Exmp. A2 reduced the limit test to a function of translational mode parameters alone, $N/Z_{tr} << 1$. When we use the expression for Z_{tr}

$$Z_{tr} = \bar{v}\left(\frac{2\pi m^* kT}{h^2}\right)^{3/2}$$

and its consequent equation of state (see Exmp. 5) $p\bar{v} = \bar{R}T$ or $p = n_v kT$ where n_v is the particle number density ($n_v \equiv N/V = N_A/\bar{v}$), we obtain

$$\left.\frac{n_j}{g_j}\right|_{max} \simeq \frac{N}{Z_{tr}} = n_v\left(\frac{h^2}{2\pi m^* kT}\right)^{3/2} = \frac{p}{(kT)^{5/2}}\left(\frac{h^2}{2\pi m^*}\right)^{3/2} \overset{?}{<<} 1 \qquad \text{(IIIC-A2)}$$

APPENDIX IIIC-B

IONIZATION, DISSOCIATION, AND CHEMICAL ENERGY

The development in the unit was restricted to the consideration of pure substances in which the subject molecule (or atom) remained unaltered. In our brief consideration of the electronic mode (based on the one electron hydrogen atom), we concluded that this mode is not excited at ordinary temperatures, $T << \theta_{el}$ Thus it normally contributes little more than a constant to the properties of a molecular gas. It was on this basis that we ignored the electronic mode within the body of the unit.

I. IONIZATION

When the temperature of a gas composed of hydrogen atoms is increased toward $\theta_{el,H}$, the electron of many of the atoms is excited to higher energy levels (or to larger Bohr

Ans. A1. The result of Exmp. A1 can be written as the difference of two integrals. The second is negligible in the limit $T >> \theta_{tr}$ and the first is available from Table IIIE-1.

$$Z_{tr} = \frac{\pi}{2}\left(\int_0^\infty q^2 e^{-q^2\theta_{tr}/T} dq - \int_0^{\sqrt{3}} q^2 e^{-q^2\theta_{tr}/T} dq\right) = \frac{\pi}{2}\frac{1}{4}\left[\pi\left(\frac{T}{\theta_{tr}}\right)^3\right]^{\frac{1}{2}} = \frac{1}{8}\left(\frac{\pi T}{\theta_{tr}}\right)^{3/2}$$

Ans. A2. The energy is defined as $\varepsilon = k\theta_{tr}q^2$. Thus $\varepsilon_{min} = 3\,k\theta_{tr}$, $\varepsilon_{max} = \infty$, $d\varepsilon = 2k\theta_{tr}q\,dq$. Thus

$$Z_{tr} = \frac{\pi}{2}\int_{\sqrt{3}}^{\infty} q^2 e^{-q^2\theta_{tr}/T} dq = \frac{\pi}{2}\int_{3k\theta_{tr}}^{\infty} \frac{\varepsilon}{k\theta_{tr}} e^{-\varepsilon/kT} \frac{d\varepsilon}{2(k\theta_{tr}\varepsilon)^{\frac{1}{2}}}$$

$$= \frac{\pi}{4}\frac{1}{(k\theta_{tr})^{3/2}}\int_{3k\theta_{tr}}^{\infty} \varepsilon^{\frac{1}{2}} e^{-\varepsilon/kT} d\varepsilon \quad \text{and} \quad g_{tr}(\varepsilon) = \frac{\pi}{4}\left[\frac{\varepsilon}{(k\theta_{tr})^3}\right]^{\frac{1}{2}}$$