the classical Russell equations in so far as the chemical equilibrium in stellar atmosphere is concerned.

In the present study, negative ion formation by both atoms and molecules as well as single ionization of atoms are taken into account and solved for simultaneously with the molecular equilibrium. We have, however, investigated only gaseous systems, and the formation of solids and liquids have not been considered.

In the actual computations, we first determine the fictitious pressure of the hydrogen nucleus,  $P(H)$ , defined by

$$P(H) = P_H + P_{H^+} + 2P_{H_2}, \quad (4)$$

where  $P_H$ ,  $P_{H^+}$ , and  $P_{H_2}$  are the partial pressures of neutral hydrogen, ionized hydrogen, and molecular hydrogen, respectively. To calculate  $P(H)$  from the above equation, we must calculate  $P_H$  for a given temperature and gas pressure from

$$P_g = P_H + P_{H^+} + P_{H_2} + P_{He} + P_e, \quad (5)$$

where  $P_{He}$  is the partial pressure of neutral helium and is equated to the fictitious pressure of the helium nuclei. The electron pressure,  $P_e$ , is equated to  $P_{H^+}$ , since otherwise the electron pressure is so small that it gives no contribution to the gas pressure. Then, the above equation and the ionization and dissociation equations are solved for  $P_H$ . After  $P(H)$  has been obtained by the above procedure, the fictitious pressure of any element,  $M$ , can be obtained from

$$P(M) = a(M) P(H), \quad (6)$$

where  $a(M)$  is the abundance of element  $M$  relative to hydrogen. These fictitious pressures are necessary in solving the Russell equations. Next, the Russell equations are solved by iteration using the Newton-Raphson method. The convergence is reasonably fast in general, even though hundreds of species are incorporated.

#### IV. Chemical Equilibrium in Stellar Atmospheres of Normal Chemical Abundance

The chemical equilibria of 36 elements are solved for the standard chemical composition shown in Table 2.

The resulting partial pressures of free neutral atoms for 35 elements are shown in Table 3 for the temperature range between 1008 °K ( $\theta = 5.0$ ) and 6300 °K ( $\theta = 0.8$ ) and for  $\log P_g$  between 0.0 and 8.0. In this table, the fictitious pressure of hydrogen,  $P(H)$ , and the electron pressure are also shown. The partial pressure of helium is not shown since it is given simply by  $P_{He} = P(H) a(He)$ . From the equilibrium partial pressures for neutral atoms, the partial pressure of any molecule can directly be evaluated from equation (2). The necessary equilibrium constants are approximated by

$$\log K_p = a_0 + a_1 \theta + a_2 \theta^2 + a_3 \theta^3 + a_4 \theta^4, \quad (7)$$

and the fitting coefficients are given in Table 4.

In Figs. 1a and 1b, we have plotted, for selected elements,  $\log n(M)/N(M)$  against  $\theta = 5040/T$  for the case of  $\log P_g = 3.0$ , where  $n(M)$  is the number density of the free neutral atom and  $N(M)$  is the number density of the nuclei of element  $M$ . The decrease of  $\log n(M)/N(M)$  is due to the effect of molecular formation at lower temperatures and to ionization at higher temperatures. At lower temperatures, the fraction of neutral atoms is fairly large for Group Ia elements (alkali metals), but it decreases in Group IIa (alkali earth metals) and especially in Group IIIa (Sc, Y, La, and lanthanides) and group IVa (Ti, Zr etc. .). It then increases again in the transition elements of Group Va (V), VIa (Cr), VIIa (Mn), VIII (Fe, Co, Ni), Ib (Cu), and IIb (Zn). Eventually, the fraction decreases in the non-metallic elements of Group IIIb (B, Al), IVb (C, Si), Vb (N, P), VIb (O, S) and VII b (halogens). It is interesting to note that the elements most strongly locked in molecules are not the ones of the strongest

TABLE 3 LOGARITHMS OF THE EQUILIBRIUM PARTIAL PRESSURE OF GASEOUS NEUTRAL ATOMS (UNIT OF PRESSURE IS DYN/CM\*\*2)

THETA=	5.0	4.5	4.0	3.5	3.0	2.8	2.6	2.4	2.2	2.0	1.8	1.6	1.4	1.2	1.0	0.8
LOG PG=0.0 ELECTRON H NUCLEI	-10.74 0.18	-9.58 0.18	-8.43 0.18	-7.33 0.18	-6.58 0.16	-6.21 0.12	-5.90 0.04	-5.71 -0.04	-5.44 -0.06	-5.20 -0.06	-4.72 -0.06	-4.22 -0.06	-4.02 -0.06	-3.69 -0.06	-2.43 -0.07	-1.01 -0.11
H	-5.60	-4.45	-3.29	-2.13	-0.99	-0.58	-0.26	-0.10	-0.07	-0.07	-0.06	-0.06	-0.06	-0.06	-0.07	-0.17
LI	-11.64	-11.17	-11.13	-11.17	-10.17	-11.23	-11.17	-12.05	-13.03	-13.27	-14.55	-15.44	-12.05	-12.77	-17.19	-17.15
BE	-16.70	-14.16	-11.69	-10.74	-10.74	-10.78	-10.86	-10.94	-10.96	-10.96	-10.96	-10.97	-11.26	-12.66	-13.65	-14.19
B	-26.26	-23.01	-19.76	-16.61	-14.38	-13.80	-13.29	-12.25	-10.63	-9.08	-8.49	-8.49	-8.97	-10.31	-10.90	-11.43
C	-29.21	-26.20	-23.19	-20.18	-17.22	-16.11	-15.05	-13.45	-11.26	-9.03	-6.80	-4.61	-3.57	-3.55	-3.85	-4.74
N	-20.41	-17.94	-15.47	-13.00	-10.54	-9.57	-8.62	-7.66	-6.67	-5.68	-4.73	-4.18	-4.14	-4.13	-4.14	-4.23
O	-17.06	-14.46	-11.86	-9.25	-6.61	-5.51	-4.40	-3.82	-3.77	-3.73	-3.69	-3.64	-3.32	-3.30	-3.30	-3.39
F	-20.82	-18.66	-16.51	-14.08	-11.93	-11.16	-10.34	-9.35	-8.24	-7.48	-7.33	-7.32	-7.31	-7.31	-7.32	-7.36
NA	-5.65	-5.64	-5.64	-5.64	-5.69	-5.82	-6.25	-7.09	-7.94	-8.83	-9.50	-10.15	-11.12	-11.99	-11.95	-11.85
MG	-4.34	-4.34	-4.34	-4.34	-4.36	-4.40	-4.48	-4.56	-4.58	-4.60	-4.76	-5.50	-6.91	-8.28	-8.75	-9.15
AL	-9.06	-7.68	-6.34	-5.52	-5.45	-5.48	-5.57	-5.66	-5.84	-6.51	-7.29	-8.10	-9.24	-10.28	-10.41	-10.47
SI	-16.30	-14.71	-13.11	-11.52	-9.98	-9.44	-8.95	-7.92	-6.31	-4.89	-4.54	-4.65	-5.69	-7.13	-7.70	-8.19
P	-14.57	-13.30	-11.91	-10.02	-7.78	-7.43	-7.31	-6.90	-6.65	-6.64	-6.63	-6.63	-6.65	-7.14	-8.03	-8.98
S	-8.91	-7.31	-5.85	-4.89	-4.68	-4.69	-4.76	-4.83	-4.85	-4.85	-4.85	-4.85	-4.86	-5.06	-5.72	-6.60
CL	-12.20	-10.81	-9.65	-8.45	-7.34	-6.96	-6.69	-6.59	-6.57	-6.57	-6.56	-6.56	-6.56	-6.57	-6.59	-6.96
K	-6.82	-6.78	-6.78	-6.91	-7.97	-8.56	-9.27	-10.11	-10.83	-11.56	-12.07	-12.56	-13.37	-14.08	-13.88	-13.62
CA	-5.90	-5.58	-5.51	-5.49	-5.51	-5.55	-5.64	-5.82	-6.36	-7.35	-8.20	-9.04	-10.21	-11.27	-11.43	-11.52
SC	-22.36	-20.20	-18.05	-15.93	-13.90	-13.20	-12.57	-10.95	-9.33	-7.74	-10.60	-11.52	-12.77	-13.92	-14.17	-14.34
TI	-15.03	-13.94	-11.86	-11.79	-10.77	-10.43	-10.14	-9.31	-8.06	-7.88	-6.62	-5.57	-4.93	-4.28	-12.38	-12.51
V	-12.34	-11.13	-10.12	-9.32	-8.70	-8.55	-8.48	-8.23	-8.17	-8.44	-9.17	-10.10	-11.39	-12.58	-12.86	-13.08
CR	-6.36	-6.36	-6.35	-6.35	-6.38	-6.41	-6.49	-6.57	-6.61	-6.86	-7.57	-8.50	-9.79	-10.98	-11.27	-11.49
MN	-6.94	-6.94	-6.94	-6.94	-6.96	-7.00	-7.08	-7.16	-7.18	-7.21	-7.42	-8.19	-9.58	-10.90	-11.33	-11.68
FE	-4.20	-4.20	-4.20	-4.20	-4.22	-4.26	-4.34	-4.42	-4.44	-4.45	-4.49	-4.90	-6.24	-7.65	-8.16	-8.60
NI	-6.74	-6.74	-6.74	-6.74	-6.76	-6.80	-6.88	-6.96	-6.98	-6.99	-7.04	-7.43	-8.71	-10.07	-10.54	-10.93
CU	-8.33	-8.32	-8.32	-8.32	-8.34	-8.38	-8.46	-8.54	-8.56	-8.57	-8.60	-8.93	-10.19	-11.57	-12.05	-12.46
BR	-12.35	-10.29	-9.26	-9.34	-9.20	-9.22	-9.29	-9.38	-9.38	-9.38	-9.38	-9.38	-9.38	-9.38	-9.61	-10.50
RB	-9.29	-9.21	-9.23	-9.56	-10.85	-11.43	-12.11	-12.92	-13.60	-14.30	-14.78	-15.24	-16.02	-16.69	-16.46	-16.17
Y	-11.01	-9.28	-9.01	-9.00	-9.03	-9.08	-9.25	-9.82	-10.70	-11.69	-12.46	-13.23	-14.31	-15.29	-15.36	-15.37
SR	-25.43	-22.96	-20.51	-18.09	-15.74	-14.91	-14.16	-12.34	-9.78	-9.10	-9.63	-10.45	-11.66	-12.78	-12.99	-13.14
ZR	-23.33	-21.21	-19.14	-17.18	-15.40	-14.80	-14.27	-13.16	-11.51	-10.08	-10.44	-11.39	-12.69	-13.90	-14.21	-14.44
I	-10.52	-10.39	-10.38	-10.37	-10.39	-10.43	-10.51	-10.59	-10.61	-10.61	-10.61	-10.62	-11.03	-11.87	-12.81	-13.81
BA	-14.61	-12.33	-10.74	-10.10	-10.03	-10.25	-10.84	-11.78	-12.66	-13.57	-14.25	-14.92	-15.90	-16.78	-16.76	-16.67
LA	-30.82	-27.93	-25.04	-22.16	-19.35	-18.34	-17.40	-16.40	-15.71	-12.67	-13.42	-14.17	-15.23	-16.20	-16.25	-16.24
CE	-28.12	-25.25	-22.34	-19.48	-16.68	-15.67	-14.71	-13.71	-12.71	-11.27	-11.37	-12.04	-13.12	-14.18	-15.19	-16.24
ND	-28.24	-25.57	-22.90	-20.25	-17.68	-16.77	-15.93	-14.91	-11.14	-11.18	-12.04	-12.92	-14.12	-15.22	-15.82	-15.55
LOG PG=1.0 ELECTRON H NUCLEI	-10.26 1.18	-9.08 1.18	-7.93 1.18	-6.78 1.18	-5.84 1.17	-5.55 1.16	-5.17 1.12	-4.86 1.04	-4.64 0.96	-4.37 0.94	-4.05 0.93	-3.49 0.93	-3.09 0.93	-2.93 0.93	-1.91 0.93	-0.48 0.92
H	-5.10	-3.95	-2.79	-1.63	-0.48	-0.02	0.40	0.73	0.89	0.93	0.93	0.93	0.93	0.93	0.93	0.90
LI	-11.90	-11.91	-10.28	-10.15	-10.15	-10.17	-10.23	-10.47	-11.14	-12.01	-12.87	-13.52	-14.34	-15.43	-15.68	-15.58
BE	-16.70	-14.16	-11.64	-9.85	-9.73	-9.74	-9.78	-9.86	-9.94	-9.96	-9.96	-9.97	-10.01	-10.94	-11.93	-12.62
B	-25.76	-22.51	-19.26	-16.05	-13.43	-12.72	-12.14	-11.60	-10.54	-8.94	-7.68	-7.47	-7.56	-8.58	-9.38	-9.86
C	-28.21	-25.20	-22.19	-19.18	-16.19	-15.01	-13.89	-12.80	-11.18	-8.99	-6.78	-4.53	-2.80	-2.52	-3.65	-4.24
N	-19.91	-17.44	-14.97	-12.50	-10.03	-9.05	-8.07	-7.12	-6.16	-5.17	-4.19	-3.36	-3.14	-3.13	-3.14	-3.16
O	-17.06	-14.46	-11.86	-9.25	-6.63	-5.57	-4.48	-3.88	-2.82	-2.77	-2.71	-2.69	-2.44	-2.30	-2.30	-2.32
F	-20.32	-18.16	-16.04	-13.77	-11.46	-10.68	-9.91	-9.10	-8.13	-7.05	-6.42	-6.32	-6.32	-6.31	-6.32	-6.33
NA	-4.65	-4.64	-4.64	-4.64	-4.65	-4.69	-4.83	-5.29	-6.14	-7.00	-7.83	-8.42	-9.19	-10.23	-10.43	-10.28
MG	-3.34	-3.34	-3.34	-3.34	-3.35	-3.36	-3.40	-3.48	-3.56	-3.58	-3.63	-3.96	-5.00	-6.53	-7.23	-7.58
AL	-8.56	-7.17	-5.81	-4.69	-4.44	-4.45	-4.48	-4.56	-4.67	-4.94	-5.65	-6.38	-7.31	-8.52	-8.89	-8.91
SI	-15.30	-13.71	-12.12	-10.53	-8.95	-8.41	-7.79	-7.27	-6.23	-5.65	-5.33	-5.35	-6.39	-7.58	-8.17	-8.63
P	-13.57	-12.32	-11.04	-9.54	-7.37	-6.58	-6.21	-6.08	-5.77	-5.64	-5.64	-5.64	-5.64	-5.78	-6.54	-7.52
S	-8.90	-7.30	-5.72	-4.38	-3.76	-3.70	-3.70	-3.76	-3.83	-3.85	-3.85	-3.85	-3.86	-3.90	-4.31	-5.06
CL	-11.93	-10.35	-9.15	-7.97	-6.81	-6.38	-5.99	-5.71	-5.59	-5.57	-5.57	-5.56	-5.56	-5.56	-5.57	-5.71
K	-5.86	-5.79	-5.78	-5.81	-6.33	-6.88	-7.46	-8.18	-9.00	-9.73	-10.39	-10.83	-11.44	-12.32	-12.36	-12.05
CA	-5.27	-4.73	-4.54	-4.50	-4.50	-4.51	-4.55	-4.65	-4.89	-5.57	-6.53	-7.32	-8.28	-9.51	-9.91	-9.96
SC	-21.36	-19.20	-17.06	-14.93	-12.84	-12.05	-11.34	-10.67	-9.16	-8.29	-8.97	-9.80	-10.85	-12.16	-12.64	-12.78
TI	-14.03	-12.94	-11.86	-10.79	-9.73	-9.33	-8.98	-8.66	-7.82	-6.82	-7.07	-7.86	-8.94	-10.32	-10.85	-11.04
V	-11.34	-10.14	-9.12	-8.32	-7.66	-7.47	-7.34	-7.29	-7.17	-7.20	-7.63	-8.40	-9.46	-10.82	-11.34	-11.51
CR	-5.39	-5.37	-5.36	-5.36	-5.36	-5.37	-5.41	-5.49	-5.57	-5.64	-6.04	-6.79	-7.86	-9.22	-9.75	-9.93
MN	-5.94	-5.94	-5.94	-5.94	-5.95	-5.96	-6.00	-6.08	-6.16	-6.18	-6.25	-6.62	-7.66	-9.15	-9.80	-10.12
FE	-3.20	-3.20	-3.20	-3.20	-3.21	-3.22	-3.26	-3.34	-3.42	-3.44	-3.46	-3.58	-4.36	-5.89	-6.64	-7.04
NI	-5.74	-5.74	-5.74	-5.74	-5.75	-5.76	-5.80	-5.88	-5.96	-5.98	-6.00	-6.11	-6.84	-8.32	-9.01	-9.37
CU	-7.34	-7.33	-7.32	-7.32	-7.33	-7.34	-7.38	-7.46	-7.54	-7.56	-7.57	-7.66	-8.33	-9.81	-10.52	-10.89
BR	-12.04	-10.62	-9.37	-8.61	-8.26	-8.21	-8.22	-8.29	-8.36	-8.38	-8.38	-8.38	-8.38	-8.39	-8.47	-9.02
RB	-8.35	-8.23	-8.21	-8.33	-9.15	-9.74	-10.30	-10.99	-11.78	-12.48	-13.11	-13.51	-14.09	-14.93	-14.94	-14.60
Y	-10.53	-8.90	-8.04	-6.01	-8.01	-8.03	-8.08	-8.29	-9.05	-10.03	-10.79	-11.50	-12.38	-13.53	-13.64	-13.60
SR	-24.42	-21.96	-19.51	-17.08	-14.69	-13.71	-12.92	-12.11	-10.29	-8.26	-6.18	-4.77	-3.99	-3.02	-15.47	-11.57
ZR	-22.33	-20.21	-18.14	-16.18	-14.36	-13.69	-13.09	-12.54	-11.44	-9.83	-8.97	-9.68	-10.77	-12.14	-12.68	-12.88
I	-9.96	-9.45	-8.99	-9.38	-9.38	-9.39	-9.43	-9.51	-9.59	-9.61	-9.61	-9.61	-9.62	-9.72	-10.40	-11.25
BA	-14.14	-12.19	-10.17	-9.32	-9.00	-9.04	-9.28	-9.91	-10.85	-11.74	-12.58	-13.19	-13.97	-15.03	-15.24	-15.11
LA	-29.82	-26.93	-24.04	-21.16	-18.30	-17.19	-16.16	-15.17	-13.18	-11.12	-11.75	-12.44	-13.30	-14.44	-14.73	-14.68
CE	-30.12	-27.23	-24.34	-21.46	-18.60	-17.49	-16.46	-15.48	-13.50	-11.19	-9.96	-10.63	-11.73	-13.12	-13.67	-13.88
ND	-29.84	-26.97	-24.01	-21.25	-18.63	-17.62	-16.69	-15.80	-11.86	-9.66	-10.39	-11.80	-12.49	-13.87	-13.90	-13.98
LOG PG=2.0 ELECTRON H NUCLEI	-9.79 2.18	-8.60 2.18	-7.43 2.18	-6.27 2.18	-5.18 2.18	-4.84 2.17	-4.51 2.16	-4.12 2.12	-3.81 2.05	-3.57 1.96	-3.29 1.94	-2.84 1.93	-2.28 1.93	-2.0		

