Thermodynamics Tutorials

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Winter 2023

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1. Indexed as number 51 in tutorial sheet 7.

   Consider the entropy change for an ideal gas:

$$\begin{aligned}\Delta S(V,T) &= S(V,T) - S(V_0,T_0)\\ &= C_V \ln\frac{T}{T_0} + nR\ln\frac{V}{V_0}.\end{aligned}$$

   For part $(a)(1)$ write this expression as:

$$\Delta S(P,T) = C_P \ln\frac{T}{T_0} - nR\ln\frac{P}{P_0}.$$

   It is important for us to recall the difference in heat capacity:

$$C_P - C_V = nR.$$

   Using this and the ideal state equation $PV = nRT$:

$$\begin{aligned}\Delta S &= (C_P - nR)\ln\frac{T}{T_0} + nR\ln\frac{V}{V_0}\\ &= C_P\ln\frac{T}{T_0} + nR\ln\left(\frac{V}{V_0}\cdot\frac{T_0}{T}\right)\\ &= C_P\ln\frac{T}{T_0} - nR\ln\frac{P}{P_0}\end{aligned}$$

   since the ideal gas equation holds for fixed physical quantities:

$$P_0V_0 = nRT_0.$$

   For part $(a)(2)$ write this expression as:

$$\Delta S(P,V) = C_P\ln\frac{V}{V_0} + C_V\ln\frac{P}{P_0}.$$

   Now we start again with our original equation and use $C_P - C_V = nR$.

$$\begin{aligned}\therefore \Delta S &= C_V\ln\frac{T}{T_0} + nR\ln\frac{V}{V_0}\\ &= C_V\ln\frac{T}{T_0} + (C_P - C_V)\ln\frac{V}{V_0}\\ &= C_P\ln\frac{V}{V_0} + C_V\ln\frac{P}{P_0}\end{aligned}$$

   The last step we used the ideal gas equation.

For part (b) we want to verify:

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$

given the following assumptions:

- $\Delta S(P,T) = C_P \ln \frac{T}{T_0} - nR \ln \frac{P}{P_0}$
- $PV = nRT$.

The right hand side of our equation is:

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{P}.$$

Now for the left hand side. Firstly we need to come up with an expression for entropy, and then take its partial derivatives to show equality.

$$\because \Delta S(P,T) = S(P,T) - S_0$$
$$\therefore S(P,T) = C_P \ln \frac{T}{T_0} - nR \ln \frac{P}{P_0} + S_0$$
$$\therefore \frac{\partial}{\partial P} S(P,T) = -\frac{nR}{P}$$

And clearly we have equality of both sides.

For part (c) show that a reversible adiabatic process implies an isentropic process:

$$PV^\gamma = \text{constant} \implies \Delta S = 0$$

where $\gamma = \dfrac{C_P}{C_V}$.

Beginning with our derived expression $\Delta S(P,V)$:

$$\begin{aligned}\Delta S(P,V) &= C_P \ln \frac{V}{V_0} + C_V \ln \frac{P}{P_0} \\ &= C_P \left(\ln \frac{V}{V_0} + \frac{1}{\gamma} \ln \frac{P}{P_0}\right).\end{aligned}$$

Now since we have that:

$$\frac{P}{P_0} = \left(\frac{V_0}{V}\right)^\gamma$$

it is clear that $\Delta S = 0$.

2. Indexed as number 52 in tutorial sheet 7.

   For part (a) show that:

$$\mathrm{d}S = \frac{C_P}{T}\mathrm{d}T - V\beta\mathrm{d}P.$$

   We take total differentials of the previously derived $S(P,T)$:

$$\mathrm{d}S = \left(\frac{\partial S}{\partial T}\right)_P \mathrm{d}T + \left(\frac{\partial S}{\partial P}\right)_T \mathrm{d}P.$$

   Since we have that:

$$S(P,T) = C_P \ln\frac{T}{T_0} - nR\ln\frac{P}{P_0} + S_0$$

   therefore:

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}.$$

   The second partial derivative we recognise as a Maxwell relation:

$$\begin{aligned}\left(\frac{\partial S}{\partial P}\right)_T &= -\left(\frac{\partial V}{\partial T}\right)_P \\ &= -V\beta\end{aligned}$$

   where β is the <u>isobaric expansivity</u>. Therefore we have that:

$$\mathrm{d}S = \frac{C_P}{T}\mathrm{d}T - V\beta\mathrm{d}P.$$

   For part (b), consider metal box subject to <u>adiabatic</u> and <u>reversible</u> increase in pressure. $(P_1 \to P_2)$

   Show that its temperature change $(T_1 \to T_2)$ satisfies the following:

$$\ln\frac{T_2}{T_1} = \frac{V\beta(P_2 - P_1)}{C_P}.$$

   Since $\Delta Q = 0$ and our process is reversible the overall entropy change is <u>zero</u>. Integrate result in previous part to obtain answer.

Integrating from initial state to final state:

$$\begin{aligned}\Delta S &= \int_{(1)}^{(2)} \mathrm{d}S \\ &= \int_{(1)}^{(2)} \left(\frac{C_P}{T} \mathrm{d}T - V\beta \mathrm{d}P \right) \\ &= 0.\end{aligned}$$

We then have that:

$$\int_{T_1}^{T_2} \frac{C_P}{T} \mathrm{d}T - \int_{P_1}^{P_2} V\beta \mathrm{d}P = 0$$

which gives:

$$\ln \frac{T_2}{T_1} = \frac{V\beta(P_2 - P_1)}{C_P}.$$

3. Indexed as number 53 in tutorial sheet 7.