

Example Problems for Diffusional Equilibrium.

1. One-component subsystems. Consider a closed, composite system formed from two single-component subsystems 1 and 2, each described by the fundamental relation $S = NA + NR \ln(U^{3/2}VN^{-5/2})$, where R is the gas constant and A is another constant. The subsystems are separated by a diathermal, rigid, permeable wall. The initial conditions are $T^{(1)} = 300$ K, $V^{(1)} = 4.0$ liters, $N^{(1)} = 1.25$, $T^{(2)} = 250$ K, $V^{(2)} = 6.0$ liters, and $N^{(2)} = 0.75$. After equilibrium is established, what are the values of $N^{(1)}$, $N^{(2)}$, T , $P^{(1)}$, and $P^{(2)}$?

Solution: The equations of state for each subsystem are

$$\frac{1}{T} = \frac{3NR}{2U}, \quad \frac{P}{T} = \frac{NR}{V}, \quad \frac{\mu}{T} = \frac{5R}{2} - A - R \ln \frac{U^{3/2}V}{N^{5/2}}.$$

When the subsystems reach diffusional equilibrium, the four unconstrained extensive variables are determined by the equations

$$T^{(1)} = T^{(2)} \Rightarrow \frac{U^{(1)}}{N^{(1)}} = \frac{U^{(2)}}{N^{(2)}} \quad (1)$$

$$U^{(1)} + U^{(2)} = U = \frac{3}{2}N^{(1)}RT^{(1)} + \frac{3}{2}N^{(2)}RT^{(2)} = 7015 \text{ J}, \quad (2)$$

$$\mu^{(1)} = \mu^{(2)} \Rightarrow \frac{U^{(1)3/2}V^{(1)}}{N^{(1)5/2}} = \frac{U^{(2)3/2}V^{(2)}}{N^{(2)5/2}}, \quad (3)$$

$$N^{(1)} + N^{(2)} = N = 2.00. \quad (4)$$

Raising Eq. (1) to the $\frac{3}{2}$ power, then dividing by Eq. (3), we obtain

$$\frac{N^{(1)}}{V^{(1)}} = \frac{N^{(2)}}{V^{(2)}} \Rightarrow \boxed{N^{(1)} = 0.80}, \quad \boxed{N^{(2)} = 1.20}.$$

Substituting these values back into Eqs. (1) and (2), we find

$$U^{(1)} = \frac{0.80}{2.00}U = 2806 \text{ J} \Rightarrow \boxed{T = 281.3 \text{ K}}.$$

Finally, we can substitute into the mechanical equation of state to obtain

$$\boxed{P^{(1)} = P^{(2)} = 4.68 \times 10^5 \text{ Pa}}.$$

Discussion:

(1) The fundamental equation above describes a monatomic ideal gas. That being the case, the final answers should come as no surprise. Since gas molecules can travel freely between the subsystems, carrying internal energy with them, the internal wall serves no real physical purpose; we could regard it merely as an imaginary boundary between two regions of a single physical system. Thus, the equilibrium state must be one in which the two subsystems have the same particle density N/V , the same energy density U/V , and the same pressure; if this were not the case, then the single combined system would not be homogeneous. It turns out, therefore, that this problem can be solved without reference to the chemical potential.

(2) Note that even though the molecules in an ideal gas don't interact with each other, the chemical potential is **not** just equal to the molar internal energy of the gas, $U/N = \frac{3}{2}RT$.

The reason is that $\mu = (\partial U/\partial N)_{S,V}$ is defined in terms of addition of particles at constant entropy, whereas U/N measures the change in energy arising from addition of particles at constant temperature.

(3) In order to see nontrivial applications of the chemical potential, one must look at equilibrium between

- single-component subsystems described by different fundamental equations, e.g., the liquid and gas phases of the same chemical species. Situations of this type are still governed by Eqs. (1)–(4), but typically the algebra becomes very messy.
- multiple-component subsystems (two or more different types of particles) separated by a wall which is permeable to certain particles and impermeable to others. See below.

2. Two-component subsystems: Callen Problem 2.8-1. This problem considers two subsystems, each containing two distinct types of particle (or two components). The key feature is that the internal wall is permeable to particles of type 1 but impermeable to type-2 particles. (Think of a wall pierced by holes which are too small to allow molecules of type 2 to pass through.) Each subsystem satisfies

$$S = NA + NR \ln \frac{U^{3/2}V}{N^{5/2}} - N_1 R \ln \frac{N_1}{N} - N_2 R \ln \frac{N_2}{N}, \quad N \equiv N_1 + N_2.$$

Given initial conditions $T^{(1)} = 300$ K, $V^{(1)} = 5.0$ liters, $N_1^{(1)} = 0.5$, $N_2^{(1)} = 0.75$, $T^{(2)} = 250$ K, $V^{(2)} = 5.0$ liters, $N_1^{(2)} = 1.0$, and $N_2^{(2)} = 0.5$, we must find the equilibrium values of $N_1^{(1)}$, $N_1^{(2)}$, T , $P^{(1)}$, and $P^{(2)}$.

Solution: The equations of state for each subsystem are

$$\frac{1}{T} = \frac{3NR}{2U}, \quad \frac{P}{T} = \frac{NR}{V}, \quad \frac{\mu_j}{T} = \frac{5R}{2} - A - R \ln \frac{U^{3/2}V}{N^{3/2}N_j}.$$

When the subsystems reach diffusional equilibrium, the four unconstrained extensive variables are determined by the equations

$$T^{(1)} = T^{(2)} \Rightarrow \frac{U^{(1)}}{N_1^{(1)} + N_2^{(1)}} = \frac{U^{(2)}}{N_1^{(2)} + N_2^{(2)}}, \quad (5)$$

$$U^{(1)} + U^{(2)} = U = \frac{3}{2}N^{(1)}RT^{(1)} + \frac{3}{2}N^{(2)}RT^{(2)} = 9353 \text{ J}, \quad (6)$$

$$\mu_1^{(1)} = \mu_1^{(2)} \Rightarrow \frac{U^{(1)3/2}V^{(1)}}{[N_1^{(1)} + N_2^{(1)}]^{3/2}N_1^{(1)}} = \frac{U^{(2)3/2}V^{(2)}}{[N_1^{(2)} + N_2^{(2)}]^{3/2}N_1^{(2)}}, \quad (7)$$

$$N_1^{(1)} + N_1^{(2)} = N_1 = 1.50. \quad (8)$$

Raising Eq. (5) to the $\frac{3}{2}$ power, then dividing by Eq. (7), we obtain

$$\frac{N_1^{(1)}}{V^{(1)}} = \frac{N_1^{(2)}}{V^{(2)}} \Rightarrow \boxed{N_1^{(1)} = N_1^{(2)} = 0.75.}$$

Substituting these values back into Eqs. (5) and (6), we find

$$U^{(1)} = \frac{1.50}{2.75}U = 5102 \text{ J} \Rightarrow \boxed{T = 272.7 \text{ K.}}$$

Finally, we can substitute into the mechanical equation of state to obtain

$$\boxed{P^{(1)} = \frac{N^{(1)}RT}{V^{(1)}} = 6.8 \times 10^5 \text{ Pa},} \quad \boxed{P^{(2)} = \frac{N^{(2)}RT}{V^{(2)}} = 5.7 \times 10^5 \text{ Pa.}}$$