Exer. 18 shows that the specific heat of gaseous methane varies at all temperature levels. Its lowest vibrational excitation is initiated below normal temperatures and one or more vibrational modes contribute variably as the temperature increases. This is representative of all polyatomic molecules. So the assumption of constant specific heats is a poor approximation for the analysis of polyatomic gas molecules.

It might be noted that both Exers. 17 and 18 require that $\bar{c}_p^*$ be evaluated at temperatures at which their respective species are not perfect gases at atmospheric pressure. Even though the substance is not within the perfect gas region its perfect gas properties can be calculated. We will find that the general method of determining imperfect gas and condensed phase properties, Units IVD and IVF, is based on their deviation from a perfect gas reference value. Thus a prediction of perfect gas properties at all temperature levels is an essential step in property determination. The methods developed in this unit have been employed to compile an exhaustive collection of perfect gas properties, the JANAF Tables.[19] Exers. 17 and 18 have shown how the $\bar{c}_p^*$ data is computed. The following problems demonstrate the compilation of enthalpy and entropy.

Example 11. Write expressions for the enthalpy and entropy change of carbon dioxide. Determine the values of these changes from 298 to 500, 1000, and 3000 K at atmospheric pressure.

Carbon dioxide is a linear polyatomic molecule. Its enthalpy is given by (see Table IIIC-1).

$$\bar{h}^*(T) = \bar{u}_{tr}^*(T) + \bar{u}_{r,n}^*(T) + \bar{u}_v^*(T) + \bar{R}T = \bar{R}\left\{\frac{7}{2}T + \sum_{p=1}^{4}\theta_{v,p}\left[\frac{1}{2} + \frac{1}{\left(e^{\theta_{v,p}/T_o} - 1\right)}\right]\right\}$$

Thus, the enthalpy change is

$$\bar{h}^*(T) - \bar{h}^*(T_o = 298\text{ K}) = \bar{R}\left\{\frac{7}{2}(T - T_o) + \sum_{p=1}^{4}\theta_{v,p}\left[\frac{1}{\left(e^{\theta_{v,p}/T} - 1\right)} - \frac{1}{\left(e^{\theta_{v,p}/T_o} - 1\right)}\right]\right\}$$

The entropy and entropy change are written in an analogous manner. We write only the entropy change, thus eliminating the constants and pressure dependent terms.

$$\bar{s}^*(T, 1\text{ atm}) - \bar{s}^*(T_o, 1\text{ atm}) = \bar{R}\left\{\frac{7}{2}\ln(T/T_o) + \sum_{p=1}^{4}\theta_{v,p}\left[\frac{1}{T\left(e^{\theta_{v,p}/T} - 1\right)} - \frac{1}{T_o\left(e^{\theta_{v,p}/T_o} - 1\right)}\right] - \ln\left(\frac{1 - e^{-\theta_{v,p}/T}}{1 - e^{-\theta_{v,p}/T_o}}\right)\right\}$$

Table IIIC-2 gives the necessary vibrational temperatures: 960.1 K (2), 1932 K, 3380 K. Thus we find

T(K)	$\left\lvert\frac{\bar{h}^*(T) - \bar{h}^*(T_o)}{\bar{R}}\right\rvert$ (K)	$\left\lvert\frac{\bar{s}^*(T, 1\text{ atm}) - \bar{s}^*(T_o, 1\text{ atm})}{\bar{R}}\right\rvert$
500	999.4	2.540
1000	3939	6.598
3000	18220	14.398

Exercise 19. Determine the enthalpy and entropy change when carbon monoxide is heated at atmospheric pressure from 298 to 1000 K. (Answer on pg. 28.)

[19]The JANAF Tables include the electronic mode, coupling between the rotational and vibrational modes, and other effects which allow greater accuracy.