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Research Note

Partition Functions and Equilibrium Constants for ScO, YO and LaO

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Partition functions and equilibrium constants for ScO, YO and LaO have been computed for temperatures between 1000—8000 °K in steps of 500 °K. It is assumed that the ground electronic state of all the three molecules is a doublet and the recent values for the spectroscopic constants and the dissociation energies have been used. The excited electronic states $A\,^2\Pi$ and $B\,^2\Sigma$ have also been considered and their contribution to partition function given.

Key words: partition function — equilibrium constant — cool stars

The oxides of Sc, Y and La are fairly abundant in the atmospheres of cool stars specially that of S- and C-stars (see e.g., Fujita and Tsuji, 1965). The electronic multiplicities of the ground state of ScO, YO and LaO have been uncertain and their dissociation energies not known accurately. Hence, it has been difficult to compute reliable values of partition functions and equilibrium constants for these molecules. Thanks to recent work, this can be accomplished now.

The recent work of Berg, Wharton and Klemperer (1965), of Kasai and Weltner (1965) and of Adams, Klemperer and Dunn (1968) has shown that the multiplicity of the electronic ground state of all the three molecules is a doublet.

Ames, Walsh and White (1967) have derived the dissociation energies by the third-law treatment of the Knudsen effusion data. They have also derived the dissociation energies for ScO and YO from the second- and third-law heats of the isomolecular reactions, taking the dissociation energy of the LaO as the standard; mean values from the three methods have been used for ScO and YO.

The vibrational spectroscopic constants have been taken from Herzberg (1950) and the rotational constants from Åkerlind (1962) and Adams *et al.* (1968).

The adopted values for the individual molecules are given in Table 1.

Partition Function

The internal partition function for a diatomic molecule AB can be written as (see e.g., Tatum, 1966)

$$Q_{AB} = \frac{1}{\sigma} \sum_i \tilde{\omega}_i \, e^{-T_i/kT} \sum_v^{v_{i,\max}} e^{-\varepsilon_{v,i}/kT} \sum_J^{J_{v,i,\max}} \cdot (2J+1)\, e^{-\varepsilon_{J,v,i}/kT} \, .$$

Here σ is the symmetry factor, which is unity for heteronuclear and two for homonuclear diatomic

Table 1. *Data for individual molecules*

Molecule	D_0^0(eV)	σ	State	g_e	T_e(cm^{-1})	ω_e (cm^{-1})	$\omega_e\, x_e$(cm^{-1})	B_e (cm^{-1})	$\alpha_e \times 10^3$ (cm^{-1})	$D_e \times 10^6$ (cm^{-1})
ScO	7.16	1	$B\,^2\Sigma$	2	20653	825.0	4.5	0.48308	3.4828	0.674
			$A\,^2\Pi$	4	16500	874.8	4.99	0.50230	3.7326	0.61
			$X\,^2\Sigma$	2	0	971.55	3.95	0.51340	2.8871	0.580
YO	7.45	1	$B\,^2\Sigma$	2	20800	765.0	7.75	0.3722	3.8713	0.38
			$A\,^2\Pi$	4	16500	810.8	2.88	0.3857	1.9077	0.35
			$X\,^2\Sigma$	2	0	852.5	2.45	0.3881	1.6033	0.32
LaO	8.38	1	$B\,^2\Sigma$	2	17890	732.9	1.84	0.3405	1.2575	0.25
			$A\,^2\Pi$	4	13100	755.3	2.13	0.3463	1.4100	0.31
			$X\,^2\Sigma$	2	0	811.6	2.23	0.3519	1.3891	0.26

molecules, $\tilde{\omega}_i$ is the statistical weight of electronic state i of energy T_i above the ground state, $\varepsilon_{v,i}$ is the vibrational energy relative to T_i of the vibrational level v in electronic state i and $\varepsilon_{J,v,i}$ is the rotational energy relative to $\varepsilon_{v,i}$ of rotational level J in vibrational level v of electronic state i. Following Vardya (1965) the summation is terminated just before $(T_i + \varepsilon_{v,i} + \varepsilon_{J,v,i})$ exceeds the dissociation energy; on this assumption, $J_{v,i,\max}$ and $v_{i,\max}$ are computed. In terms of spectroscopic constants

