TABLE IIIC-B1. IONIZATION AND DISSOCIATION TEMPERATURES

IONIZATION TEMPERATURES		DISSOCIATION TEMPERATURES	
Symbol	Θ_I (K)	Symbol	Θ_d (K)
He	$2.855 \cdot 10^5$	H_2	$5.20 \cdot 10^4$
Ne	$2.500 \cdot 10^5$	N_2	$4.18 \cdot 10^4$
A	$1.830 \cdot 10^5$	O_2	$5.90 \cdot 10^4$
H	$1.579 \cdot 10^5$	Cl_2	$2.87 \cdot 10^4$
N	$1.690 \cdot 10^5$	CH	$4.03 \cdot 10^4$
O	$1.582 \cdot 10^5$	CO	$12.9 \cdot 10^4$
Cl	$1.512 \cdot 10^5$	HCl	$5.15 \cdot 10^4$
C	$1.308 \cdot 10^5$	NO	$7.53 \cdot 10^4$
S	$1.203 \cdot 10^5$	OH	$5.11 \cdot 10^4$
Na	$0.596 \cdot 10^5$		

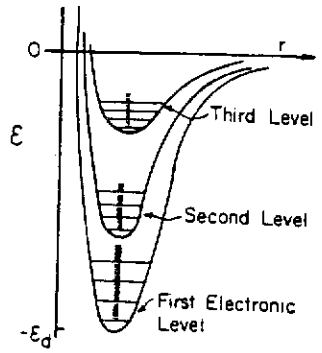

Fig. IIIC-B1. Electronic Levels of a Diatomic Molecule (Schematic)

smaller rotational levels above each vibrational level. If the temperature is increased sufficiently, electrons will be excited to higher electronic levels. But like the atom, molecular electron excitation is not appreciable unless the temperature is raised to a very high level. At sufficiently high temperatures the molecule will dissociate. For the diatomic molecule represented in Fig. IIIC-B1, the dissociation level is represented by the depth of the potential well corresponding to the lowest electronic level, ε_d. Values of the dissociation energy for several atoms are reported in units of temperature in Table IIIC-B1, $\theta_d = \varepsilon_d/k$. Notice that molecular dissociation temperatures are about one order smaller than atomic ionization temperatures. After the molecules have dissociated, further increases in temperature cause the atoms to ionize.

We are now equipped to discuss chemical reactions. When atoms (or molecules) are combined to produce new molecular species the principal energy change results from the dissociation energy. To study this change, we must first formulate the electronic partition function for the molecule. For purposes of discussion, we arbitrarily choose the unionized atoms in their lowest electronic energy level as the zero level of electronic energy. Then the electronic partition function of the molecule can be written in the standard infinite series formulation. However at normal temperatures this partition function can be evaluated using low temperature limit, $T << \theta_d$, as consisting of its first term

$$Z_{el|T<<\theta_D} = \sum_{\ell=1}^{\infty} g_{el,\ell}\, e^{-\varepsilon_{el,\ell}/kT} \approx g_{el,1}\, e^{\theta_d/T} \qquad \text{IIIC-B1)}$$

The partition function allows us to formulate the electronic contribution to molecular properties (based on an atomic reference level).

Exercise B1. Formulate an expression for the energy, entropy, and specific heat of the electronic mode of a gas in the low temperature limit. (Answer on Pg. 34.)

Exer. B1 shows that the electronic contribution to the energy of a gas is a constant proportional to the dissociation temperature.