TABLE 3 (CONTINUED)

THETA=	5.0	4.5	4.0	3.5	3.0	2.8	2.6	2.4	2.2	2.0	1.8	1.6	1.4	1.2	1.0	0.8
LOG PG=3.0 ELECTRON H NUCLEI	-9.33 3.18	-8.13 3.18	-6.94 3.18	-5.77 3.18	-4.62 3.18	-4.20 3.18	-3.83 3.17	-3.47 3.16	-3.07 3.13	-2.75 3.05	-2.49 2.97	-2.15 2.94	-1.59 2.93	-1.12 2.93	-0.75 2.93	0.55 2.93
H	-4.10	-2.95	-1.79	-0.63	0.53	1.00	1.46	1.92	2.35	2.70	2.88	2.93	2.93	2.93	2.93	2.93
LI	-10.35	-9.71	-8.79	-8.22	-8.15	-8.15	-8.17	-8.25	-8.25	-8.56	-9.22	-10.18	-10.84	-11.62	-12.52	-12.54
BE	-16.69	-14.15	-11.63	-9.15	-7.79	-7.74	-7.73	-7.74	-7.77	-7.85	-7.93	-7.96	-7.97	-8.02	-8.83	-9.59
B	-24.75	-21.50	-18.25	-15.02	-11.91	-10.88	-10.08	-9.41	-8.81	-8.22	-7.13	-5.80	-5.97	-5.54	-6.29	-6.84
C	-26.21	-23.20	-20.19	-17.18	-14.18	-12.97	-11.78	-10.59	-9.44	-8.29	-6.63	-4.48	-2.25	-0.70	-0.53	-0.66
N	-18.91	-16.44	-13.97	-11.50	-9.03	-8.04	-7.05	-6.06	-5.08	-4.12	-3.16	-2.18	-1.35	-1.14	-1.13	-1.14
O	-17.07	-14.47	-11.86	-9.25	-6.64	-5.59	-4.54	-3.47	-2.39	-1.35	-0.83	-0.72	-0.68	-0.60	-0.30	-0.30
F	-19.35	-17.17	-15.05	-12.95	-10.64	-9.75	-8.94	-8.18	-7.42	-6.62	-5.68	-4.73	-4.35	-4.32	-4.31	-4.32
NA	-2.67	-2.66	-2.64	-2.64	-2.64	-2.64	-2.65	-2.70	-2.86	-3.38	-4.24	-5.08	-5.70	-6.42	-7.27	-7.24
MG	-1.37	-1.35	-1.34	-1.34	-1.34	-1.34	-1.35	-1.36	-1.39	-1.47	-1.55	-1.61	-1.84	-2.74	-4.07	-4.54
AL	-7.55	-6.17	-4.79	-3.45	-2.55	-2.46	-2.44	-2.44	-2.48	-2.56	-2.72	-3.18	-3.84	-4.71	-5.73	-5.87
SI	-13.29	-11.71	-10.13	-8.54	-6.95	-6.31	-5.68	-5.07	-4.49	-3.91	-2.84	-1.70	-1.51	-1.84	-3.03	-3.59
P	-11.57	-10.32	-9.08	-7.82	-6.41	-5.70	-4.91	-4.21	-3.87	-3.75	-3.65	-3.64	-3.63	-3.64	-3.81	-4.44
S	-8.90	-7.29	-5.68	-4.09	-2.66	-2.23	-1.95	-1.79	-1.74	-1.77	-1.83	-1.85	-1.85	-1.86	-1.91	-2.23
CL	-11.50	-9.64	-8.19	-7.00	-5.82	-5.35	-4.89	-4.45	-4.05	-3.74	-3.60	-3.57	-3.57	-3.56	-3.57	-3.58
K	-3.98	-3.87	-3.79	-3.78	-3.83	-3.95	-4.25	-4.73	-5.28	-5.99	-6.79	-7.49	-7.94	-8.51	-9.20	-9.01
CA	-4.419	-3.42	-2.88	-2.57	-2.51	-2.50	-2.50	-2.51	-2.55	-2.68	-3.13	-4.00	-4.79	-5.70	-6.75	-6.92
SC	-19.35	-17.19	-15.05	-12.93	-10.63	-9.75	-8.94	-8.18	-7.42	-6.62	-5.68	-4.73	-4.35	-4.32	-4.31	-4.32
TI	-12.05	-10.94	-9.86	-8.79	-7.72	-7.29	-6.86	-6.45	-6.07	-5.69	-4.97	-4.84	-5.50	-6.51	-7.69	-8.01
V	-9.37	-8.16	-7.12	-6.32	-5.65	-5.43	-5.26	-5.14	-5.08	-5.10	-5.14	-5.39	-6.03	-7.01	-8.18	-8.48
CR	-3.64	-3.51	-3.44	-3.39	-3.37	-3.37	-3.37	-3.38	-3.41	-3.48	-3.58	-3.82	-4.43	-5.42	-6.59	-6.89
MN	-3.94	-3.94	-3.94	-3.94	-3.94	-3.94	-3.95	-3.96	-3.99	-4.07	-4.15	-4.21	-4.47	-5.36	-6.65	-7.08
NI	-1.20	-1.20	-1.20	-1.20	-1.20	-1.20	-1.21	-1.22	-1.25	-1.33	-1.41	-1.45	-1.54	-2.17	-3.48	-4.00
FE	-3.75	-3.74	-3.74	-3.74	-3.74	-3.74	-3.75	-3.76	-3.79	-3.87	-3.95	-3.99	-4.06	-4.62	-5.86	-6.33
CU	-5.48	-5.46	-5.36	-5.34	-5.33	-5.33	-5.33	-5.34	-5.38	-5.45	-5.53	-5.57	-5.63	-6.13	-7.37	-7.86
BR	-11.52	-10.00	-8.66	-7.53	-6.74	-6.52	-6.36	-6.27	-6.25	-6.29	-6.36	-6.38	-6.38	-6.38	-6.39	-6.50
RB	-6.54	-6.37	-6.23	-6.21	-6.36	-6.58	-6.99	-7.51	-8.05	-8.74	-9.51	-10.17	-10.59	-11.12	-11.78	-11.56
SR	-9.40	-8.24	-6.56	-6.06	-6.01	-6.01	-6.01	-6.03	-6.10	-6.42	-7.23	-8.16	-8.88	-9.72	-10.68	-10.76
Y	-22.42	-19.95	-17.51	-15.08	-12.67	-11.70	-10.75	-9.82	-8.95	-8.06	-6.56	-6.01	-6.39	-7.23	-8.31	-8.53
ZR	-20.32	-18.21	-16.14	-14.17	-12.34	-11.65	-10.97	-10.33	-9.72	-9.12	-8.02	-6.86	-7.33	-8.34	-9.52	-9.84
I	-9.67	-8.27	-7.57	-7.42	-7.39	-7.38	-7.38	-7.39	-7.43	-7.50	-7.58	-7.61	-7.61	-7.62	-7.75	-8.30
BA	-13.00	-11.58	-9.51	-8.00	-7.26	-7.09	-7.02	-7.07	-7.35	-8.05	-8.98	-9.85	-10.48	-11.21	-12.08	-12.07
LA	-27.81	-24.92	-22.04	-19.16	-16.28	-15.13	-13.99	-12.81	-11.40	-10.78	-9.12	-9.11	-9.81	-10.63	-11.57	-11.65
CE	-28.11	-25.22	-22.34	-19.46	-16.58	-15.43	-14.29	-13.18	-12.14	-11.10	-9.63	-7.92	-8.28	-9.31	-10.51	-10.84
ND	-25.23	-22.56	-19.90	-17.25	-14.61	-13.56	-12.62	-11.80	-10.54	-9.55	-7.80	-7.93	-8.71	-9.66	-10.74	-10.95
LOG PG=4.0 ELECTRON H NUCLEI	-8.87 4.18	-7.67 4.18	-6.45 4.18	-5.27 4.18	-4.10 4.18	-3.64 4.18	-3.21 4.18	-2.82 4.17	-2.43 4.16	-2.01 4.13	-1.68 4.06	-1.39 3.97	-0.95 3.94	-0.36 3.93	0.02 3.93	1.06 3.93
H	-3.60	-2.45	-1.29	-0.13	1.03	1.50	1.97	2.43	2.89	3.33	3.69	3.88	3.93	3.93	3.93	3.93
LI	-9.54	-8.97	-8.16	-7.35	-7.16	-7.15	-7.17	-7.15	-7.17	-7.26	-7.62	-8.42	-9.20	-9.85	-10.75	-11.03
BE	-16.68	-14.15	-11.63	-9.12	-7.05	-6.81	-6.75	-6.74	-6.74	-6.77	-6.84	-6.93	-6.96	-6.97	-7.28	-8.10
B	-24.75	-21.50	-18.25	-15.02	-11.91	-10.88	-10.08	-9.41	-8.81	-8.22	-7.13	-5.80	-5.97	-5.54	-6.29	-6.84
C	-26.21	-23.20	-20.19	-17.18	-14.18	-12.97	-11.78	-10.59	-9.44	-8.29	-6.63	-4.48	-2.25	-0.70	-0.53	-0.66
N	-18.91	-16.44	-13.97	-11.50	-9.03	-8.04	-7.05	-6.06	-5.08	-4.12	-3.16	-2.18	-1.35	-1.14	-1.13	-1.14
O	-17.07	-14.47	-11.86	-9.25	-6.64	-5.59	-4.54	-3.47	-2.39	-1.35	-0.83	-0.72	-0.68	-0.60	-0.30	-0.30
F	-19.35	-17.17	-15.05	-12.95	-10.64	-9.75	-8.94	-8.18	-7.42	-6.62	-5.68	-4.73	-4.35	-4.32	-4.31	-4.32
NA	-2.67	-2.66	-2.64	-2.64	-2.64	-2.64	-2.65	-2.70	-2.86	-3.38	-4.24	-5.08	-5.70	-6.42	-7.27	-7.24
MG	-1.37	-1.35	-1.34	-1.34	-1.34	-1.34	-1.35	-1.36	-1.39	-1.47	-1.55	-1.61	-1.84	-2.74	-4.07	-4.54
AL	-7.55	-6.17	-4.79	-3.45	-2.55	-2.46	-2.44	-2.44	-2.48	-2.56	-2.72	-3.18	-3.84	-4.71	-5.73	-5.87
SI	-13.29	-11.71	-10.13	-8.54	-6.95	-6.31	-5.68	-5.07	-4.49	-3.91	-2.84	-1.70	-1.51	-1.84	-3.03	-3.59
P	-11.57	-10.32	-9.08	-7.82	-6.41	-5.70	-4.91	-4.21	-3.87	-3.75	-3.65	-3.64	-3.63	-3.64	-3.81	-4.44
S	-8.90	-7.29	-5.68	-4.09	-2.66	-2.23	-1.95	-1.79	-1.74	-1.77	-1.83	-1.85	-1.85	-1.86	-1.91	-2.23
CL	-11.50	-9.64	-8.19	-7.00	-5.82	-5.35	-4.89	-4.45	-4.05	-3.74	-3.60	-3.57	-3.57	-3.56	-3.57	-3.58
K	-3.98	-3.87	-3.79	-3.78	-3.83	-3.95	-4.25	-4.73	-5.28	-5.99	-6.79	-7.49	-7.94	-8.51	-9.20	-9.01
CA	-4.419	-3.42	-2.88	-2.57	-2.51	-2.50	-2.50	-2.51	-2.55	-2.68	-3.13	-4.00	-4.79	-5.70	-6.75	-6.92
SC	-19.35	-17.19	-15.05	-12.93	-10.63	-9.75	-8.94	-8.18	-7.42	-6.62	-5.68	-4.73	-4.35	-4.32	-4.31	-4.32
TI	-12.05	-10.94	-9.86	-8.79	-7.72	-7.29	-6.86	-6.45	-6.07	-5.69	-4.97	-4.84	-5.50	-6.51	-7.69	-8.01
V	-9.37	-8.16	-7.12	-6.32	-5.65	-5.43	-5.26	-5.14	-5.08	-5.10	-5.14	-5.39	-6.03	-7.01	-8.18	-8.48
CR	-3.64	-3.51	-3.44	-3.39	-3.37	-3.37	-3.37	-3.38	-3.41	-3.48	-3.58	-3.82	-4.43	-5.42	-6.59	-6.89
MN	-3.94	-3.94	-3.94	-3.94	-3.94	-3.94	-3.95	-3.96	-3.99	-4.07	-4.15	-4.21	-4.47	-5.36	-6.65	-7.08
NI	-1.20	-1.20	-1.20	-1.20	-1.20	-1.20	-1.21	-1.22	-1.25	-1.33	-1.41	-1.45	-1.54	-2.17	-3.48	-4.00
FE	-3.75	-3.74	-3.74	-3.74	-3.74	-3.74	-3.75	-3.76	-3.79	-3.87	-3.95	-3.99	-4.06	-4.62	-5.86	-6.33
CU	-5.48	-5.46	-5.36	-5.34	-5.33	-5.33	-5.33	-5.34	-5.38	-5.45	-5.53	-5.57	-5.63	-6.13	-7.37	-7.86
BR	-11.52	-10.00	-8.66	-7.53	-6.74	-6.52	-6.36	-6.27	-6.25	-6.29	-6.36	-6.38	-6.38	-6.38	-6.39	-6.50
RB	-6.54	-6.37	-6.23	-6.21	-6.36	-6.58	-6.99	-7.51	-8.05	-8.74	-9.51	-10.17	-10.59	-11.12	-11.78	-11.56
SR	-9.40	-8.24	-6.56	-6.06	-6.01	-6.01	-6.01	-6.03	-6.10	-6.42	-7.23	-8.16	-8.88	-9.72	-10.68	-10.76
Y	-22.42	-19.95	-17.51	-15.08	-12.67	-11.70	-10.75	-9.82	-8.95	-8.06	-6.56	-6.01	-6.39	-7.23	-8.31	-8.53
ZR	-20.32	-18.21	-16.14	-14.17	-12.34	-11.65	-10.97	-10.33	-9.72	-9.12	-8.02	-6.86	-7.33	-8.34	-9.52	-9.84
I	-9.67	-8.27	-7.57	-7.42	-7.39	-7.38	-7.38	-7.39	-7.43	-7.50	-7.58	-7.61	-7.61	-7.62	-7.75	-8.30
BA	-13.00	-11.58	-9.51	-8.00	-7.26	-7.09	-7.02	-7.07	-7.35	-8.05	-8.98	-9.85	-10.48	-11.21	-12.08	-12.07
LA	-27.81	-24.92	-22.04	-19.16	-16.28	-15.13	-13.99	-12.81	-11.40	-10.78	-9.12	-9.11	-9.81	-10.63	-11.57	-11.65
CE	-28.11	-25.22	-22.34	-19.46	-16.58	-15.43	-14.29	-13.18	-12.14	-11.10	-9.63	-7.92	-8.28	-9.31	-10.51	-10.84
ND	-25.23	-22.56	-19.90	-17.25	-14.61	-13.56	-12.62	-11.80	-10.54	-9.55	-7.80	-7.93	-8.71	-9.66	-10.74	-10.95
LOG PG=5.0 ELECTRON H NUCLEI	-8.43 5.18	-7.22 5.18	-5.99 5.18	-4.78 5.18	-3.59 5.18	-3.12 5.18	-2.66 5.18	-2.21 5.18	-1.80 5.17	-1.38 5.16	-0.94 5.13	-0.59 5.06	-0.25 4.97	0.31 4.94	0.85 4.93	1.60 4.93
H	-3.10	-1.95	-0.79	0.37	1.53	2.00	2.47	2.94	3.41	3.87	4.31	4.67	4.88	4.93	4.93	4.93
LI	-8.77	-8.18	-7.49	-6.60	-6.20	-6.17	-6.16	-6.15	-6.16	-6.18	-					