$$\varepsilon_{v,i}/hc = \omega_{0,i}\, v - \omega_{0,i}\, x_{0,i}\, v^2\,,$$

$$\varepsilon_{J,v,i}/hc = B_{v,i}\, J(J+1) - D_{v,i}\, J^2(J+1)^2,$$

where

$$\omega_{0,i} = \omega_{e,i} - \omega_{e,i}\, x_{e,i} + \frac{3}{4}\, \omega_{e,i}\, J_{e,i} + \ldots,$$

$$\omega_{0,i}\, x_{0,i} = \omega_{e,i}\, x_{e,i} - \frac{3}{2}\, \omega_{e,i}\, J_{e,i} + \ldots,$$

$$B_{v,i} = B_{e,i} - \alpha_{e,i}\left(v + \frac{1}{2}\right) + \ldots,$$

$$D_{v,i} = D_{e,i} + \ldots.$$

Here $\omega_{e,i}$, $\omega_{e,i}\, x_{e,i}$, etc. are the usual spectroscopic constants.

For the partition functions of atoms, one needs to consider only the electronic levels.

Equilibrium Constants

For a reaction of the type

$$AB \rightleftharpoons A + B$$

in equilibrium, the equilibrium constant can be written as (Tatum, 1966)

$$\log_{10} K_{AB}(T) \equiv \log_{10}\frac{p_A\, p_B}{p_{AB}} = -\frac{5040.39\, D_0^0}{T} + \frac{5}{2} \cdot \log_{10} T + \frac{3}{2}\log_{10}\mu + \log_{10}\frac{Q_A\, Q_B}{Q_{AB}} + 4.41405$$

where p's are partial pressures in dyn/cm^2, D_0^0 the dissociation energy in eV from the level relative to which electronic energies have been measured in computing Q_{AB}, μ is the reduced mass and T is the temperature in °K.

Atomic partition functions have been computed, using the energy levels as given in Moore's (1949, 1952, 1958) tables for energies up to 40000 cm^{-1}.

Molecular partition functions, Q, have been computed using the spectroscopic constants given in Table 1, and are listed in Tables 2, 3 and 4. Contributions Q_X, Q_A and Q_B, respectively, to the partition function by the electronic states X, A and B have also been given in the tables. As expected, only at high temperatures the contributions from excited state A become significant. The contribution from B to the total partition function is negligible in all cases considered.

These partition functions have been used using the dissociation energies as given in Table 1 to compute the equilibrium constants K_P; these are given in Tables 2, 3 and 4 for ScO, YO and LaO, respectively. These equilibrium constants should be far more reliable than those given earlier, say by Tsuji (1964).

For practical application, the following polynomial fits of the numerical values of the equilibrium constants as a function of $\theta = 5040.39/T$ will be

Table 2. *Partition functions and equilibrium constants for* ScO

T (°K)	Q_X	Q_A	Q_B	$\log_{10} Q$	$\log_{10} K_P$ (dyn/cm^2)
1000	3.6438 (3)	4.1344 (−7)	5.8402 (−10)	3.5616	−24.2764
1500	6.8337 (3)	2.1086 (−3)	2.1752 (−5)	3.8347	−12.0471
2000	1.1059 (4)	1.7846 (−1)	4.9790 (−3)	4.0437	− 5.9119
2500	1.6344 (4)	2.8384 (0)	1.4393 (−1)	4.2134	− 2.2184
3000	2.2714 (4)	1.9256 (1)	1.4546 (0)	4.3567	+ 0.2541
3500	3.0193 (4)	7.9545 (1)	7.9897 (0)	4.4812	2.0307
4000	3.8809 (4)	2.3961 (2)	2.9807 (1)	4.5919	3.3744
4500	4.8590 (4)	5.8254 (2)	8.5598 (1)	4.6925	4.4310
5000	5.9567 (4)	1.2158 (3)	2.0412 (2)	4.7852	5.2876
5500	7.1771 (4)	2.2663 (3)	4.2434 (2)	4.8719	5.9988
6000	8.5237 (4)	3.8755 (3)	7.9456 (2)	4.9538	6.6004
6500	1.0000 (5)	6.1941 (3)	1.3709 (3)	5.0317	7.1171
7000	1.1610 (5)	9.3772 (3)	2.2154 (3)	5.1062	7.5661
7500	1.3357 (5)	1.3580 (4)	3.3936 (3)	5.1777	7.9604
8000	1.5245 (5)	1.8955 (4)	4.9727 (3)	5.2465	8.3095

