

Problem 4.1

Let the molar internal energy and molar entropy of an ideal gas at standard temperature and pressure be $\overline{U}_0(P_0, T_0)$ and $\overline{S}_0(P_0, T_0)$.

Derive expressions for the state functions $\overline{U}(P, T)$, $\overline{U}(V, T)$, $\overline{U}(P, V)$ and $\overline{S}(P, T)$, $\overline{S}(V, T)$, $\overline{S}(P, V)$.

Solution 4.1

The molar internal energy of an ideal gas is only a function of temperature.

$$d\overline{U} = \overline{C}_v dT \quad (1)$$

$$\overline{U} - \overline{U}_0 = \overline{C}_v(T - T_0) \quad (2)$$

Therefore with substitution:

$$\overline{U}(T, P) - \overline{U}_0(T_0, P_0) = \overline{C}_v(T - T_0) \quad (3)$$

$$\overline{U}(T, \overline{V}) - \overline{U}_0(T_0, \overline{V}_0) = \overline{C}_v(T - T_0) \quad (4)$$

$$\overline{U}(P, \overline{V}) - \overline{U}_0(P_0, \overline{V}_0) = \frac{\overline{C}_v}{R}(P\overline{V} - P_0\overline{V}_0) \quad (5)$$

To derive the expression for the molar entropy for an ideal gas we begin with the first law.

$$d\overline{U} = d\overline{q} - Pd\overline{V} = \overline{C}_v dT \quad (6)$$

$$d\overline{S} = \frac{d\overline{q}}{T} = \frac{\overline{C}_v}{T} dT + \frac{P}{T} d\overline{V} \quad (7)$$

$$\overline{S} - \overline{S}_0 = \overline{C}_v \log \frac{T}{T_0} + R \log \frac{\overline{V}}{\overline{V}_0} \quad (8)$$

Substituting using the ideal gas law and the relation $\overline{C}_p = \overline{C}_v + R$ gives the following.

$$\overline{S}(T, \overline{V}) - \overline{S}_0(T_0, \overline{V}_0) = \overline{C}_v \log \frac{T}{T_0} + R \log \frac{\overline{V}}{\overline{V}_0} \quad (9)$$

$$\overline{S}(T, P) - \overline{S}_0(T_0, P_0) = \overline{C}_p \log \frac{T}{T_0} + R \log \frac{P_0}{P} \quad (10)$$

$$\overline{S}(P, \overline{V}) - \overline{S}_0(P_0, \overline{V}_0) = \overline{C}_v \log \frac{P}{P_0} + \overline{C}_p \log \frac{\overline{V}}{\overline{V}_0} \quad (11)$$

Problem 4.2

The molar heat capacity of solid aluminum is a weak function of temperature $\overline{C}_p = 20.7 + 12.4 \cdot 10^{-3}T$ ($\frac{\text{joule}}{\text{degree mole}}$) for $300\text{K} < T < 900\text{K}$.

Suppose c grams of aluminum at temperature $T_c = 600(1 - \frac{\theta}{2})$ (Kelvin) are put in thermal contact with h grams of aluminum at $T_h = 600(1 + \frac{\theta}{2})$ (Kelvin).

1-2-i Calculate an expression for the final temperature as a function of the ratio c/h and θ ($0 < \theta < 1$).

1-2-ii Plot the change in total entropy per mole of aluminum as a function of θ for values of $c/h = (1/16, 1/8, 1/4, 1/2, 1)$.

Solution 4.2

a) Take the two aluminum masses together as an isolated system. The heat transferred from the hot to the cold aluminum piece is equal to the heat adsorbed by the cold from the hot after they reach the final temperature, T_f .

$$dq_{h \rightarrow c} = -dq_{c \rightarrow h} \quad (12)$$

Use the relation $dq = C_p dT = n \overline{C_p} dT$. In the following, M is the atomic weight of aluminum.

$$C_p^{cold} dT = -C_p^{hot} dT \quad (13)$$

$$\frac{c}{M} \int_{T_c}^{T_f} \overline{C_p^{Al}} dT + \frac{h}{M} \int_{T_h}^{T_f} \overline{C_p^{Al}} dT = 0 \quad (14)$$

$$\left(1 + \frac{c}{h}\right) \int_{T_c}^{T_f} \overline{C_p^{Al}} dT - \int_{T_c}^{T_h} \overline{C_p^{Al}} dT = 0 \quad (15)$$

Evaluation in Mathematica gives the following output where $\gamma = \frac{c}{h}$. The quadratic expression has two roots.

$$T_f = 0.5(-20.7 - 20.7\gamma \pm ((20.7 + 20.7\gamma)^2 - 4(0.0062 + 0.0062\gamma)(-12420\gamma(1 - \frac{\theta}{2}) - 2232\gamma(1 - \frac{\theta}{2})^2 - 12420(1 - \frac{\theta}{2}) - 2232(1 - \frac{\theta}{2})^2))^{\frac{1}{2}})/(0.0062 + 0.0062\gamma)$$

Only the first makes sense (+).

b) The total change in entropy for the system is given by the sum of the change in entropy for the hot block and the cold block.

$$dS = \frac{c}{M} \int_{T_c}^{T_f} \frac{\overline{C_p^{Al}}}{T} dT + \frac{h}{M} \int_{T_h}^{T_f} \frac{\overline{C_p^{Al}}}{T} dT \quad (16)$$

The change in entropy per unit mole is given below.

$$d\overline{S} = \frac{c}{c+h} \int_{T_c}^{T_f} \frac{\overline{C_p^{Al}}}{T} dT + \frac{h}{c+h} \int_{T_h}^{T_f} \frac{\overline{C_p^{Al}}}{T} dT \quad (17)$$

Using Mathematica and substituting expressions for $\overline{C_p^{Al}}$, T_c , T_h , and T_f gives the following results for the plot of entropy change per mole of aluminum. The lowest curve corresponds to the $\gamma = 1/16$ and the highest to $\gamma = 1$. Also, the curves are all monotonically increasing. These trends follow because the entropy change approaches that for a reversible or quasi-static process (zero in an isolated system) as γ and θ get infinitesimally small.

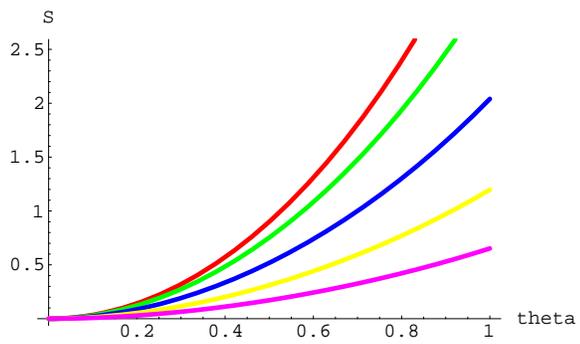


Figure 1: The entropy change per mole of aluminum as a function of θ the initial temperature difference for different mass ratios of cold to hot blocks of aluminum, γ . $\gamma = \frac{1}{16}$ is pink, $\gamma = \frac{1}{8}$ is yellow, $\gamma = \frac{1}{4}$ is blue, $\gamma = \frac{1}{2}$ is green, and $\gamma = 1$ is red.