

# Thermodynamics Tutorials

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## 1 Set 6

1. ?!
- 2.

## 2 Set 7

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:

$$P_0 V_0 = nRT_0.$$

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.

$$\therefore \Delta S(P, T) = S(P, T) - S_0$$

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

$$\therefore \frac{\partial}{\partial P} S(P, T) = -\frac{nR}{P}$$

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  $\gamma = \frac{C_P}{C_V}$ .

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:

$$dS = \frac{C_P}{T}dT - V\beta dP.$$

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

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP.$$

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  $\beta$  is the isobaric expansivity. Therefore we have that:

$$dS = \frac{C_P}{T}dT - V\beta dP.$$

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

Show that its temperature change ( $T_1 \rightarrow T_2$ ) 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 zero. Integrate result in previous part to obtain answer.

Integrating from initial state to final state:

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

We then have that:

$$\int_{T_1}^{T_2} \frac{C_P}{T} dT - \int_{P_1}^{P_2} V\beta dP = 0$$

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.

For part (a) show that:

$$\mu_{JK} = \left( \frac{\partial T}{\partial P} \right)_H = \frac{V}{C_P}(\beta T - 1).$$

We begin by using the cyclic relations of partial derivatives:

$$\left( \frac{\partial T}{\partial P} \right)_H \left( \frac{\partial H}{\partial T} \right)_P \left( \frac{\partial P}{\partial H} \right)_T = -1$$

and hence:

$$\begin{aligned} \left( \frac{\partial T}{\partial P} \right)_H &= - \left( \frac{\partial H}{\partial T} \right)_P^{-1} \left( \frac{\partial P}{\partial H} \right)_T^{-1} \\ &= - \left( \frac{\partial H}{\partial T} \right)_P^{-1} \left( \frac{\partial H}{\partial P} \right)_T. \end{aligned}$$

The first one is by definition  $C_P$ :

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

Since we have that:

$$dH = TdS + VdP$$

dividing through by  $dP$  at fixed  $T$  gives:

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

and hence for the second partial derivative:

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

via a Maxwell relation.

For part (b) since  $V = \frac{nRT}{P}$  and using the definition of isobaric expansivity we get that  $\mu_{JK} = 0$ .



4. Indexed as number 54 in tutorial sheet 7.

For part (a) show that:

$$\frac{\kappa_T}{\kappa_S} = \frac{C_P}{C_V}$$

where we define:

$$\kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T$$

and

$$\kappa_S = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_S.$$

Firstly using the definition we have that:

$$\frac{\kappa_T}{\kappa_S} = \left( \frac{\partial V}{\partial P} \right)_T \left( \frac{\partial V}{\partial P} \right)_S^{-1}.$$

Note the following cyclic relations:

$$\left( \frac{\partial V}{\partial P} \right)_T \left( \frac{\partial T}{\partial V} \right)_P \left( \frac{\partial P}{\partial T} \right)_V = -1$$

and

$$\left( \frac{\partial V}{\partial P} \right)_S \left( \frac{\partial S}{\partial V} \right)_P \left( \frac{\partial P}{\partial S} \right)_V = -1.$$

Then our first expression becomes:

$$\begin{aligned} \frac{\kappa_T}{\kappa_S} &= \left( \frac{\partial T}{\partial V} \right)_P^{-1} \left( \frac{\partial P}{\partial T} \right)_V^{-1} \left( \frac{\partial S}{\partial V} \right)_P \left( \frac{\partial P}{\partial S} \right)_V \\ &= \left( \frac{\partial S}{\partial V} \right)_P \left( \frac{\partial V}{\partial T} \right)_P \left[ \left( \frac{\partial S}{\partial P} \right)_V \left( \frac{\partial P}{\partial T} \right)_V \right]^{-1} \\ &= T \left( \frac{\partial S}{\partial T} \right)_P \left[ T \left( \frac{\partial S}{\partial T} \right)_V \right]^{-1} \\ &= \frac{C_P}{C_V}. \end{aligned}$$

For part (b) show that:

$$\kappa_T - \kappa_S = \frac{VT\beta^2}{C_P}.$$

Using previous results:

$$C_P - C_V = \frac{VT\beta^2}{\kappa_T}$$

and

$$C_V = C_P \frac{\kappa_S}{\kappa_T}$$

the result follows after substituting in  $C_V$ .

For part (c) find  $\kappa_S$  for an ideal gas and verify part (b).

Let  $\gamma = \frac{C_P}{C_V}$ . We then have the following relation:

$$\kappa_S = \frac{\kappa_T}{\gamma}.$$

Now since  $PV = nRT$ :

$$\begin{aligned}\kappa_T &= -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T \\ &= \frac{1}{p}\end{aligned}$$

and so:

$$\kappa_S = \frac{1}{\gamma p}.$$