TABLE 3 (CONTINUED)

THETA=	5.0	4.5	4.0	3.5	3.0	2.8	2.6	2.4	2.2	2.0	1.8	1.6	1.4	1.2	1.0	0.8
LOG PG=6.0 ELECTRON H NUCLEI	-8.01 6.18	-6.78 6.18	-5.55 6.18	-4.30 6.18	-3.10 6.18	-2.62 6.18	-2.14 6.18	-1.67 6.18	-1.21 6.18	-0.77 6.17	-0.32 6.16	0.13 6.13	0.52 6.06	0.95 5.97	1.57 5.94	2.21 5.93
H	-2.60	-1.45	-0.29	0.87	2.03	2.50	2.97	3.44	3.91	4.38	4.85	5.29	5.66	5.87	5.93	5.93
LI	-8.14	-7.49	-6.80	-5.94	-5.31	-5.22	-5.19	-5.17	-5.16	-5.17	-5.19	-5.32	-5.76	-6.53	-7.20	-7.88
BE	-17.40	-14.76	-11.82	-9.13	-6.67	-5.83	-5.24	-4.95	-4.82	-4.77	-4.76	-4.78	-4.84	-4.93	-4.97	-5.24
B	-23.96	-20.61	-16.94	-13.53	-10.28	-9.01	-7.79	-6.71	-5.84	-5.12	-4.46	-3.84	-3.21	-2.57	-2.48	-2.64
C	-24.94	-20.93	-17.35	-14.19	-11.17	-9.97	-8.76	-7.56	-6.35	-5.14	-3.94	-2.76	-1.51	-0.18	2.01	2.47
N	-17.42	-14.95	-12.48	-10.00	-7.53	-6.54	-5.55	-4.55	-3.55	-2.56	-1.56	-0.57	0.40	1.31	1.83	1.86
O	-16.71	-14.16	-11.77	-9.25	-6.64	-5.59	-4.54	-3.49	-2.43	-1.38	-0.32	0.74	1.71	2.22	2.47	2.70
F	-19.48	-16.14	-13.57	-11.48	-9.40	-8.54	-7.65	-6.76	-5.95	-5.19	-4.44	-3.69	-2.92	-2.06	-1.44	-1.32
NA	0.26	0.28	0.32	0.35	0.35	0.36	0.36	0.35	0.35	0.34	0.27	0.05	-0.53	-1.32	-1.95	-2.58
MG	0.81	1.35	1.60	1.64	1.65	1.65	1.65	1.65	1.65	1.65	1.64	1.61	1.54	1.41	1.03	0.10
AL	-6.31	-4.89	-3.36	-1.92	-0.57	-0.10	0.24	0.43	0.50	0.53	0.53	0.51	0.41	0.09	-0.47	-1.22
SI	-10.63	-8.99	-7.21	-5.55	-3.96	-3.33	-2.69	-2.06	-1.42	-0.78	-0.15	0.44	1.01	1.44	1.42	0.93
P	-8.97	-7.54	-6.19	-4.92	-3.69	-3.20	-2.71	-2.23	-1.77	-1.34	-1.00	-0.78	-0.67	-0.64	-0.64	-0.68
S	-8.83	-7.24	-5.66	-4.07	-2.46	-1.82	-1.19	-0.58	-0.01	0.48	0.85	1.08	1.17	1.16	1.14	1.13
CL	-11.12	-9.05	-7.15	-5.60	-4.36	-3.89	-3.41	-2.94	-2.47	-2.01	-1.56	-1.13	-0.79	-0.61	-0.57	-0.57
K	-1.18	-1.08	-0.95	-0.82	-0.78	-0.78	-0.79	-0.82	-0.91	-1.14	-1.52	-2.02	-2.71	-3.39	-3.87	-4.35
CA	-3.23	-3.21	-3.19	-3.17	-3.19	-3.22	-3.41	-3.66	-3.88	-4.09	-4.28	-4.45	-4.62	-4.78	-4.93	-5.08
SC	-17.06	-14.80	-12.24	-9.94	-7.82	-6.98	-6.15	-5.34	-4.57	-3.90	-3.39	-3.09	-3.03	-3.43	-3.19	-3.08
TI	-9.39	-8.47	-7.66	-6.96	-6.42	-6.29	-6.35	-6.42	-6.48	-6.55	-6.62	-6.69	-6.76	-6.83	-6.90	-6.97
V	-7.07	-5.79	-4.45	-3.35	-2.65	-2.43	-2.25	-2.11	-2.02	-1.97	-1.95	-1.96	-2.04	-2.31	-2.93	-3.82
CR	-1.85	-1.53	-1.25	-0.99	-0.77	-0.69	-0.63	-0.57	-0.52	-0.47	-0.45	-0.45	-0.51	-0.75	-1.34	-2.24
MN	-1.02	-1.00	-0.99	-0.99	-0.98	-0.98	-0.98	-0.97	-0.97	-0.97	-0.98	-1.00	-1.07	-1.20	-1.55	-2.44
NI	1.31	1.76	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.79	1.78	1.75	1.68	1.58	1.38	0.61
FE	-0.93	-0.83	-0.79	-0.77	-0.76	-0.76	-0.75	-0.75	-0.75	-0.75	-0.76	-0.79	-0.86	-0.96	-1.11	-1.75
CU	-3.50	-3.20	-2.93	-2.71	-2.55	-2.50	-2.46	-2.43	-2.40	-2.38	-2.38	-2.39	-2.45	-2.54	-2.67	-3.29
BR	-11.15	-9.38	-7.78	-6.40	-5.26	-4.88	-4.52	-4.20	-3.90	-3.65	-3.46	-3.34	-3.32	-3.36	-3.38	-3.39
RB	-3.79	-3.67	-3.47	-3.26	-3.20	-3.21	-3.24	-3.30	-3.46	-3.77	-4.19	-4.70	-5.35	-6.01	-6.45	-6.90
SR	-7.24	-6.46	-5.41	-3.98	-3.26	-3.15	-3.08	-3.04	-3.03	-3.02	-3.05	-3.20	-3.75	-4.62	-5.35	-6.10
Y	-20.13	-17.56	-14.70	-12.09	-9.66	-8.70	-7.73	-6.77	-5.82	-4.89	-4.06	-3.41	-3.00	-2.92	-3.23	-3.91
ZR	-18.03	-15.79	-13.31	-11.18	-9.34	-8.64	-7.96	-7.29	-6.63	-5.97	-5.33	-4.72	-4.10	-3.68	-4.26	-5.19
I	-9.51	-7.96	-6.48	-5.32	-4.76	-4.63	-4.54	-4.48	-4.45	-4.43	-4.42	-4.44	-4.50	-4.58	-4.61	-4.65
BA	-10.82	-9.81	-8.69	-7.72	-7.49	-7.41	-7.36	-7.32	-7.29	-7.27	-7.26	-7.25	-7.24	-7.23	-7.22	-7.21
LA	-25.83	-22.83	-19.53	-16.47	-13.57	-12.42	-11.28	-10.14	-9.01	-7.93	-6.95	-6.09	-5.30	-4.64	-4.23	-3.98
CE	-22.95	-20.17	-17.09	-14.26	-11.60	-10.55	-9.50	-8.45	-7.41	-6.38	-5.40	-4.59	-4.23	-4.67	-5.43	-6.29
LOG PG=7.0 ELECTRON H NUCLEI	-7.61 7.18	-6.37 7.18	-5.13 7.18	-3.86 7.18	-2.61 7.18	-2.13 7.18	-1.64 7.18	-1.16 7.18	-0.67 7.18	-0.20 7.18	0.27 7.17	0.75 7.16	1.22 7.13	1.66 7.07	2.22 6.98	2.88 6.94
H	-2.10	-0.95	0.21	1.37	2.53	3.00	3.47	3.94	4.41	4.89	5.36	5.83	6.28	6.65	6.87	6.93
LI	-7.49	-6.82	-6.18	-5.38	-4.54	-4.36	-4.27	-4.23	-4.20	-4.19	-4.19	-4.22	-4.36	-4.84	-5.54	-6.21
BE	-17.37	-14.91	-12.42	-9.60	-6.75	-5.79	-5.04	-4.52	-4.17	-3.96	-3.85	-3.80	-3.81	-3.86	-3.94	-4.04
B	-23.43	-20.26	-17.04	-13.50	-10.88	-9.54	-8.27	-6.99	-5.10	-4.29	-3.57	-2.91	-2.29	-1.75	-1.47	-1.51
C	-25.92	-21.73	-17.58	-13.68	-10.26	-9.00	-7.77	-6.56	-5.35	-4.14	-2.93	-1.73	-0.53	0.73	2.39	3.42
N	-16.97	-14.47	-11.99	-9.51	-7.03	-6.04	-5.05	-4.05	-3.05	-2.05	-1.05	-0.05	0.94	1.90	2.68	2.86
O	-16.73	-14.09	-11.47	-9.01	-6.59	-5.57	-4.53	-3.49	-2.43	-1.38	-0.32	0.74	1.80	2.76	3.27	3.66
F	-20.96	-17.40	-13.89	-10.99	-8.90	-8.07	-7.21	-6.33	-5.49	-4.70	-3.94	-3.20	-2.45	-1.69	-0.88	-0.39
NA	1.22	1.25	1.28	1.32	1.35	1.35	1.35	1.35	1.35	1.34	1.33	1.26	1.01	0.63	-0.27	-0.91
MG	1.20	1.90	2.36	2.59	2.64	2.64	2.65	2.65	2.65	2.64	2.64	2.63	2.60	2.53	2.33	1.70
AL	-5.80	-4.45	-3.09	-1.60	-0.09	0.44	0.89	1.20	1.37	1.45	1.49	1.50	1.49	1.38	1.02	0.41
SI	-9.64	-8.07	-6.50	-4.78	-3.01	-2.35	-1.70	-1.06	-0.42	0.22	0.85	1.46	1.99	2.37	2.48	2.30
P	-9.19	-7.49	-5.88	-4.38	-3.01	-2.50	-2.02	-1.57	-1.15	-0.76	-0.41	-0.10	0.13	0.29	0.35	0.35
S	-8.83	-7.22	-5.62	-4.03	-2.44	-1.80	-1.16	-0.53	0.09	0.69	1.22	1.66	1.97	2.12	2.14	2.14
L	-11.17	-9.00	-6.96	-5.21	-3.88	-3.40	-2.92	-2.45	-1.97	-1.50	-1.04	-0.58	-0.15	0.20	0.38	0.43
K	-0.18	-0.13	-0.03	0.12	0.21	0.21	0.21	0.20	0.17	0.09	-0.11	-0.47	-0.96	-1.60	-2.19	-2.68
CA	-2.95	-1.88	-1.00	-0.06	0.82	1.07	1.25	1.36	1.43	1.46	1.48	1.46	1.38	0.99	0.22	-0.99
SC	-16.03	-13.95	-11.84	-9.42	-6.92	-6.02	-5.14	-4.26	-3.57	-2.89	-2.38	-2.06	-1.94	-2.04	-2.60	-3.42
TI	-9.37	-8.32	-7.26	-6.04	-5.37	-5.31	-5.28	-5.28	-5.28	-5.28	-5.28	-5.28	-5.28	-5.28	-5.28	-5.28
V	-6.02	-4.91	-3.87	-2.67	-1.70	-1.44	-1.25	-1.11	-1.02	-0.97	-0.94	-0.93	-0.96	-1.06	-1.44	-2.18
CR	-1.34	-1.01	-0.71	-0.42	-0.14	-0.03	0.07	0.17	0.26	0.34	0.42	0.48	0.50	0.45	0.12	-0.59
MN	-0.15	-0.12	-0.09	-0.07	-0.06	-0.05	-0.04	-0.03	-0.03	-0.02	-0.01	-0.01	-0.03	-0.09	-0.27	-0.85
FE	1.50	2.45	2.77	2.80	2.80	2.80	2.80	2.80	2.80	2.80	2.79	2.78	2.75	2.68	2.55	2.13
NI	-0.23	0.02	0.11	0.17	0.20	0.21	0.22	0.23	0.23	0.24	0.24	0.23	0.21	0.14	0.02	-0.29
CU	-2.98	-2.66	-2.35	-2.07	-1.83	-1.74	-1.66	-1.59	-1.53	-1.48	-1.44	-1.42	-1.42	-1.46	-1.56	-1.84
BR	-11.08	-9.28	-7.57	-6.08	-4.95	-4.44	-4.05	-3.68	-3.36	-3.06	-2.76	-2.46	-2.16	-1.86	-1.56	-1.36
RB	-2.76	-2.70	-2.57	-2.35	-2.21	-2.21	-2.21	-2.23	-2.29	-2.43	-2.71	-3.10	-3.59	-4.21	-4.77	-5.23
SR	-6.43	-5.67	-4.88	-3.70	-2.61	-2.38	-2.22	-2.12	-2.07	-2.04	-2.04	-2.07	-2.27	-2.88	-3.68	-4.43
Y	-19.09	-16.71	-14.30	-11.57	-8.76	-7.73	-6.74	-5.77	-4.82	-3.89	-3.05	-2.38	-1.97	-1.83	-1.94	-2.36
ZR	-16.99	-14.94	-12.88	-10.58	-8.41	-7.67	-6.97	-6.29	-5.63	-4.97	-4.32	-3.69	-3.12	-2.66	-2.77	-3.53
I	-9.49	-7.92	-6.39	-5.02	-4.16	-3.96	-3.80	-3.67	-3.58	-3.51	-3.47	-3.45	-3.45	-3.50	-3.58	-3.62
BA	-9.97	-8.98	-7.93	-6.46	-4.96	-4.50	-4.09	-3.71	-3.39	-3.17	-3.08	-3.18	-3.59	-4.32	-5.07	-5.73
CE	-24.48	-21.68	-18.43	-15.65	-12.88	-11.63	-10.48	-9.33	-8.18	-7.06	-6.01	-5.08	-4.31	-3.87	-3.71	-3.87
ND	-21.91	-19.32	-16.89	-13.74	-10.71	-9.59	-8.51	-7.46	-6.41	-5.38	-4.38	-3.55	-3.14	-3.22	-3.82	-4.62
LOG PG=8.0 ELECTRON H NUCLEI	-7.33 8.18	-5.96 8.18	-4.68 8.18	-3.44 8.18	-2.16 8.18	-1.66 8.18	-1.16 8.18	-0.67 8.18	-0.18 8.18	0.32 8.18	0.81 8.18	1.30 8.17	1.81 8.16	2.33 8.14	2.86 8.07	3.53 7.98
H	-1.60	-0.45	0.71	1.87	3.03	3.50	3.97	4.44	4.91	5.39	5.87	6.34	6.81	7.26	7.65	7.87
LI	-6.95	-6.16	-5.46	-4.81	-4.04	-3.74	-3.52	-3.39	-3.32	-3.29	-3.27	-3.26	-3.28	-3.43	-3.49	-4.55
BE	-17.39	-14.87	-12.42	-9.96	-7.37	-6.28	-5.24	-4.47	-3.96	-3.56	-3.33	-3.04	-2.92	-2.88	-2.90	-2.97
B	-22.95	-19.71	-16.55	-13.36	-10.04	-8.62	-7.19	-5.86	-4.76	-3.82	-3.10	-2.37	-1.66	-1.02	-0.57	-

