1. Problem 2.16

We have a collection of molecules that can exist in two (and only two) energy states. The total number $N$ of molecules is constant:

$$\bar{N}_u + \bar{N}_l = N$$

With this equation and the equation for the ratio of number densities we obtain

$$\bar{N}_l = \frac{N}{1 + (g_u/g_l) \exp \left\{ -(E_u - E_l) / k_B T \right\}}$$

$$\bar{N}_u = \frac{N (g_u/g_l) \exp \left\{ -(E_u - E_l) / k_B T \right\}}{1 + (g_u/g_l) \exp \left\{ -(E_u - E_l) / k_B T \right\}}$$

In the limit as $k_B T$ becomes very small relative to the energy level difference

$$\bar{N}_l \to N$$

$$\bar{N}_u \to 0$$

In the limit as $T$ becomes indefinitely large we have

$$\lim_{T \to \infty} \bar{N}_l = \frac{N}{1 + (g_u/g_l)}$$

$$\lim_{T \to \infty} \bar{N}_u = \frac{N (g_u/g_l)}{1 + (g_u/g_l)}$$

According to this result the number of molecules in the upper state is greater than the number in the lower state (in this limit) only if the multiplicity of upper states is greater than that of lower states.

2. Problem 2.25
Collisional broadening is the result of interactions between molecules. Water molecules obviously interact more strongly with each other than with foreign molecules (at least the foreign molecules nitrogen and oxygen). “Obviously” because if you compress water vapor sufficiently (in air) it becomes liquid water, which is much more cohesive than the vapor.

3. Problem 2.27

First we have to assume that absorption coefficients are additive. This is true only if each of the absorbing gases does not appreciably foreign-broaden the others. With this assumption, the transmissivity is the product of transmissivities:

\[ T = T_c T_a \]

where \( T \) is the total transmissivity, \( T_c \) is that of an atmosphere containing only carbon dioxide as the absorbing gas, and \( T_a \) is that transmissivity of the atmosphere without any carbon dioxide.

What we want is

\[ A_c = 1 - T_c \]

what we calculate is

\[ A = 1 - T_c T_a \]

and

\[ A_a = 1 - T_a \]

Combine these to obtain

\[ A = 1 - (1 - A_c) (1 - A_a) \]

which yields

\[ 1 - A_c = \frac{1 - A}{1 - A_a} \]
and finally
\[ A_c = \frac{A - A_a}{1 - A_a} \]

So, only if \( A_a \ll 1 \) can we subtract absorptivities

\[ A_c \simeq A - A_a \]

4. Problem 2.28

The spectral emissivity is
\[ \varepsilon = 1 - \exp \left\{ -\sum_i N_i \sigma_i H \right\} \]

where \( H \) is the thickness of the atmosphere, \( N_i \) is the concentration of the \( i^{th} \) species and \( \sigma_i \) is its absorption cross-section. Take the derivative of this with respect to \( N_j \)

\[ \frac{d\varepsilon}{dN_j} = \exp \left\{ -\sum_i N_i \sigma_i H \right\} \sigma_j H \]

The exponential term is the transmissivity \( T \), so we have

\[ \frac{d\varepsilon}{dN_j} = T \sigma_j H \]

This decreases with decreasing \( T \) for a given \( \sigma_j \)

5. Problem 2.29

First it is necessary to try to understand just exactly what is meant by “ten times more effective.” Does this mean that the absorption cross-section of methane is 10 times that of carbon dioxide? If so, at what wavelength of wavelengths? The key to answering this is Fig. 2.12, which shows the absorption spectrum of both methane and carbon dioxide. At the short end of the atmospheric window region between 8 and 12 \( \mu \)m, the absorption cross-
section of methane is appreciably higher than that of carbon dioxide, although at the long end the reverse is true. The text say that the spike at 15 µm in the absorption spectrum of carbon dioxide is what is playing the role in global warming. But at this wavelength the absorption cross-section of methane is very small. Cross-sections, however, aren’t the entire story. Methane is characterized by weak-line absorption whereas as carbon dioxide by strong-line absorption, so, to an approximation, a linear increase in methane corresponds to a linear increase in spectral absorption, whereas as a linear increase for carbon dioxide corresponds to a square root dependence in absorption.