

Thermodynamics Tutorials

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Contents

Set 6	3
Set 7	4

Set 6

1. ?!
- 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 β 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 κ_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:

$$\kappa_S = \frac{1}{\gamma P}$$

where γ is our adiabatic exponent. To verify part (b):

$$\begin{aligned}\kappa_T - \kappa_S &= \frac{1}{P} - \frac{1}{\gamma P} \\ &= \frac{1}{P} \left(\frac{C_P - C_V}{C_P} \right) \\ &= \frac{VT\beta^2}{C_P}\end{aligned}$$

via the difference in heat capacities.

5. Consider the following:

$$C_P - C_V = \frac{VT\beta^2}{\kappa_T} > 0$$

since $\beta > 0$ and $\kappa_T > 0$. Explain physically why $\kappa_T > 0$ must be true.

Firstly recall the definition of κ_T :

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

Physically a compression results in a reduction of volume:

$$+\Delta P \implies -\Delta V$$

and that vice versa:

$$-\Delta P \implies +\Delta V.$$

If we think of partial derivatives as infinitesimal fractions of change then it is clear that κ_T is always positive.

We can also contradict ourself by assuming:

$$-\Delta P \implies -\Delta V$$

or that a reduction in pressure results in compression of solid. This eventually forms a black hole which is impossible. (for 'normal' matter)

6. For part (a) express μ_{JK} using the Van der Waals state equation.

So we have that:

$$\mu_{JK} = \frac{V}{C_P}(\beta T - 1)$$

and the molar Van der Waals state equation:

$$\left(P + \frac{a}{v^2}\right)(v - b) = RT$$

which states that at pressure P one mole of gas with volume v has temperature T . Now everything is all well and good except when finding β which is defined as follows:

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_P$$

and is known as the isobaric expansivity constant.

But we can use the inverse relations for partial derivatives:

$$\left(\frac{\partial T}{\partial v} \right)_P = \frac{1}{Rv^3} (Pv^3 - av + 2ab)$$

and so

$$\beta = Rv^2 (Pv^3 - av + 2ab)^{-1}.$$

After some rearranging we get:

$$\beta T = RTv^{-1} \left[\frac{RT}{v - b} - \frac{2a(v - b)}{v^3} \right]^{-1}$$

and therefore our Joule-Kelvin coefficient is:

$$\mu_{JK} = \frac{v}{c_P} \left(RTv^{-1} \left[\frac{RT}{v - b} - \frac{2a(v - b)}{v^3} \right]^{-1} - 1 \right).$$

For part (b) find temperature T such that $\mu_{JK} = 0$.

Setting the previous result to zero implies:

$$RTv^{-1} \left[\frac{RT}{v-b} - \frac{2a(v-b)}{v^3} \right]^{-1} - 1 = 0$$

and solving for T gives:

$$T = \frac{2a}{bR} \left(\frac{v-b}{v} \right)^2.$$

Now when $b = 0$ our T is maximised:

$$T_{max} = \frac{2a}{bR}$$

which is part (c).