TABLE 4 FITTING COEFFICIENTS TO LOK KP

MOLECULE	A(0)	A(1)	A(2)	A(3)	A(4)	MOLECULE	A(0)	A(1)	A(2)	A(3)	A(4)
HH	1.2739E 01	-5.1172E 00	1.2572E-01	-1.4149E-02	6.3021E-04	MGCL	1.1318E 01	-4.2224E 00	2.1137E-01	-3.0174E-02	1.5480E-03
LTH	1.1782E 01	-3.4443E 00	3.2741E-01	-4.8456E-02	2.5336E-03	MGCL2	2.4666E 01	-8.9557E 00	2.6264E-01	-3.9593E-02	2.0922E-03
L10	1.2362E 01	-4.5737E 00	3.6095E-01	-5.0059E-02	2.6013E-03	CACL	1.2314E 01	-5.1814E 00	5.6532E-01	-8.2868E-02	4.2822E-03
L1F	1.449E 01	-6.859E 00	2.857E-01	-4.1622E-02	2.1577E-03	CACL2	2.4611E 01	-1.0617E 01	4.4397E-01	-7.0992E-02	3.7140E-03
L1C1	1.2014E 01	-5.7321E 00	2.5558E-01	-3.6937E-02	1.9054E-03	ACCL	1.1976E 01	-5.2228E 00	-1.0263E-02	3.9344E-03	-2.6236E-04
L1BR	1.2069E 01	-5.2789E 00	2.7930E-01	-4.0121E-02	2.0533E-03	ADCL	2.5274E 01	-1.1345E 01	1.8101E-01	-2.6949E-02	1.8245E-03
L1I	1.1937E 01	-4.5689E 00	2.7869E-01	-4.0036E-02	2.0486E-03	SIH3CL	4.8899E 01	-1.5218E 01	4.0856E-01	-3.518E-03	-7.1176E-04
L1OH	2.5122E 01	-1.0625E 01	5.0357E-01	-7.2141E-02	3.7183E-03	KH	1.1417E 01	-2.9459E 00	2.8707E-01	-4.0954E-02	2.0897E-03
BEH	1.1416E 01	-3.1385E 00	2.3509E-01	-3.2702E-02	1.6565E-03	KO	1.1940E 01	-4.0743E 00	4.4901E-01	-6.5741E-02	3.3940E-03
BEH2	2.4160E 01	-7.3693E 00	1.4740E-01	-2.0183E-02	1.0453E-03	KOH	2.4798E 01	-9.7458E 00	4.7803E-01	-6.7612E-02	3.4511E-03
BE0	1.2695E 01	-5.4813E 00	2.5206E-01	-3.5618E-02	1.8152E-03	CAH	1.1340E 01	-3.0144E 00	4.2349E-01	-6.1467E-02	3.1639E-03
BEF	2.5093E 01	-7.1310E 00	2.2863E-01	-3.8140E-02	1.6248E-03	CAO	1.2280E 01	-6.0525E 00	5.8284E-01	-8.5805E-02	4.4425E-03
BECL	1.1749E 01	-4.8045E 00	2.3793E-01	-3.5532E-02	1.7088E-03	CAS	1.2309E 01	-4.9728E 00	6.0546E-01	-8.8967E-02	4.5993E-03
BECL2	2.4864E 01	-1.0132E 01	1.4191E-01	-2.0619E-02	1.0798E-03	CAOH	2.4611E 01	-1.0911E 01	6.0803E-01	-8.7197E-02	4.4736E-03
BEOH	2.4521E 01	-1.0424E 01	2.8415E-01	-3.8203E-02	1.9178E-03	CA(OH)2	4.9549E 01	-1.9354E 01	4.5536E-01	-6.5841E-02	3.4252E-03
BE(OH)2	4.9720E 01	-2.0514E 01	1.1864E-01	-1.5389E-02	8.0412E-04	SCO	1.3747E 01	-8.6420E 00	4.8072E-01	-6.9670E-02	3.5747E-03
BH	1.2399E 01	-3.9819E 00	1.3174E-01	-1.6723E-02	8.1003E-04	SC02	2.6909E 01	-1.5824E 01	3.9999E-01	-5.9363E-02	3.0875E-03
BH2	2.3468E 01	-8.5831E 00	4.5053E-02	-3.9934E-03	1.7376E-04	SCS	1.3500E 01	-6.4640E 00	5.0458E-01	-7.3117E-02	3.7488E-03
BH3	3.7848E 01	-1.2113E 01	6.3985E-02	-6.6538E-03	1.0482E-04	TIC2	2.7018E 01	-1.3534E 01	4.5875E-01	-6.6158E-02	3.3834E-03
BO	1.3111E 01	-8.8640E 00	1.2714E-01	-1.6313E-02	7.9408E-04	TIC4	5.3496E 01	-2.6027E 01	3.3495E-01	-5.0249E-02	2.6337E-03
BO2	2.5766E 01	-1.4065E 01	3.4383E-02	-4.4398E-03	2.2852E-04	TIN	1.4033E 01	-6.4552E 00	5.3710E-01	-7.6826E-02	3.9056E-03
BS	1.2822E 01	-5.8147E 00	1.7034E-01	-2.3020E-02	1.1454E-03	TIO	1.3398E 01	-8.5956E 00	4.0973E-01	-5.7972E-02	2.9287E-03
BF	1.3080E 01	-8.2826E 00	1.2575E-01	-1.6313E-02	7.9645E-04	TIO2	2.7901E 01	-1.4031E 01	4.1256E-01	-6.1271E-02	3.1478E-03
BCL	1.2634E 01	-6.0398E 00	1.2536E-01	-1.6225E-02	7.8846E-04	TIS	1.3316E 01	-6.2216E 00	4.5829E-01	-6.4903E-02	3.7876E-03
HBO	2.5377E 01	-1.1824E 01	5.0180E-02	-5.3856E-03	2.5485E-04	TIF	1.2575E 01	-7.4975E 00	3.8424E-01	-5.6623E-02	2.9179E-03
HBO2	3.8934E 01	-1.9624E 01	9.8403E-02	-1.0894E-02	5.1783E-04	TIF2	2.5682E 01	-1.4600E 01	1.9921E-01	-2.9451E-02	1.5353E-03
C2	2.2804E 01	-6.4178E 00	9.7719E-02	-1.2739E-02	6.2603E-04	TICL	1.2305E 01	-5.6564E 00	3.8665E-01	-5.6760E-02	2.9204E-03
C3	2.5290E 01	-1.4445E 01	1.2547E-01	-1.7390E-02	8.8594E-04	TICL2	2.5157E 01	-1.0936E 01	1.1766E-01	-2.6875E-02	1.3754E-03
C4	1.2139E 01	-4.0760E 00	1.2768E-01	-1.5473E-02	7.2661E-04	TIOF	2.8068E 01	-1.4706E 01	5.9173E-01	-8.2933E-02	4.1629E-03
CH2	2.5052E 01	-8.4195E 00	8.2200E-02	-8.4261E-03	3.8461E-04	TIOCL	2.6387E 01	-1.2475E 01	4.0173E-01	-5.8149E-02	2.9758E-03
CH3	3.7198E 01	-1.3462E 01	8.7214E-02	-7.1230E-03	2.7670E-04	VC2	2.7279E 01	-1.3337E 01	3.6999E-01	-5.2661E-02	2.6894E-03
CH4	5.0777E 01	-1.7911E 01	1.4135E-02	-4.4553E-03	-3.0176E-04	VC4	5.3793E 01	-2.5670E 01	3.7307E-01	-4.1437E-02	2.2108E-03
C2H	2.5063E 01	-1.2291E 01	-1.9036E-02	4.4498E-03	-2.3073E-04	VO	1.3811E 01	-7.7520E 00	3.7056E-01	-5.1467E-02	2.5861E-03
C2H2	3.8184E 01	-1.7365E 01	2.1512E-02	-8.8961E-05	-8.2720E-05	VO2	2.7754E 01	-1.4040E 01	3.3613E-01	-4.8215E-02	2.4780E-03
C2H4	6.3500E 01	-2.3854E 01	-2.9033E-02	9.2219E-03	-4.9573E-04	CRH	1.2297E 01	-4.4505E 00	5.5079E-01	-7.1306E-02	3.6224E-03
C3H	4.0791E 01	-2.1345E 01	9.3377E-02	-1.3863E-01	7.4549E-03	CR2	2.6747E 01	-1.2469E 01	5.6737E-01	-8.1535E-02	4.0267E-03
C2-	2.3845E 01	-1.1852E 01	6.7867E-01	-8.8402E-02	4.2770E-04	CRH	1.9513E 01	-6.1702E 00	5.8789E-01	-8.4809E-02	4.3322E-03
CH-	2.2955E 01	-7.6855E 00	6.5284E-01	-8.3850E-02	4.0331E-03	CNO	1.3591E 01	-1.6834E 01	4.6809E-01	-6.0528E-02	3.2475E-03
N2	1.3590E 01	-1.0585E 00	2.2067E-01	-2.9997E-02	1.4993E-03	MNO	1.3246E 01	-5.4769E 00	4.1225E-01	-6.3093E-02	2.6066E-03
NH	1.2033E 01	-3.8435E 00	1.3629E-01	-1.6643E-02	7.8691E-04	MNS	1.3151E 01	-4.3821E 00	4.5737E-01	-6.6849E-02	3.4521E-03
NH2	2.4603E 01	-8.6300E 00	2.0048E-01	-2.4124E-02	1.1484E-03	FEO	1.2984E 01	-5.3318E 00	3.1745E-01	-4.4565E-02	2.524E-03
NH3	3.7554E 01	-1.3059E 01	1.2910E-01	-1.2338E-02	5.3429E-04	FES	1.3855E 01	-4.6198E 00	4.1556E-01	-5.9026E-02	2.9960E-03
CN	1.2805E 01	-8.2793E 00	6.4162E-02	-7.3627E-03	3.4666E-04	FEF	1.3057E 01	-5.8254E 00	3.7447E-01	-5.3035E-02	2.6903E-03
HCN	2.5635E 01	-1.3827E 01	1.3827E-01	-1.8124E-02	7.845E-04	PEF2	2.4970E 01	-1.0699E 01	2.3078E-01	-3.2535E-02	1.8581E-03
C2N	2.5666E 01	-1.4450E 01	1.5941E-01	-2.3830E-02	1.2585E-03	FECL	1.2148E 01	-4.0158E 00	3.4488E-01	-4.5908E-02	2.5088E-03
C2N2	4.1357E 01	-2.2172E 01	1.6700E-01	-2.3499E-02	1.2586E-03	FECL2	4.9585E 01	-2.9957E 01	2.9957E-01	-3.8825E-02	1.8575E-03
GN	1.2831E 01	-7.1964E 00	1.7349E-01	-2.3065E-02	1.1380E-03	FE(OH)2	4.9403E 01	-1.8136E 01	2.0682E-01	-3.0943E-02	1.6499E-03
HNO	2.5258E 01	-9.5542E 00	1.9462E-01	-2.4812E-02	1.2129E-03	NIH	1.2520E 01	-3.4331E 00	1.9630E-01	-2.5377E-02	1.2412E-03
CN-	2.4123E 01	-1.4422E 01	7.0477E-01	-9.2137E-02	4.4771E-03	NIO	1.3013E 01	-5.0171E 00	2.1076E-01	-2.8251E-02	1.4000E-03
OH	1.3228E 01	-5.5181E 00	6.9935E-02	-8.1511E-03	3.7970E-04	CUH	1.2152E 01	-3.9190E 00	3.0976E-01	-4.3389E-02	2.1933E-03
OH2	1.2371E 01	-5.0578E 00	1.3822E-01	-1.6547E-02	7.7224E-04	CUO	1.2176E 01	-4.2827E 00	2.0485E-01	-2.8217E-02	1.4075E-03
H2O	2.5420E 01	-1.0522E 01	1.6939E-01	-1.8368E-02	8.1730E-04	CUS	1.2511E 01	-4.2636E 00	3.7475E-01	-5.4068E-02	2.7545E-03
C2O	1.3820E 01	-1.1795E 01	1.7127E-01	-2.2888E-02	1.1349E-03	HR	1.2301E 01	-4.0444E 00	1.1751E-01	-1.3231E-02	6.1881E-03
CO2	2.7478E 01	-1.7098E 01	9.5012E-02	-1.2579E-02	6.4058E-04	NABR	1.1933E 01	-4.8744E 00	3.1557E-01	-4.2930E-02	2.3478E-03
C2O2	2.5724E 01	-1.4651E 01	4.6094E-02	-7.1122E-03	4.0529E-04	KBR	1.2088E 01	-5.1959E 00	4.2982E-01	-6.2876E-02	3.4383E-03
HCO	2.5363E 01	-1.3213E 01	1.8451E-01	-2.2973E-02	1.1114E-03	RBR	1.1294E 01	-4.3923E 00	1.0285E-01	-1.3374E-02	6.4687E-04
HCHO	3.3838E 01	-1.6397E 01	8.3773E-02	-7.4410E-03	3.1337E-04	MGR	1.1438E 01	-4.0782E 00	2.7446E-01	-3.9608E-02	2.0331E-03
OH-	2.3621E 01	-8.8212E 00	6.3799E-01	-8.0888E-02	3.8591E-03	MGBR2	2.4153E 01	-7.5523E 00	1.7436E-01	-2.6626E-02	1.4081E-03
HF	1.2444E 01	-6.0199E 00	-5.5059E-02	1.3363E-02	-8.1880E-04	CABR	1.2083E 01	-5.3048E 00	4.7701E-01	-6.9871E-02	3.6055E-03
NF	1.2187E 01	-5.8118E 00	2.7848E-01	-4.0864E-02	2.1223E-03	CABR2	2.3566E 01	-9.5378E 00	4.5884E-01	-6.9266E-02	3.6274E-03
KA	1.2448E 01	-6.3832E 00	4.2974E-01	-6.2720E-02	3.2339E-03	RBH	1.0602E 01	-1.7516E 00	-4.4476E-02	9.26461E-03	-5.4739E-04
MGF	1.1727E 01	-5.4169E 00	2.4672E-01	-3.5752E-02	1.8465E-03	RB	1.1654E 01	-5.6299E 00	1.0078E-01	-1.2876E-02	6.1709E-04
MGF2	2.5587E 01	-1.1733E 01	3.2973E-01	-5.0152E-02	2.6559E-03	RBCL	1.1366E 01	-4.8565E 00	1.0116E-01	-1.2629E-02	5.9743E-04
CAF	1.2357E 01	-7.1372E 00	5.6024E-01	-8.2266E-02	4.2527E-03	SRH	1.1827E 01	-3.6194E 00	6.7189E-01	-9.8927E-02	5.1226E-03
CAF2	2.4485E 01	-1.3238E 01	5.5677E-01	-8.1420E-02	4.1998E-03	SRO	1.2458E 01	-6.2098E 00	6.9168E-01	-1.0216E-01	5.2955E-03
ALF	1.2756E 01	-7.4947E 00	1.7507E-01	-2.4848E-02	1.2738E-03	SRS	1.2520E 01	-5.2793E 00	7.1405E-01	-1.0527E-01	5.4491E-03
ALOF	2.1300E 01	-1.3890E 01	2.5776E-01	-3.9461E-02	2.1030E-03	SRS	1.2318E 01	-7.2384E 00	5.6010E-01	-8.1994E-02	4.2281E-03
SIH3F	4.9315E 01	-7.282E 01	5.7304E-01	-1.2804E-02	-5.8634E-05	SRF2	2.4400E 01	-1.3345E 01	6.6768E-01	-9.8245E-02	5.0839E-03
NAH	1.1415E 01	-2.7508E 00	1.9646E-01	-2.7383E-02	1.3844E-03	SRCL	1.2231E 01	-5.7706E 00	6.7316E-01	-9.9303E-02	5.1241E-03
NAO	1.1799E 01	-3.8242E 00	3.3266E-01	-4.8423E-02	2.4970E-03	SRCL2	2.3875E 01	-1.1348E 01	5.7865E-01	-8.6621E-02	4.5257E-03
NAOH	2.4604E 01	-9.4104E 00	3.6408E-01	-5.0732E-02	2.5799E-03	SROH	2.4863E 01	-1.1153E 01	7.1421E-01	-1.0306E-01	5.2983E-03
MGO	1.1285E 01	-2.7164E 01	1.9658E-01	-2.7310E-02	1.3816E-03	SR(OH)2	4.9563E 01	-1.9535E 01	5.6241E-01	-8.1992E-02	4.2684E-03
MGO2											

