Thermodynamics Tutorials

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1. Indexed as number 51 in tutorial sheet 7.

   Consider the entropy change for an <u>ideal</u> gas:

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

   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 $PV = nRT$:

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

   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 $C_P - C_V = nR$.

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

   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 $\Delta S(P,V)$:

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

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:

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

where β is the isobaric expansivity. 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 adiabatic and reversible 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 zero. Integrate result in previous part to obtain answer.

Integrating from initial state to final state:

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

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.

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:

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

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

The first one is by definition C_P:

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

Since we have that:

$$\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}P$$

dividing through by $\mathrm{d}P$ 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 $V = \dfrac{nRT}{P}$ 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 $\gamma = \dfrac{C_P}{C_V}$. We then have the following relation:

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

Now since $PV = nRT$:

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

and so:

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

where γ is our <u>adiabatic exponent</u>.