It should be noted that the determination of these property changes were independent of both the symmetry number and the rotational characteristic temperature, σ and θ_r. A determination of the absolute entropy requires these parameters. The JANAF Tables tabulate absolute entropy, but the tabulated enthalpy is relative. Hence the constants employed are different from those of the above formulations.[20] In other respects the results of this section are compatible with the JANAF compilation.

[20]The entropies of the JANAF Table are referenced to absolute zero temperature. The tables permit a determination of absolute enthalpy using the enthalpy of formation of each molecule from its constituent elements. This determination is dependent on the electronic dissociation mode, see Appendix IIIC-B.

Ans. 17. Nitrogen is a homonuclear diatomic element, hence

$$\bar{c}_p^* = \bar{c}_{v,tr}^* + \bar{c}_{v(r,n)}^* + \bar{c}_{v,v}^* + \bar{R} = \bar{R}\left[\frac{3}{2} + 1 + \left(\frac{\theta_v}{T}\right)^2 \frac{e^{\theta_v/T}}{\left(e^{\theta_v/T} - 1\right)^2} + 1\right]$$

For nitrogen $\theta_v = 3392$ K. Then substituting we obtain

T(K)	50	300	600	1500	3500	5000
$\frac{\bar{c}_p^*}{\bar{R}}$	3.50	3.502	3.613	4.164	4.425	4.363

The normal boiling point of nitrogen is 77 K. Thus at 50 K atmospheric nitrogen is condensed and $\bar{c}_p^*$ is not appropriate. Up to 600 K the vibrational mode is unexcited, $c_p^* \approx (7/2)\ \bar{R}$, the "near room temperature value." At 5000 K the vibrational mode is almost fully excited ($\bar{c}_p^* \Rightarrow 9/2\ \bar{R}$); but at this level electronic excitation is beginning and cannot be overlooked.

Ans. 18. Methane, CH_4, is a nonlinear molecule with 5 atoms. It has 9 vibrational modes. Hence

$$\bar{c}_p^* = \bar{c}_v^* + \bar{R} = \bar{R}\left[\frac{3}{2} + \frac{3}{2} + \sum_{p=1}^{9} \left(\frac{\theta_{v,p}}{T}\right)^2 \frac{e^{\theta_{v,p}/T}}{\left(e^{\theta_{v,p}/T} - 1\right)^2} + 1\right]$$

Fortunately there are only four distinct values of $\theta_{v,p}$: 1879 K (3), 2207 (2), 4196 K, and 4343 K (3). Thus,

T(K)	200	400	800	1600	3200
$\frac{\bar{c}_p^*}{\bar{R}}$	4.026	4.871	7.569	10.65	12.29

Ans. 19. Carbon monoxide is heteronuclear diatomic. Thus, its enthalpy and entropy change are

$$\bar{h}^*(T) - \bar{h}^*(T_o) = \bar{R}\left\{\frac{7}{2}(T - T_o) + \theta_v\left[\frac{1}{\left(e^{\theta_v/T} - 1\right)} - \frac{1}{\left(e^{\theta_v/T_o} - 1\right)}\right]\right\}$$

$$\bar{s}^*(T, 1\text{ atm}) - \bar{s}^*(T_o, 1\text{ atm}) = \bar{R}\left\{\frac{7}{2}\ln\left(\frac{T_o}{T}\right) + \theta_v\left[\frac{1}{T}\frac{1}{\left(e^{\theta_v/T} - 1\right)} - \frac{1}{T_o}\frac{1}{\left(e^{\theta_v/T_o} - 1\right)}\right] - \ln\left(\frac{1 - e^{-\theta_v/T}}{1 - e^{-\theta_v/T_o}}\right)\right\}$$

Then substituting $\theta_v = 3121$ K, we obtain $[\bar{h}^*(1000\text{ K}) - \bar{h}^*(298\text{ K})]/\bar{R} = 2601$ K, $[\bar{s}^*(1000\text{ K}, 1\text{ atm}) - \bar{s}^*(298\text{ K}, 1\text{ atm})]/\bar{R} = 4.336$.