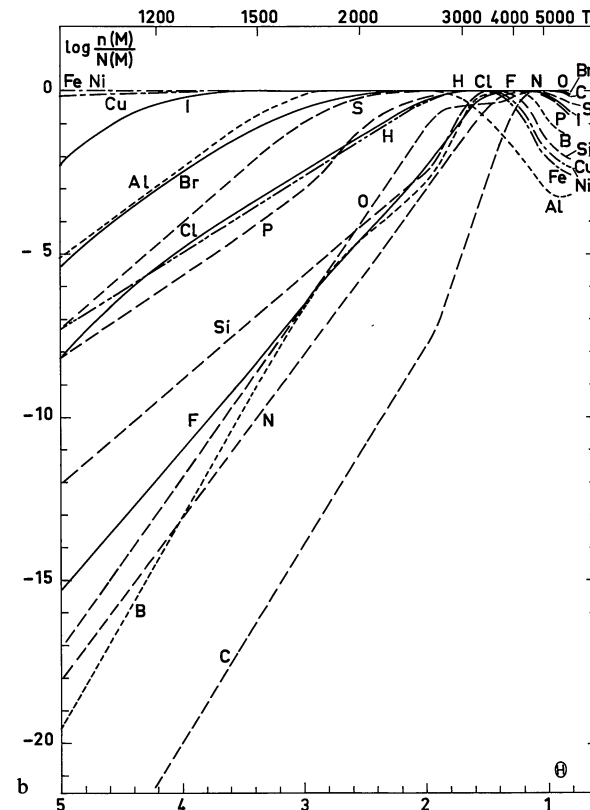
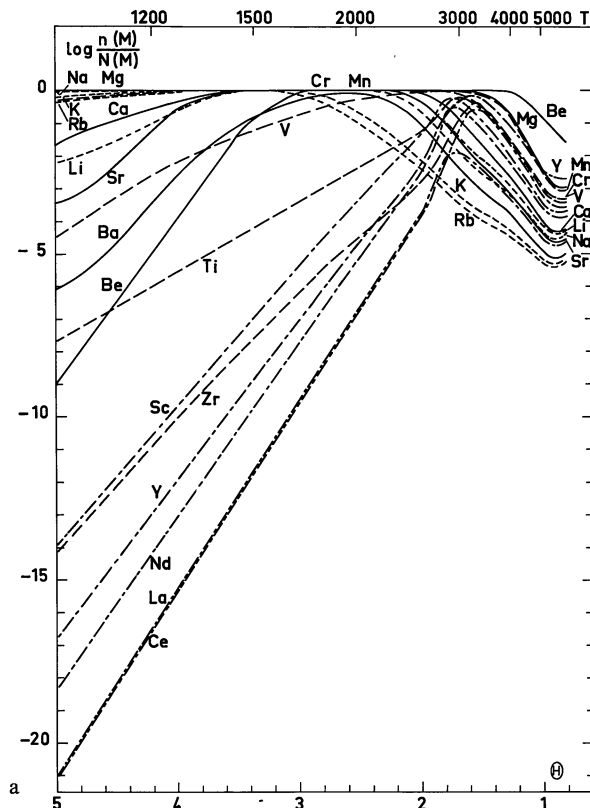


Fig. 1a and b. The values of  $\log n(M)/N(M)$ , where  $n(M)$  and  $N(M)$  are the number densities of free neutral atom and the fictitious number density of the nucleus of element  $M$ , respectively are plotted against the reciprocal temperature  $\theta = 5040/T$  for the case of the solar composition and  $\log P_g = 3.0$

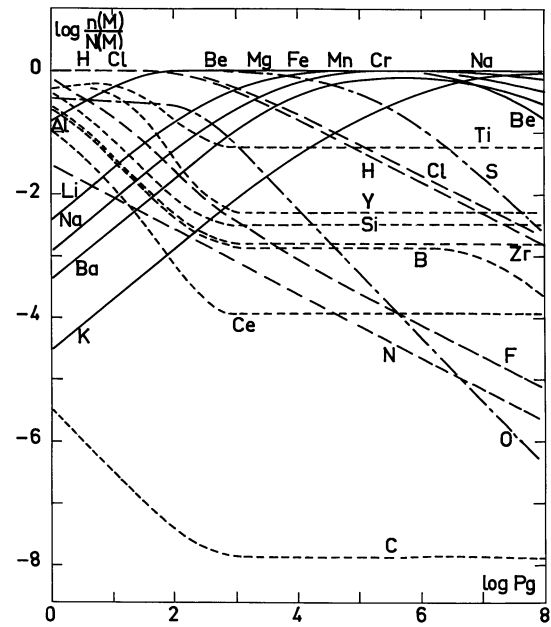


Fig. 2. The values of  $\log n(M)/N(M)$  are plotted against  $\log P_g$  for the case of the solar composition and  $\theta = 5040/T = 2.0$

metallic or non-metallic character, but the ones in Group III, IV, V, or VI. This can be understood by the fact that, in general, covalent bonding is relatively more stable than ionic bonding.

In Figs. 1a and 1b, it is also to be noted that, for each Group of metallic elements, the degree of molecular association is generally largest for heavier elements except for the lightest element that shows exceptional behaviour. In non-metallic elements, on the other hand, the degree of molecular association is smaller for heavier elements. These results correspond to the well known property of the periodic table that the elements at the lower left corner in the periodic table have the stronger metallic character while those at the upper right corner have the stronger non-metallic character.

The above conclusion is based on results for  $\log P_g = 3.0$ . To see the effect of the gas pressure on molecular association, we have plotted in Fig. 2 the value of  $\log n(M)/N(M)$  against  $\log P_g$ , at  $\theta = 2.0$  ( $T = 2520$  °K). Inspection of Fig. 2 reveals that the behaviour of  $\log n(M)/N(M)$  can be classified in several characteristic patterns as follows: a) inversely proportional to the gas pressure (O), b) inversely proportional to the square root of the gas pressure (H, N, F, Cl, etc. . .), c) independent of the gas pressure (B, C, Si, Ti, Zr, Y, Ce, etc. . .), and d) remaining almost zero except for the effect of ionization (Groups Ia, IIa, VIa, VIIa, VIII). The reason why different elements show such different behaviour again depends on the chemical property of each element or, more directly, on the major species of each element. Case a) is a rather special case which applies only to oxygen and sulphur at

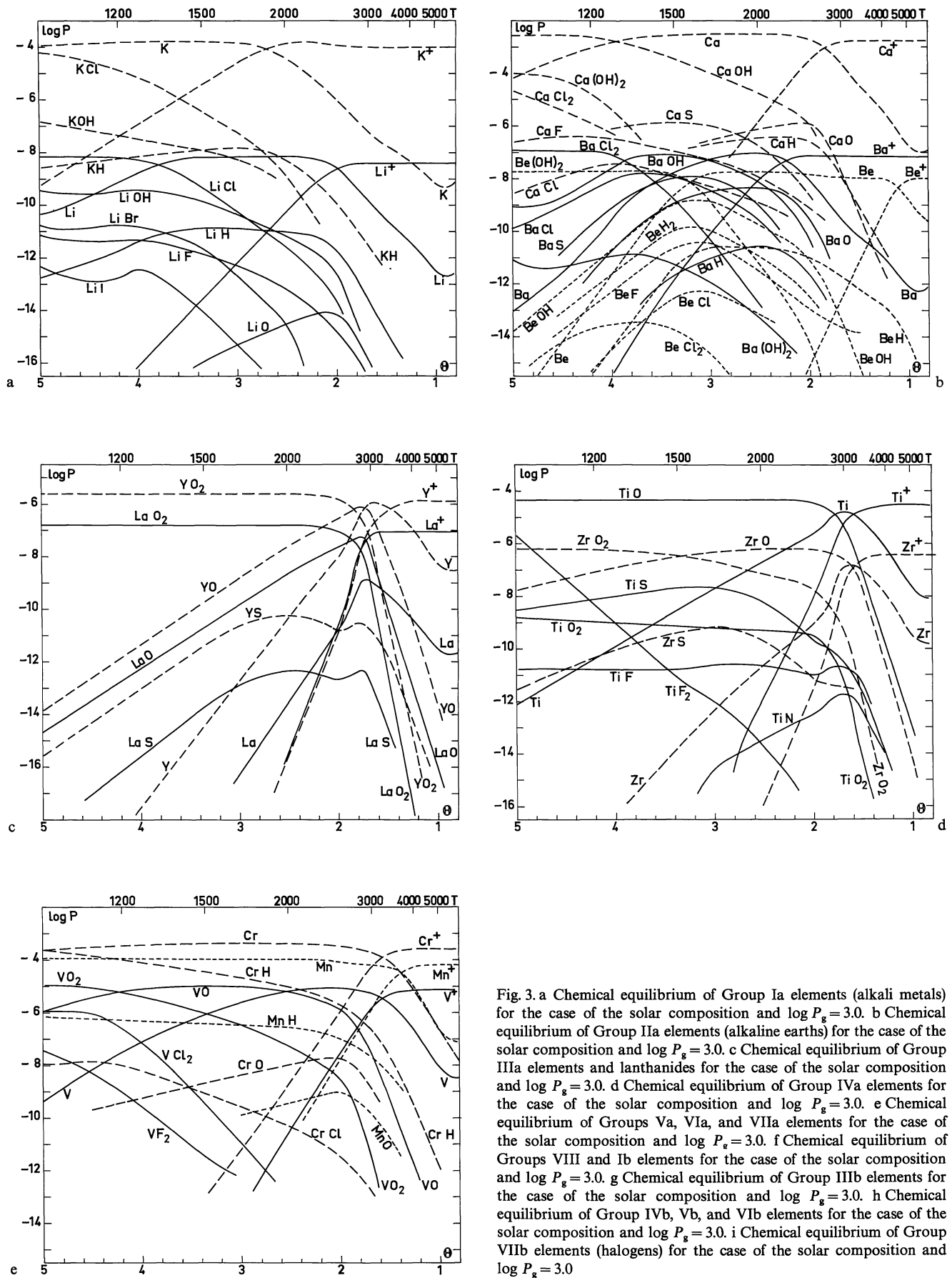
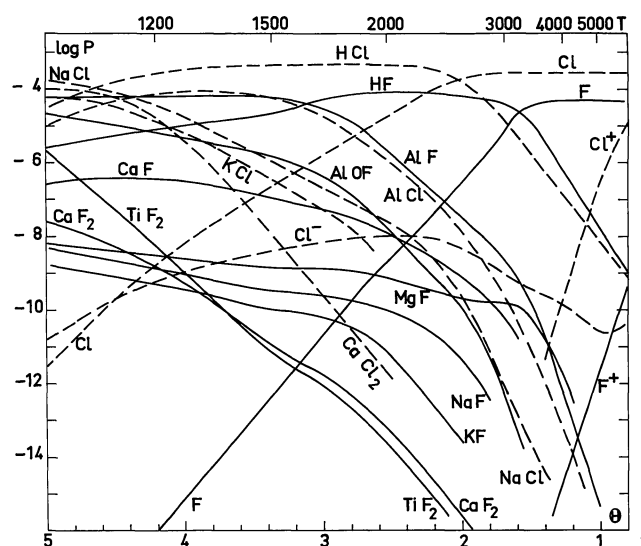
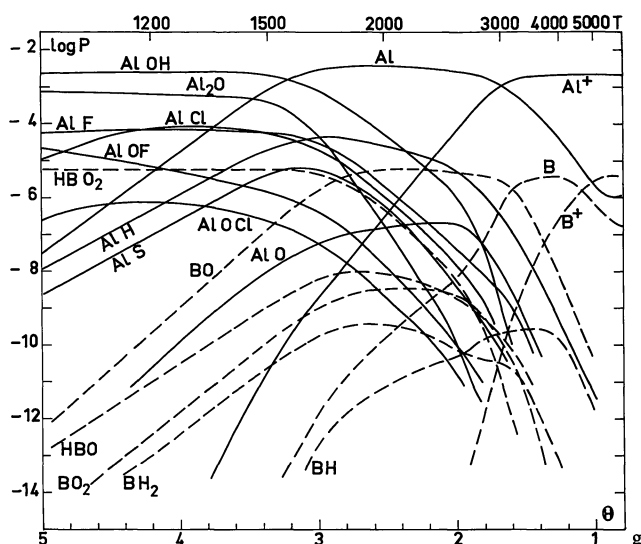