Table 3. *Partition functions and equilibrium constants for* YO

T(°K)	Q_X	Q_A	Q_B	$\log_{10} Q$	$\log_{10} K_P$ (dyn/cm^2)
1000	5.1252 (3)	5.3540 (−7)	6.2127 (−10)	3.7097	−27.4058
1500	9.7821 (3)	2.7884 (−3)	2.5624 (−5)	3.9904	−14.6673
2000	1.5983 (4)	2.3829 (−1)	6.2064 (−3)	4.2037	− 8.2753
2500	2.3760 (4)	3.8082 (0)	1.8654 (−1)	4.3759	− 4.4262
3000	3.3140 (4)	2.5891 (1)	1.9458 (0)	4.5207	− 1.8480
3500	4.4156 (4)	1.0700 (2)	1.0996 (1)	4.6461	+ 0.0062
4000	5.6839 (4)	3.2207 (2)	4.2157 (1)	4.7574	1.4101
4500	7.1224 (4)	7.8172 (2)	1.2433 (2)	4.8581	2.5154
5000	8.7345 (4)	1.6276 (3)	3.0422 (2)	4.9507	3.4122
5500	1.0524 (5)	3.0250 (3)	6.4818 (2)	5.0371	4.1569
6000	1.2495 (5)	5.1550 (3)	1.2419 (3)	5.1184	4.7869
6500	1.4651 (5)	8.2078 (3)	2.1886 (3)	5.1956	5.3276
7000	1.6996 (5)	1.2376 (4)	3.6051 (3)	5.2694	5.7973
7500	1.9534 (5)	1.7850 (4)	5.6180 (3)	5.3401	6.2093
8000	2.2269 (5)	2.4812 (4)	8.3585 (3)	5.4080	6.5737

Table 4. *Partition functions and equilibrium constants for* LaO

T(°K)	Q_X	Q_A	Q_B	$\log_{10} Q$	$\log_{10} K_P$ (dyn/cm^2)
1000	5.7983 (3)	8.3305 (−5)	4.4419 (−8)	3.7633	−32.1942
1500	1.1141 (4)	8.5397 (−2)	4.5194 (−4)	4.0469	−17.8258
2000	1.8272 (4)	3.2386 (0)	5.3989 (−2)	4.2619	−10.5733
2500	2.7227 (4)	3.1786 (1)	1.0546 (0)	4.4355	− 6.1819
3000	3.8041 (4)	1.5611 (2)	8.1925 (0)	4.5821	− 3.2289
3500	5.0748 (4)	5.1132 (2)	3.7226 (1)	4.7101	− 1.1023
4000	6.5386 (4)	1.2926 (3)	1.2027 (2)	4.8248	+ 0.5050
4500	8.1994 (4)	2.7386 (3)	3.0830 (2)	4.9296	1.7643
5000	1.0061 (5)	5.1136 (3)	6.7034 (2)	5.0269	2.7789
5500	1.2129 (5)	8.6928 (3)	1.2904 (2)	5.1182	3.6149
6000	1.4406 (5)	1.3752 (4)	2.2639 (3)	5.2043	4.3162
6500	1.6898 (5)	2.0563 (4)	3.6937 (3)	5.2861	4.9136
7000	1.9610 (5)	2.9385 (4)	5.6868 (3)	5.3639	5.4290
7500	2.2547 (5)	4.0470 (4)	8.3518 (3)	5.4382	5.8785
8000	2.5714 (5)	5.4052 (4)	1.1796 (4)	5.5092	6.2743

found useful:

$$\log K(\mathrm{ScO}) = +\,2.0510\times10^{-2}\,\theta^4 - 0.24620\,\theta^3 + 1.04696\,\theta^2 - 9.1882\,\theta + 13.726\,,$$

$$\log K\,(\mathrm{YO}) = +\,2.1725\times10^{-2}\,\theta^4 - 0.26239\,\theta^3 + 1.12580\,\theta^2 - 9.6602\,\theta + 12.262\,,$$

$$\log K\,(\mathrm{LaO}) = -\,2.2881\times10^{-2}\,\theta^3 + 0.26375\,\theta^2 - 9.5512\,\theta + 12.175\,.$$

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