1. Write =, <, >, or X (for cannot be determined). Formaldehyde is CH_2O

Compound	Melting Point	Boiling Point
Formaldehyde	181 K	254 K
Boron tribromide	227 K	364 K

(a) ΔS_{CH_2O} heating 0 K→150 K ___<___ ΔS_{BBr_3} heating 0 K→ 150 K

(b) ΔS_{BBr_3} heating 350 K→375 K ___>___ ΔS_{BBr_3} heating 375 K→ 400 K

(c) $\Delta S_{CH_2O,\,\text{melt}}$ ___<___ $\Delta S_{CH_2O,\,\text{vap}}$

(d) ΔS_{CH_2O} heating 375 K→ 400 K ___>___ ΔS_{BBr_3} heating 400 K→ 425 K

2. Two ideal gases, gas A (n_A, V_A) and gas B (n_B, V_B), are mixed in a isolated container. Initially, gas A is confined to the left half of the container, and gas B occupies the right half. The two gases are at the same temperature and pressure.

(a) Calculate the total entropy change ΔS_{mix} for the process of mixing the two ideal gases.

Isothermal, only volume changes

$$\begin{aligned}\Delta S &= \Delta S_A + \Delta S_B \\ &= n_A R \ln\left(\frac{V_A + V_B}{V_A}\right) + n_B R \ln\left(\frac{V_A + V_B}{V_B}\right)\end{aligned}$$

(b) Rewrite the entropy using mol fractions $X_A = \frac{n_A}{n_A+n_B}$ and $X_B = \frac{n_B}{n_A+n_B}$.

$$\begin{aligned}PV = nRT &\implies V \propto n \\ \Delta S &= n_A R \ln\left(\frac{V_A + V_B}{V_A}\right) + n_B R \ln\left(\frac{V_A + V_B}{V_B}\right) \\ &= n_A R \ln\left(\frac{n_A + n_B}{n_A}\right) + n_B R \ln\left(\frac{n_A + n_B}{n_B}\right) \\ &= -n_A R \ln(X_A) - n_B R \ln(X_B)\end{aligned}$$

(c) Draw a conclusion about the sign of ΔS.

Both mol fractions are less than one, so both $\ln(X_A)$ and $\ln(X_B)$ are negative, making ΔS strictly positive as expected.

3. Consider a system of 6 distinguishable particles with total energy 12. The accessible single particle energy levels are: $E = 1, 3, 5, 7$

   (a) List all possible macrostates for this system.

   $(1, 1, 1, 1, 3, 5),\ (1, 1, 1, 3, 3, 3),\ (1, 1, 1, 1, 1, 7)$

   (b) For each macrostate, determine the number of microstates W

$$(1, 1, 1, 1, 3, 5) : W = \frac{6!}{4!1!1!} = 30$$

$$(1, 1, 1, 3, 3, 3) : W = \frac{6!}{3!3!} = 20$$

$$(1, 1, 1, 1, 1, 7) : W = \frac{6!}{5!1!} = 6$$

   (c) Determine the residual entropy for this system, no longer subject to the energy constraint.

   Ground state means all particles occupy the lowest energy level $E = 1$:

$$(1, 1, 1, 1, 1, 1)$$

   Only one microstate, so $\Omega_0 = 1$

$$S_{\text{residual}} = k_B \ln \Omega_0 = k_B \ln 1 = 0$$

   (d) Now suppose each energy level is 2-fold degenerate. How would your answers change?

   Macrostates remain the same $(1, 1, 1, 1, 3, 5),\ (1, 1, 1, 3, 3, 3),\ (1, 1, 1, 1, 1, 7)$
   Microstates would increase

$$(1, 1, 1, 1, 3, 5) : W = 30 \cdot 2^4 \cdot 2^1 \cdot 2^1 = 1920$$

$$(1, 1, 1, 3, 3, 3) : W = 20 \cdot 2^3 \cdot 2^3 = 1280$$

$$(1, 1, 1, 1, 1, 7) : W = 6 \cdot 2^5 \cdot 2^1 = 384$$

   For ground state we have 6 particles each with 2 choices:

$$\Omega_0 = 2^6 = 64$$

$$S_{\text{residual}} = k_B \ln \Omega_0 = k_B \ln 64 = 5.74 \times 10^{-23}\ \tfrac{\text{J}}{\text{K}}$$

Homework Problem 18

1. Consider a system of 8 distinguishable particles with total energy 12. The accessible single particle energy levels are: $E = 0, 1, 4, 9$
   (a) List all possible macrostates.

   (b) For each macrostate, determine the number of microstates W, then determine the most probable microstate and its associated probability.