Fig. 3. a Chemical equilibrium of Group Ia elements (alkali metals) for the case of the solar composition and  $\log P_g = 3.0$ . b Chemical equilibrium of Group IIa elements (alkaline earths) for the case of the solar composition and  $\log P_g = 3.0$ . c Chemical equilibrium of Group IIIa elements and lanthanides for the case of the solar composition and  $\log P_g = 3.0$ . d Chemical equilibrium of Group IVa elements for the case of the solar composition and  $\log P_g = 3.0$ . e Chemical equilibrium of Groups Va, VIa, and VIIa elements for the case of the solar composition and  $\log P_g = 3.0$ . f Chemical equilibrium of Groups VIII and Ib elements for the case of the solar composition and  $\log P_g = 3.0$ . g Chemical equilibrium of Group IIIb elements for the case of the solar composition and  $\log P_g = 3.0$ . h Chemical equilibrium of Group IVb, Vb, and VIb elements for the case of the solar composition and  $\log P_g = 3.0$ . i Chemical equilibrium of Group VIIb elements (halogens) for the case of the solar composition and  $\log P_g = 3.0$ .





Some details of the equilibrium features that give the general conclusions above will now be discussed for

<sup>1)</sup> In contrast to the oxygen-rich atmospheres now under discussion, the equilibrium partial pressure of free carbon atoms is independent of the gas pressure in carbon-rich stars and the reason of this is given in Paper I. In the present case, we know that  $P_{\text{H}} \propto P_g^{1/2}$  and, as  $\text{H}_2\text{O}$  is the major species,  $P_{\text{H}_2\text{O}} \approx P(\text{O}) - P(\text{C}) \propto P_g$ . Thus, from the equilibrium equation for  $\text{H}_2\text{O}$ , we have  $P_{\text{O}} = K_p P_{\text{H}_2\text{O}}/P_{\text{H}}^2 \approx \text{independent of the gas pressure}$ . Then,  $n(\text{O})/N(\text{O}) \approx P_{\text{O}}/a(\text{O}) P_g \propto P_g^{-1}$ .

each group. The results are shown only for the case of  $\log P_g = 3.0$ , since the effect of the gas pressure can be inferred from the discussion above.

**Group Ia (Li, Na, K, Rb).** The results for the alkali metals are shown in Fig. 3a taking lithium and potassium as examples. It is found that the alkali metals are generally little affected by molecular formation. Though some halogen compounds are formed, they do not consume the atoms enough to effect the partial pressures of the neutral free atoms, except for Li. This result is obvious for Na which is more abundant than any of the halogens. But the results for K and Rb, which have abundances less than those assumed for some halogens, indicate that the chemical stability of alkali-halogen compounds is generally not sufficient to effect the equilibrium features in general. Only Li is appreciably locked up in halides, especially in LiCl, and this is because halogen compounds of Li are exceptionally stable (see Table 1). At higher gas pressure, hydroxyl compounds are as important as halides. Even at the higher pressures, however, alkali metals except Li remain mostly as free neutral atoms in the physical conditions of normal atmospheres in cool stars (see Table 3), and the reason for this is partly that the assumed abundance of the halogens is almost comparable to that of the alkali metals. If the abundance of the halogens is much larger than assumed, as in some hot stars, the effect of molecular association in alkali metals will also increase at higher gas pressure, since the major species are halides or hydroxyl compounds.

**Group IIa (Be, Mg, Ca, Sr, Ba).** The results for alkaline earth metals are shown in Fig. 3b for beryllium, calcium and barium. The major species of Be is  $\text{Be}(\text{OH})_2$ , those of Mg and Ca are  $\text{MgOH}$  and  $\text{CaOH}$ , respectively, and in Sr and Ba, dichlorides ( $\text{SrCl}_2$  and  $\text{BaCl}_2$ ) are also important. The effect of molecular formation is not very important in Mg and Ca, but it is increasingly important in Sr and Ba. Be shows exceptional behaviour in that the degree of molecular association is quite large, as was expected from the nature of the chemical bonds. While compounds of Group IIa metals, except for Be, are usually bound by ionic bonds, Be compounds have non-ionic bonds. At higher pressures, the effect of molecular formation generally increases, since the major species are halides and hydroxyl compounds.

**Group IIIa (Sc, Y) and Lanthanides (La, Ce, Nd).** The results for yttrium and lanthanum are shown in Fig. 3c. The elements of these groups are the most strongly locked up in molecules among all the metallic elements. The major species are always dioxides. It is to be noted, however, that no direct determination of the atomization energies for dioxides of Group IIIa metals and lanthanides is yet available and this is urgently needed. The atomization energies used are all estimated values as discussed in Section II. Nevertheless, the main conclusion – that dioxides are the major species in the

chemical equilibria of Group IIIa metals and lanthanides – should be correct. As expected, the degree of molecular association is larger in heavier elements (in order, Sc, Y and La) in Group IIIa. In lanthanides, the dissociation energies of monoxides given by Ames *et al.* (1967) show complicated differences between them, and these differences may be connected with the nature of the chemical bond which depends on the number of electrons in the unfilled 4f orbit. This fact suggests that the degree of molecular association may differ considerably among lanthanides and that no simple rule that depends on the atomic weight can be expected. In this Group, the major species are always oxides, even at very high pressures, and the degree of molecular association remains unchanged throughout the range of physical conditions considered (see Table 3). This comment is also valid for Groups IVa and Va.

**Group IVa (Ti, Zr).** The results for titanium and zirconium are shown in Fig. 3d. For Ti, the major species is the monoxide ( $\text{TiO}$ ), but for Zr, the dioxide ( $\text{ZrO}_2$ ) is more important than the monoxide ( $\text{ZrO}$ ) at very low temperatures. It is to be noted that the recent revision of the dissociation energy of  $\text{TiO}$  (7.2 eV) makes the monoxide more important than the dioxide. If we adopt the old value of  $D(\text{Ti}-\text{O}) = 6.8$  eV, the monoxide is less important than the dioxide at very low temperatures.

**Group Va (V).** Vanadium shows a behaviour similar to that of zirconium (Fig. 3e). The degree of molecular association of V, however, is smaller than that of Zr and even than that of Ti. The chemical equilibria of heavier elements of Group Va have not been calculated. From the results for Groups Ia–IVa, it is to be expected that the degree of molecular association should also be larger in the heavier elements in this Group (Nb, Ta). In fact,  $\text{TaO}$ , for example, is much more stable than  $\text{VO}$  (Gaydon, 1968).

**Group VIa (Cr).** In chromium, the formation of the oxide is greatly reduced and the hydride is the most abundant species (Fig. 3e). The degree of molecular association is also greatly reduced and atoms remain largely as free atoms. In this case and also in the Groups VIIa, VIII, and Ib, the effect of molecular formation is increasingly important at higher pressures, since hydrides are the major species in these Groups.

**Group VIIa (Mn).** In manganese, the formation of molecules is further reduced as compared with chromium. Though the hydride is the most abundant molecule formed from Mn, it does not consume any appreciable amount of Mn atoms, even not at very low temperatures at  $\log P_g = 3.0$  (Fig. 3e).

**Group VIII (Fe, Ni).** As has been shown above, the degree of molecular association continues to decrease from scandium to manganese in the transition elements. This tendency continues and ends at the transition

elements of Group VIII, which are least affected by molecular formation (Fig. 3f). Both iron and nickel, remain practically as free neutral atoms down to temperatures as low as 1000 °K. In the case of Fe, however, FeH was not considered in the equilibrium computation because of the lack of laboratory data. As hydrides are the most abundant species in the equilibria of transition elements neighbouring Fe, FeH may also be the most abundant compound in the equilibrium of iron compounds. At the same time, however, hydrides of Mn, Ni, Cu etc... are not abundant enough to consume any appreciable fraction of the atoms, at least at  $\log P_g = 3.0$ , and, accordingly even if FeH is appreciably abundant, it will not disturb the equilibrium features shown in Fig. 3f.

*Group Ib (Cu).* In the case of copper, which is the transition element of Group Ib, atoms are slightly consumed by forming the hydride (Fig. 3f).

*Group IIb (Zn).* For zinc, the computation was not carried out. Inspection of Table 1 indicates that the known compounds containing Zn are quite unstable and it is not likely that the effect of molecular formation is of any importance for Zn.

*Group IIIb (B, Al).* The chemical equilibria of boron and aluminum are again quite complicated (Fig. 3g). In boron, the major species is BO at relatively high temperatures and changes to the rather unfamiliar molecule HBO<sub>2</sub> at low temperatures. The high stability of this species, however, can be understood by the fact that the boron atom has a sp<sup>2</sup> hybrid configuration. The degree of molecular association of aluminum is considerably smaller than that of boron. The major species are AlOH and Al<sub>2</sub>O. In the heavier elements of Group IIIb (Ga, In and Tl) and also of Groups IVb – VIIb, the degree of molecular association may decrease in contrast to the behaviour of the Groups Ia – IVa metals. This fact can be inferred from the available dissociation energies as given by Gaydon (1968), and also from the general properties of the periodic table.

*Group IVb (C, Si).* Monoxides are the most stable compounds both for carbon and silicon (Fig. 3h, as to equilibrium features of C as well as of N and O, see Paper I). At very high pressures and low temperatures, SiH<sub>4</sub> is the major species of Si. This is quite consistent with the fact that CH<sub>4</sub> is the major species of carbon even in oxygen rich atmospheres at high pressures and low temperatures (Paper I).

*Group Vb (N, P).* For nitrogen, N<sub>2</sub> is the major species as is well known. On the other hand, the major species of phosphorus are PS, PO, PN, PH etc..., and P<sub>2</sub> is of no importance (Fig. 3h). At very high pressures, however, PH<sub>3</sub> and NH<sub>3</sub> are the major species of P and N, respectively.

*Group VIb (O, S).* For oxygen, CO, H<sub>2</sub>O, and OH are the major species. For sulphur, analogously, SiS, H<sub>2</sub>S and SH are the major species (Fig. 3h).

*Group VIIb (F, Cl, Br, I).* The major species are halogen hydrides but, at low temperatures, alkali halides and alkaline earth halides are the most important (Fig. 3i). At very high pressures, SiH<sub>3</sub>F and SiH<sub>3</sub>Cl are the major species. As the cosmic abundances of fluorine and chlorine are quite large according to Suess and Urey (1956), combinations with metals whose abundances are smaller than those of these halogens are of little importance in consuming an appreciable amount of the halogens. For this reason, only compounds including Al, Ca, Na and K are important for Cl and F. On the other hand, halogens of small abundance such as bromine and iodine may more easily be consumed by the many metals whose abundances are larger than those of Br and I. This effect, however, turns out to be unimportant because of the low chemical activity of Br and I, and only alkali halides and alkaline earth halides are important in addition to hydrides. The abundance of the negative chlorine ion, Cl<sup>-</sup>, is considerable, as has been noted previously by Vardya (1967). On the other hand, even though the electronegativity of F is larger than that of Cl, the abundance of F<sup>-</sup> is much smaller than that of Cl<sup>-</sup>. This is because the number of free fluorine atoms is much reduced for the reason given above.

*Ionization Equilibrium.* The ionization equilibrium in the atmosphere of cool stars is supposed to be fairly complicated. For example, Vardya (1966b) has shown that the effect of negative ions such as Cl<sup>-</sup> is important while Kandel (1967) has shown that alkali metals such as K and Na, which are the main electron sources in cool atmospheres, are largely locked in halides such as KCl and NaCl. In the evaluation of the electron pressures given in Table 3, all these effects have been taken into account. The alkali metals that supply most of the electrons, however, are in general little affected by molecular formation, as has been shown before. For example, at  $\log P_g = 6.0$  and  $\theta = 3.5$  ( $T = 1440$  °K),  $n(K)/N(K) = 0.896$ . The effect of this decrease of the free potassium atom on the electron pressure is still smaller, since the electron pressure is nearly proportional to the square root of the partial pressure of the electron source. At the same physical conditions,  $P_{Cl^-}/P_e = 0.05$  and  $P_{SH^-}/P_e = 0.03$  and the effect of negative ion formation on the electron pressure will be negligible. For the extreme case of  $\log P_g = 8.0$  and  $\theta = 5.0$  ( $T = 1008$  °K),  $P_{SH^-}/P_e = 4.85$  and  $P_{Cl^-}/P_e = 0.05$ . Even here, the decrease of free electrons due to negative ion formation is largely compensated for by the increasing ionization of alkali metals (at the same gas pressure), and the decrease of electron pressure due to SH<sup>-</sup> formation is  $\Delta \log P_e = -0.37$ .

It is to be noted that the physical conditions examined above may not actually be realized in normal stellar atmospheres, not even in the coolest dwarf stars. Consequently, the evaluation of the electron pressure by the simple method usually applied (e.g. Tsuji, 1966)



is justified for the numerical computation of model atmospheres or for spectral analysis. Only in the case of very peculiar dense stars, such as black dwarfs or the so-called red degenerate stars, is a detailed computation including the effect of molecular and negative ion formation necessary. These effects, however, are also sensitive to the halogen abundance and, if the halogen abundance is very large, they may be of some importance in the coolest dwarf stars as has been noted by Vardya (1966b) and by Kandel (1967).

## V. Chemical Equilibrium in Carbon-Rich Atmospheres

As is well known, the chemical equilibrium in gaseous systems in which carbon is more abundant than oxygen is characterized by a large reduction of free oxygen atoms, since oxygen atoms are mostly locked in CO. On the other hand, free carbon atoms are relatively more abundant than in oxygen-rich atmospheres. The problem then is to determine the effect of the large reduction of free oxygen on the chemical equilibria of other elements. For a large number of elements, oxygen compounds are the most important major species in oxygen-rich atmospheres, as has been shown in Section IV. The large reduction of free oxygen atoms in carbon-rich atmospheres naturally results in the decrease of the oxygen compounds. On the other hand, the  $C_2$  radical, which is more abundant in carbon-rich than in oxygen-rich atmospheres, has the chemical property of pseudo-oxygen (see Section II). Accordingly, it is expected that oxygen compounds in oxygen-rich atmospheres are replaced by carbon compounds such as metal dicarbides or metal tetracarbides in carbon-rich atmospheres.

To examine this possibility, we have made a calculation of the chemical equilibria in a carbon-rich mixture. The chemical composition assumed for the carbon-rich mixture is based on a preliminary result of an abundance analysis of the carbon star HD 156074 (Tsuji, 1972), and we assumed that carbon is overabundant by a factor of 4 as compared with the standard composition given in Table 2. The equilibrium features of the species composed of H, C, N and O are essentially the same as those reported in Paper I and need not be repeated here. In Fig. 4, the results for titanium and cerium are given for the case of  $\log P_g = 3.0$ . As is expected, the abundances of dicarbides ( $TiC_2$  and  $CeC_2$ ) are considerable at relatively high temperatures. At lower temperature, however, oxides such as  $TiO$ ,  $CeO$  and  $CeO_2$  are quite abundant even in the carbon-rich atmosphere. Thus,  $TiO$  is again the major species of Ti, and  $CeO$  and  $CeO_2$  are the major species of Ce. Both Ti and Ce remain almost as free atoms in the temperature range where dicarbides are abundant. As soon as oxides are the major species, the effect of molecular association on the concentration of free atoms becomes important. The degree of molecular

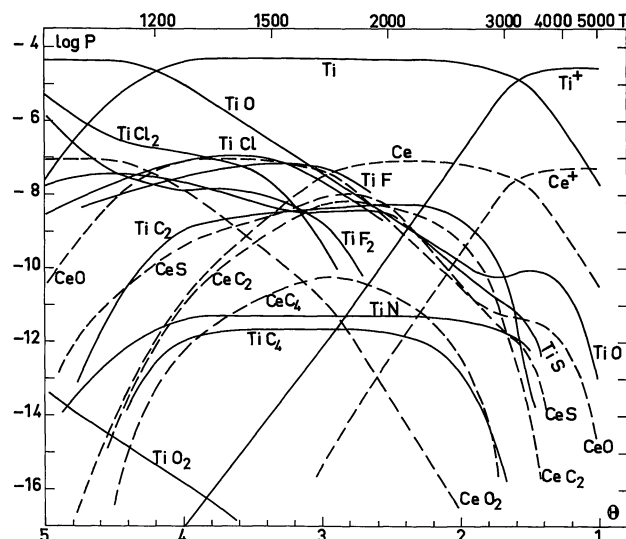


Fig. 4. Chemical equilibrium of titanium and cerium in carbon rich atmosphere of  $\log P_g = 3.0$

association, however, is definitely much smaller in carbon-rich atmosphere than in oxygen-rich atmosphere at the same temperature and gas pressure. This conclusion is valid for most of the elements since Ce is one of the elements for which the degree of molecular association is the largest in oxygen-rich atmospheres (Fig. 1a). Only for elements for which the major species are halides or hydrides, the degree of molecular association may be almost the same in oxygen-rich and carbon-rich atmospheres.

If we compare carbon-rich and oxygen-rich atmospheres of the same temperature and gas pressure, the partial pressure of free oxygen in oxygen-rich atmospheres is generally larger than the partial pressure of free carbon as well as of the  $C_2$  radical in carbon-rich atmospheres (Paper I). This is because carbon atoms are mostly locked up in several stable polyatomic molecules and little carbon is left as free atoms even in the carbon-rich atmospheres. Moreover, for any particular element M,  $D(M-O) > D(M-C_2)$  in general, as has been noted in section II. For these two reasons, a metal dicarbide in a carbon-rich atmosphere is much less abundant as compared to the corresponding metal monoxide in a oxygen-rich atmosphere. In fact, the chemical activity of oxygen is so high that oxides are more abundant than carbides even in carbon-rich atmospheres.

The decrease of free oxygen in carbon-rich atmospheres reveals some other effects that are rather masked in oxygen-rich atmospheres because of the very high chemical activity of oxygen. For example, it may be expected that a slight difference in the Si/S ratio, just like the C/O ratio, should result in a large difference in the equilibrium features of silicon and sulphur. This is due to the formation of SiS which is quite stable and also chemically analogous to CO. To show this effect, equilibrium features of silicon and sulphur in



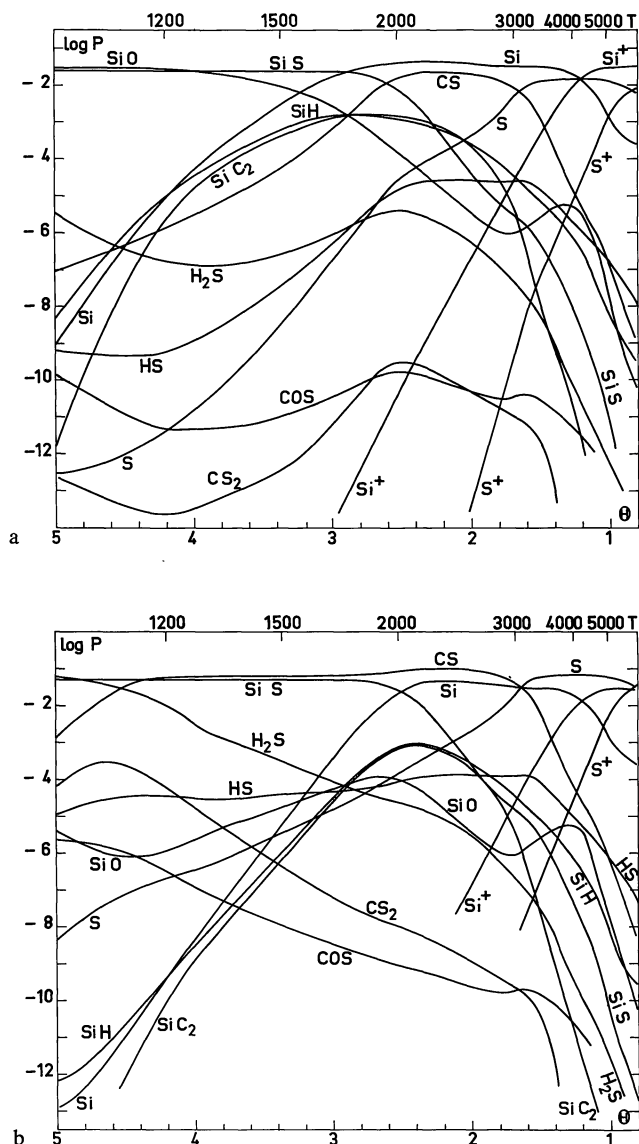


Fig. 5a. Chemical equilibrium of silicon and sulphur in carbon rich atmosphere of  $\text{Si} > \text{S}$  and  $\log P_g = 3.0$ . b Chemical equilibrium of silicon and sulphur in carbon rich atmosphere of  $\text{Si} < \text{S}$  and  $\log P_g = 3.0$

carbon-rich atmospheres of  $\log P_g = 3.0$  have been calculated for the case of  $\text{Si} > \text{S}$  and  $\text{Si} < \text{S}$ , and the results are shown in Figs. 5a and 5b, respectively. The  $\text{Si}/\text{S}$  ratio for the case of  $\text{Si} > \text{S}$  is the solar value of 2.2. In this case, Si remains mostly as neutral atoms until it becomes largely locked up in SiO at very low temperatures. Note that SiO is again the major species of Si even in a carbon-rich atmosphere. On the other hand, S is strongly locked up in SC and SiS and little free sulphur is left. Thus, the atmosphere is silicon-rich as well as carbon-rich. The  $\text{Si}/\text{S}$  ratio for the case of  $\text{Si} < \text{S}$  is assumed to be the reciprocal of the solar  $\text{Si}/\text{S}$  ratio and is 0.45. In this case, the free silicon atoms decrease rapidly as soon as SiS is formed. On the

other hand, even after large amounts of SiS and CS are formed, the partial pressure of free sulphur remains relatively high. Also, sulphur compounds such as CS,  $\text{CS}_2$ , HS,  $\text{H}_2\text{S}$  etc. are quite abundant in this case. Thus, the atmosphere is sulphur-rich as well as carbon-rich. The effects of variations in the  $\text{Si}/\text{S}$  ratio are, however, not important in oxygen-rich atmosphere because of the predominance of SiO which is more stable than SiS, irrespective of whether  $\text{Si} > \text{S}$  or  $\text{Si} < \text{S}$ .

## VI. Discussions and Conclusion

### a) Molecules in Stellar Atmospheres

In the sun and stars many molecules have already been found. Recent progress in observational work especially in the infrared spectral region has opened new possibilities of identifying a number of molecules not previously observed. Even in the photographic spectral region, there are still many possibilities of identifying new molecules.

In normal stellar atmospheres, metal oxides are generally the most stable molecules. Recently, the first overtone vibration-rotation band of SiO at  $4\mu$  has been identified in the M-supergiant star  $\alpha$  Orionis (Cudabach *et al.*, 1971) and this is consistent with the large abundance of SiO predicted by calculations. Generally speaking, many metal monoxides of the Group IIIa, IVa, Va, VIa metals and of the lanthanides have been observed in agreement with the calculated molecular abundances, and still more will be found in the future. For example, Davis and Keenan (1969) have suggested that NbO may be present in the S-type star R Geminorum. Though the dissociation energy of NbO is highly uncertain ( $D(\text{Nb}-\text{O}) = 7 \pm 2$  eV according to Gaydon, 1968) and the computation of the chemical equilibrium has not been carried out for niobium (Group Va), the general rule obtained in the present study suggests that  $\text{NbO}/\text{Nb}$  may be larger than  $\text{VO}/\text{V}$ . Some metal dioxides especially of Groups IIIa, IVa and of the lanthanides are also very abundant in an oxygen-rich atmosphere, but none of them is yet identified. It is also interesting to note that some metal monoxides can be observed even in the coolest carbon stars (see Fig. 4). Moreover, some metals, especially lanthanides, are oxidized to dioxides in oxygen-rich atmospheres, whereas monoxides are more abundant in very cool carbon stars than in normal stars. Some sulphur compounds such as SH, SiS,  $\text{H}_2\text{S}$  etc. are quite abundant both in oxygen-rich and in carbon-rich atmospheres. In the atmosphere of carbon stars, SC is also quite abundant. The infrared vibration-rotation transitions of such sulphur compounds could certainly be observed. Some metal sulphides such as AlS, TiS, FeS etc. can also be observed in very cool stars. The dissociation energy of a metal sulphide is

generally lower than that of the corresponding oxides. This does not mean, however, that a metal sulphide is always less abundant than the corresponding metal oxide, since the abundance of free oxygen atoms is generally lower than that of free sulphur atoms, oxygen atoms being chemically so active that they are mostly locked up in more stable molecules. Thus, the low dissociation energy of a metal sulphide is sometimes compensated for by the high abundance of sulphur atoms. The possibility of observing some metal sulphides is especially strong in carbon stars in which the abundance of metal sulphides is relatively high.

The dissociation energy of a metal nitride is almost comparable to that of the sulphide. The abundance of a metal nitride, however, is generally very low, since nitrogen is mostly locked up in the very stable  $N_2$  molecule. Accordingly, there is, in general, a low probability of detecting metal nitrides in stellar spectra. On the other hand, phosphorus, which is in the same Group as nitrogen in the periodic table, shows quite different equilibrium features. Instead of being locked in  $P_2$ , phosphorus is distributed in several active molecules such as PO, PH, PN, PS... and it would be interesting to try to observe such molecules in stellar spectra.

Some hydrides, especially of alkali and alkaline earth metals, have been observed in the solar and stellar spectra and the further possibility may exist of identifying some hydrides not only of Groups Ia and IIa, but also of Groups VIa, VIIa, VIII and Ib metals. For example, CuH has recently been identified in sunspot spectrum (Hauge, 1971). Also, hydroxyl compounds of alkalis, alkaline earths, and aluminum can be expected to be found.

The observation of some halides in stellar spectra is of particular interest, since halogens are quite abundant in the solar system while the observation of their atomic spectra is difficult, especially in cool stars. Recently, in the high resolution spectra taken by Connes by means of Fourier spectroscopy, some lines of the fundamental vibration-rotation band of HF were identified in  $\alpha$  Orionis and the HF/CO ratio is estimated to be about  $6 \times 10^{-4}$  (Spinrad *et al.*, 1970). The result shown in Fig. 3i indicates that most of the fluorine atoms are locked up in HF in the temperature range roughly between 1700 °K and 3000 °K ( $\log P_g = 3.0$ ). In the same physical conditions, almost all the carbon is locked up in CO (Paper I). Thus, the HF/CO ratio roughly represents the F/C ratio, or, as HF generally dissociates more easily than CO at lower pressures and/or at higher or lower temperatures, the HF/CO ratio generally gives a lower limit to the F/C ratio. There is also some possibility of identifying other metal halides especially of Groups Ia and IIa. So far, CaCl has been identified in a carbon star by Sanford (1942). Though calcium is mostly locked up in CaOH rather than in CaCl in a oxygen-rich atmosphere

(Fig. 3b), CaCl should certainly be more abundant in the atmosphere of carbon stars in which calcium will no longer be locked up in hydroxyl compounds.

In carbon stars, it is to be expected that many carbon compounds could be observed. In Paper I, we have suggested the possibility of observing several polyatomic carbon molecules such as HCN,  $C_2H_2$ ,  $CH_4$  etc... in the infrared spectra of cool carbon stars, and tentative identifications of some of them have been made recently (e.g. Connes *et al.*, 1968; Querci and Querci, 1970). Also, some metal carbides, especially dicarbides can be observed in carbon stars. One metal dicarbide,  $SiC_2$ , has long been known as the source of the so-called Merrill-Sanford bands (Kleman, 1956). Up to the present time, this is the only known metal carbide in stellar spectra. It is expected, however, that some of the other metal carbides especially those of Groups IIIa, IVa, Va, VIa metals and also of the lanthanides could be identified in the spectra of carbon stars. Though the thermochemical study of metal carbides has made considerable progress in recent years (see Section II), little spectroscopic data for them is yet available from the laboratory, and it is highly desirable that these data should be obtained in the near future.

An attempt to understand the behaviour of Merrill-Sanford bands in the spectra of carbon stars has been presented in Paper I, where we had not incorporated SiS in the equilibrium computations. The results were approximately correct for the case of  $Si/S > 1$ , but not correct for the case  $Si/S < 1$ . The computed  $SiC_2$  abundance increased towards cooler carbon stars while the observations show that there is a maximum  $SiC_2$  absorption at about C5 stars. This difficulty, however, is removed if we take SiS into account and if we further assume that  $Si/S < 1$  (see Fig. 5b). If this interpretation is correct, very cool carbon stars would be either silicon deficient or sulphur rich. The Merrill-Sanford bands, however, show a large variation in their intensity among carbon stars of the same spectral type, and they are extremely strong in some carbon stars of type about C5. If a large variation of  $SiC_2$  abundance is to be attributed to the difference in Si abundance itself, this difference would be unreasonably large! However, in this connection, it is interesting to remember that a slight change in the Si/S ratio results in a large change in the equilibrium features of Si in carbon-rich atmospheres. As has been shown in section V, if  $Si > S$ , a relatively large amount of free Si atoms are left to form  $SiC_2$ . On the other hand, if  $Si < S$ , most of the Si atoms are locked in SiS and little is left for  $SiC_2$ . In this way, only slight differences in the Si/S ratio are, so to speak, amplified by SiS formation and result in a large difference in the  $SiC_2$  abundance. Thus, a careful study of the Merrill-Sanford bands in carbon stars may reveal the presence of silicon-rich and sulphur-rich carbon stars.

### b) Interpretation and Quantitative Analysis of the Spectra of Cool Stars

The analysis of the chemical equilibrium for each element is important for a detailed interpretation and quantitative analysis not only of molecular spectra but also of atomic spectra of cool stars. The effect of molecular association on the observed atomic line intensity in the spectra of cool stars has been noted, for example by Merrill *et al.* (1962). They noted a weakening of zero-volt lines of Sc, Ti, V, Y and Zr in Mira, when its temperature decreased from maximum phase, and suggested that this might be a result of increased formation of oxides. Deutsch (1968) has also noted that Fe lines do not weaken down to the coolest M giant stars, while Ti lines show a considerable decrease in their intensities towards later spectral types, and has emphasised the importance of a detailed study of the effect of molecular association on atomic line intensities in the spectra of cool stars.

The behaviour of atomic line spectra noted above is quite consistent with the results outlined in Section IV. This problem has further been studied in detail, following the method of Cayrel and Jugaku (1963), by the calculation of theoretical line intensities based on model atmospheres of cool stars and it has been confirmed that molecular formation plays a dominant role in determining the spectral line intensities of cool stars (Tsuji, 1972). Furthermore, it turns out that the effect of molecular formation also produces complicated stratification effects in atomic line formation. Usually, atomic lines of an element easily locked up in molecules are formed in the layer of the stellar atmosphere where the atoms are released from the molecules because of the high temperature. On the other hand, atomic lines of the elements not easily associated in molecules are formed at the surface layer of the stellar atmosphere. Thus, the so-called excitation temperatures for atomic line formation are generally higher for the elements easily bound in molecules than for the elements chemically inactive.

For the elements that are very strongly bound in molecules, atomic lines may even not be observed at all especially in the coolest M-dwarf stars. This may be the case for lanthanides, Zr, Si etc. . . It is also interesting to consider this possibility for the case of lithium whose atomic line intensities rapidly decrease towards later spectral types and almost disappear in M-dwarf stars. It is true that considerable amounts of Li are locked in molecules especially in halides, at temperatures below about 1500 °K. It is, however, not likely that this effect alone could account for the observed decrease of the Li line strengths towards cooler main sequence stars, and Li atoms may be really deficient in the atmospheres of cool dwarf stars, as is generally accepted. In interstellar space, however, Li may be locked in molecules or in solids (salts). In the case of beryllium and boron, the effect of molecular formation

is more important than for lithium at the physical conditions in the atmospheres of cool stars.

Also, the effect of molecular formation may be important in comparative studies of chemical abundances in M, S and C type stars. The so-called s-process elements that show abundance anomalies in S or C type stars are also the elements that are strongly locked up in molecules in M stars. This fact suggests that molecular association may produce some apparent anomalies in observed atomic spectra. Certainly, simultaneous analysis of atomic and molecular spectra will be necessary to solve such a problem.

### c) Chemical Equilibrium in Stellar Atmospheres and Envelopes

It is well known that the abundance ratios of some elements, especially the oxygen to carbon ratio, has a decisive effect upon the chemical equilibrium in stellar atmospheres. The sulphur to silicon ratio in carbon-rich atmospheres plays an analogous role to the oxygen to carbon ratio. For most other elements, however, the equilibrium feature is well correlated with the chemical property of each element in the periodic table and the relative abundances do not generally seem to play as critical a role as the O/C ratio. The equilibrium feature of each element is generally determined by several major species which are the most stable compounds containing that element. The most important problem then is to know the major species for each element. Until now, it seems that the compounds considered in chemical equilibria have been chosen rather arbitrarily. For this reason, in the present study we have made a careful survey of the species which ought to be considered in equilibrium calculations.

The results obtained in the present study may still be invalid if some major species have been omitted. It is true that thermochemical data are still missing for many compounds listed in Table 1. This fact, however, does not mean that our results will be seriously effected, because the species for which atomization energies are not available in Table 1 are not major species. For example, dissociation energies of metal sulphides and metal nitrides are not known for many compounds, but it is not likely that these sulphides and nitrides are the major species of the metal concerned, since, in no case studied so far, are sulphides and nitrides the major species for a normal chemical composition. There is also the possibility that some species not considered at all in the present study are the major compounds of some elements. However, the consistency of our results for many elements and the fact that the results obtained correspond well to the chemical properties of the elements in the periodic table suggest that they are not seriously in error.

We stopped our computations at a temperature of 1000 °K. At lower temperatures or even at higher



temperatures than 1000 °K, the formation of solid particles or liquid droplets should be of some importance. Thus our results might represent a pseudo-equilibrium which is unstable against phase changes in some cases. The problem of condensation in cool stellar atmospheres has been discussed recently by several authors. For example, Fix (1970) has suggested that VO, TiO<sub>2</sub> and ZrO<sub>2</sub> are supersaturated in the atmospheres of cool stars, while Gilman (1969) has indicated that more complex compounds might be important. We have not explicitly examined the problem of condensation, but the possibility of precipitation of solid metal carbides, sulphides, nitrides and halides should also be investigated, since these metal solids are well known and quite stable.

Though the effect of the formation of solids is not taken into account in our calculations, our results for very low temperatures (near 1000 °K) might be of some use in the study of the physical and chemical conditions in very cool objects such as infrared stars. Also, a detailed analysis of the chemical equilibrium of each element might be important in the study of the chemical history of pre-planetary systems or of pre-stellar gaseous nebulae. Recently, Tomley, *et al.* (1970) have suggested that the abundance anomaly in the peculiar silicon star HD 34452 shows some correlation with the chemical properties of the elements in the sense that the elements easily locked up in molecules are overabundant. They suggest that the surface composition of the star might represent the chemical composition of condensed matter at a pre-stellar stage. In this connection, we note that lanthanides are most strongly bound in molecules, and that some elements of the lanthanide group are substantially overabundant in many peculiar stars of a relatively young population. Thus, a detailed study of the chemical equilibrium for each element should be useful for our understanding of the spectra not only of cool stars but also of some hot stars.

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## References

- Ames, L.L., Walsh, P.N., White, D. 1967, *J. Phys. Chem.* **71**, 2707.  
 Bashek, B., Garz, T., Holweger, H., Richter, J. 1970, *Astron. & Astrophys.* **4**, 229.  
 Balducci, G., Capalbi, A., De Maria, G., Guido, M. 1965, *J. Chem. Phys.* **43**, 2136.  
 Balducci, G., Capalbi, A., De Maria, G., Guido, M. 1968, *J. Chem. Phys.* **48**, 5275.  
 Balducci, G., Capalbi, A., De Maria, G., Guido, M. 1969, *J. Chem. Phys.* **50**, 1969.  
 Bautista, R.G., Margrave, J.L. 1963, *J. Phys. Chem.* **67**, 2411.  
 Berry, R.S. 1969, *Chem. Rev.* **69**, 533.  
 Brewer, L., Rosenblatt, G.M. 1961, *Chem. Rev.* **61**, 257.  
 Brewer, L., Somayajulu, G.R., Brackett, E. 1963, *Chem. Rev.* **63**, 111.  
 Cayrel, R., Jugaku, J. 1963, *Ann. Astrophys.* **26**, 495.  
 Chao, J. 1965–1968, JANAF Thermochemical Tables and its addenda, Clearinghouse, Springfield-Virginia.  
 Chupka, W.A., Berkowitz, J., Giese, C.F., Inghram, M.G. 1958, *J. Phys. Chem.* **62**, 611.  
 Connes, P., Connes, J., Bouigue, R., Querci, M., Chauville, J., Querci, F. 1968, *Ann. Astrophys.* **31**, 485.  
 Coppens, P., Smoes, S., Drowart, J. 1967, *Trans. Farad. Soc.* **63**, 2140.  
 Cotton, D.H., Jenkins, D.R. 1968, *Trans. Farad. Soc.* **64**, 2988.  
 Cudaback, D.D., Gaustad, J.E., Knacke, R.F. 1971, *Astrophys. J. Letters* **166**, L 49.  
 Davis, D.N., Keenan, P.C. 1969, *Publ. Astron. Soc. Pacific* **81**, 230.  
 De Maria, G. 1968, in *Proceeding of the first International Conference on Material Science* (in press).  
 De Maria, G., Balducci, G., Capalbi, A., Guido, M. 1967, *Proc. Brit. Ceram. Soc.* **8**, 127.  
 De Maria, G., Guido, M., Malaspina, L., Pesce, B. 1965, *J. Chem. Phys.* **43**, 4449.  
 Deutsch, A.J. 1968, Private communication.  
 Dibeler, V.H., Liston, S.K. 1968, *J. Chem. Phys.* **48**, 4765.  
 Dolan, J.F. 1965, *Astrophys. J.* **142**, 1621.  
 Fix, J.D. 1970, *Astrophys. J.* **161**, 359.  
 Fujita, Y. 1939, *Jap. J. Astron. Geophys.* **17**, 17.  
 Fujita, Y. 1940, *Jap. J. Astron. Geophys.* **18**, 45.  
 Fujita, Y. 1941, *Jap. J. Astron. Geophys.* **18**, 177.  
 Garz, T., Holweger, H., Koch, M., Richter, J. 1969, *Astron. & Astrophys.* **2**, 446.  
 Gaydon, A.G. 1968, *Dissociation Energies*, 3rd ed., Chapman and Hall, London.  
 Gilman, R.C. 1969, *Astrophys. J. Letters* **155**, L 185.  
 Gingerich, K.A. 1968a, *J. Chem. Phys.* **49**, 14.  
 Gingerich, K.A. 1968b, *J. Chem. Phys.* **49**, 19.  
 Goldberg, L., Müller, E., Aller, L.H. 1960, *Astrophys. J. Suppl.* **5**, 1.  
 Grevesse, N. 1968, *Solar phys.* **5**, 159.  
 Hauge, O. 1971, *Astron. & Astrophys.* **10**, 73.  
 Hauge, O., Engvold, O. 1968, *Astrophys. Letters* **2**, 235.  
 Herzberg, G. 1945, *Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of polyatomic Molecules*, D. Van Nostrand Co. Inc. Princeton-New Jersey.  
 Herzberg, G. 1967, *Molecular Spectra and Molecular Structure. III. Electronic Spectra and electronic Structure of polyatomic molecules*, D. Van Nostrand Co. Inc. Princeton-New Jersey.  
 Hildenbrand, D.L. 1968, *J. Chem. Phys.* **48**, 3657.  
 Kalf, P.J., Alkemade, C.Th.J. 1970, *J. Chem. Phys.* **52**, 1006.  
 Kandel, R. 1969, *Ann. Astrophys.* **30**, 439.  
 Kent, R.A., Ehbort, T.C., Margrave, J.L. 1964, *J. Am. Chem. Soc.* **86**, 5090.  
 Kent, R.A., Margrave, J.L. 1965, *J. Am. Chem. Soc.* **87**, 3582.  
 Kleman, B. 1956, *Astrophys. J.* **123**, 162.  
 Kohl, F.J., Stearns, C.A. 1970a, NASA TN D-5646.  
 Kohl, F.J., Stearns, C.A. 1970b, NASA TN D-5719.  
 Lambert, D.L. 1968, *Monthly Notices Roy. Astron. Soc.* **138**, 143.  
 Lambert, D.L., Mallia, E.A., Warner, B. 1966, *Nature* **211**, 56.  
 Lambert, D.L., Warner, B. 1968a, *Monthly Notices Roy. Astron. Soc.* **138**, 181.  
 Lambert, D.L., Warner, B. 1968b, *Monthly Notices Roy. Astron. Soc.* **138**, 213.  
 Lambert, D.L., Warner, B. 1968c, *Monthly Notices Roy. Astron. Soc.* **140**, 197.  
 Marquert, J.R., Berkowitz, J. 1963, *J. Chem. Phys.* **39**, 283.



- McBride, B.J., Heimerl, S., Ehlers, J.G., Gordon, S. 1963, NASA SP-3001.
- Merrill, P.W., Deutsch, A.J., Keenan, P.C. 1962, *Astrophys. J.* **136**, 21.
- Morris, S., Wyller, A.A. 1967, *Astrophys. J.* **150**, 877.
- Novikov, M.M., Gurvich, L.V. 1966, *Opt. Spectr.* **19**, 76.
- O'Hara, D.A.G. 1970, *J. Chem. Phys.* **52**, 2992.
- Peach, J.V. 1968, *Monthly Notices Roy. Astron. Soc.* **139**, 403.
- Querci, M., Querci, F. 1970, *Astron. & Astrophys.* **9**, 1.
- Russell, H.N. 1934, *Astrophys. J.* **79**, 281.
- Sanford, R.F. 1942, *Publ. Astron. Soc. Pacific* **54**, 158.
- Shenyavskaya, E.A., Maltsev, A.A., Gurvich, L.V. 1966, *Opt. Spectr.* **21**, 374.
- Spinrad, H., Kaplan, L.D., Connes, P., Connes, J., Kunde, V.G., Maillard, J.P. 1970, Proceedings of the conference on late-type stars, Kitt Peak National Observatory Contribution No. 554, p. 59.
- Stearns, C.A., Kohl, F.J. 1969, NASA TN D-5027.
- Stearns, C.A., Kohl, F.J. 1970, NASA TN D-5653.
- Stearns, C.A., Kohl, F.J. 1971, NASA TM X-67844.
- Suess, H.E., Urey, H.C. 1956, *Rev. Mod. Phys.* **28**, 53.
- Swings, P. 1958, *Handbuch der Physik*, Ed. S. Flügge **50**, 109, Springer, Berlin · Göttingen · Heidelberg.
- Tomley, L.J., Wallerstein, G., Wolff, S.C. 1970, *Astron. & Astrophys.* **9**, 380.
- Tsuji, T. 1964, *Ann. Tokyo Astron. Obs.*, 2nd ser. **9**, 1.
- Tsuji, T. 1966, *Publ. Astron. Soc. Japan* **18**, 127.
- Tsuji, T. 1972, To be published.
- Vardya, M.S. 1966a, *Monthly Notices Roy. Astron. Soc.* **134**, 347.
- Vardya, M.S. 1966b, *Observatory* **86**, 32.
- Vardya, M.S. 1967, *Mem. Roy. Astron. Soc.* **71**, 249.
- Wahlbeck, P.G., Gilles, P.W. 1967, *J. Chem. Phys.* **46**, 2465.
- Warner, B. 1968, *Monthly Notices Roy. Astron. Soc.* **138**, 229.
- White, W.B., Johnson, S.M., Dantzig, G.B. 1958, *J. Chem. Phys.* **28**, 751.
- Wiehr, E., Stellmacher, G., Schröter, E.H. 1968, *Astrophys. Letters* **1**, 181.
- Zambov, K.F., Margrave, J.L. 1966, *J. Chem. Phys.* **45**, 3167.
- Zambov, K.F., Margrave, J.L. 1967, *J. Phys. Chem.* **71**, 2893.

T. Tsuji  
Department of Astronomy  
Faculty of Science  
University of Tokyo  
Bunkyo-ku, Tokyo 113  
Japan