EP2827: Thermodynamics
Homework Set III Solutions*

February 26, 2019

1.

Regarding the internal energy of a hydrostatic system to be a function of θ and P, derive the following equations:
(a) $\left(\frac{\partial U}{\partial \theta}\right)_P = C_P - P\,V\,\beta$,
(b) $\left(\frac{\partial U}{\partial P}\right)_\theta = PV\kappa - (C_P - C_V)\,\frac{\kappa}{\beta}$
(c) $\left(\frac{\partial U}{\partial P}\right)_V = \frac{C_V\kappa}{\beta}$
(d) $\left(\frac{\partial U}{\partial V}\right)_P = \frac{C_P}{\beta V} - P.$

(3 × 4 = 12 points)

Solution:
(a) We start with the first law,

$$\begin{aligned}
dQ &= dU + PdV \\
&= \left(\frac{\partial U}{\partial \theta}\right)_P d\theta + \left(\frac{\partial U}{\partial P}\right)_\theta dP + PdV \\
\Longrightarrow \left(\frac{dQ}{d\theta}\right)_P &= \left(\frac{\partial U}{\partial \theta}\right)_P + P\left(\frac{\partial V}{\partial \theta}\right)_P \\
\Longrightarrow C_P &= \left(\frac{\partial U}{\partial \theta}\right)_P + P\,V\,\underbrace{\frac{1}{V}\left(\frac{\partial V}{\partial \theta}\right)_P}_{=\beta} \\
\Longrightarrow C_P - P\,V\,\beta &= \left(\frac{\partial U}{\partial \theta}\right)_P .
\end{aligned}$$

(b) We start from the second line of part (a),

$$dQ = \left(\frac{\partial U}{\partial \theta}\right)_P d\theta + \left(\frac{\partial U}{\partial P}\right)_\theta dP + PdV$$

*Due in class on Tuesday, Feb. 26th

Now we divide both sides by $d\theta$ holding V fixed, to get,

$$\begin{aligned}\left(\frac{dQ}{d\theta}\right)_V &= \left(\frac{\partial U}{\partial \theta}\right)_P + \left(\frac{\partial U}{\partial P}\right)_\theta \left(\frac{\partial P}{\partial \theta}\right)_V, \\ \implies C_V &= \underline{\left(\frac{\partial U}{\partial \theta}\right)_P} + \left(\frac{\partial U}{\partial P}\right)_\theta \left(\frac{\partial P}{\partial \theta}\right)_V \\ &= C_P - PV\beta + \left(\frac{\partial U}{\partial P}\right)_\theta \left(\frac{\partial P}{\partial \theta}\right)_V,\end{aligned}$$

where we have substituted the expression for $\left(\frac{\partial U}{\partial \theta}\right)_P$ from part (a). So now we have,

$$\left(\frac{\partial U}{\partial P}\right)_\theta = -\frac{C_P - C_V - PV\beta}{\left(\frac{\partial P}{\partial \theta}\right)_V}$$

Finally, for the denominator we need to use the lemma,

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

to obtain,

$$\left(\frac{\partial P}{\partial \theta}\right)_V = -\frac{1}{\left(\frac{\partial \theta}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_\theta} = \frac{\frac{1}{V}\left(\frac{\partial V}{\partial \theta}\right)_P}{-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_\theta} = \frac{\beta}{\kappa}.$$

Thus we get,

$$\left(\frac{\partial U}{\partial P}\right)_\theta = -\frac{C_P - C_V - PV\beta}{\frac{\beta}{\kappa}} = PV\kappa - (C_P - C_V)\frac{\kappa}{\beta}.$$

(c) Next, we manipulate,

$$\left(\frac{\partial U}{\partial P}\right)_V = \left(\frac{\partial U}{\partial \theta}\right)_V \left(\frac{\partial \theta}{\partial P}\right)_V.$$

Recalling that (no need to derive this),

$$\left(\frac{\partial U}{\partial \theta}\right)_V = C_V$$

and following some steps,

$$\begin{aligned}\left(\frac{\partial \theta}{\partial P}\right)_V &= \underbrace{\left(\frac{\partial \theta}{\partial P}\right)_V \left(\frac{\partial P}{\partial V}\right)_\theta \left(\frac{\partial V}{\partial \theta}\right)_P}_{=-1} \left(\frac{\partial V}{\partial P}\right)_\theta \left(\frac{\partial \theta}{\partial V}\right)_P \\ &= -\left(\frac{\partial V}{\partial P}\right)_\theta \left(\frac{\partial \theta}{\partial V}\right)_P \\ &= \frac{-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_\theta}{\frac{1}{V}\left(\frac{\partial V}{\partial \theta}\right)_P} \\ &= \frac{\kappa_\theta}{\beta}.\end{aligned}$$

Thus,

$$\left(\frac{\partial U}{\partial P}\right)_V = \left(\frac{\partial U}{\partial \theta}\right)_V \left(\frac{\partial \theta}{\partial P}\right)_V = C_V\frac{\kappa_\theta}{\beta},$$

(d) For the last one, we start with the expression,

$$\left(\frac{\partial U}{\partial V}\right)_P = \left(\frac{\partial U}{\partial \theta}\right)_P \left(\frac{\partial \theta}{\partial V}\right)_P = \frac{\left(\frac{\partial U}{\partial \theta}\right)_P}{\left[\underbrace{\frac{1}{V}\left(\frac{\partial V}{\partial \theta}\right)_P}_{=\beta}\right] V}$$

Next we plug in the numerator the result from part (a) and get,

$$\left(\frac{\partial U}{\partial V}\right)_P = \frac{C_P - P\,V\,\beta}{\beta\,V} = \frac{C_P}{\beta V} - P.$$

2.

(a) Starting from the assumption that the internal energy function of a hydrostatic system is a function of P, V i.e., $U = U(P, V)$, show that one can express the first law in the form,

$$đQ = C_V \frac{\kappa_\theta}{\beta} dP + \frac{C_P}{V\beta} dV.$$

Show that this leads to the relation,

$$\frac{C_P}{C_V} = \frac{\kappa_\theta}{\kappa_s}.$$

Here κ_θ and κ_s are respectively the isothermal and adiabatic compressibility.

(4 + 2 = 6 points)

Solution:
For this problem we consider the internal energy to be a function of pressure and volume, $U = U(P, V)$. The infinitesimal change in internal energy is then,

$$dU = \left(\frac{\partial U}{\partial P}\right)_V dP + \left(\frac{\partial U}{\partial V}\right)_P dV.$$

Using the same set of steps as in part (c) of the previous problem, we get $\left(\frac{\partial U}{\partial P}\right)_V = C_V \frac{\kappa_\theta}{\beta}$ and substitute, to get,

$$dU = C_V \frac{\kappa_\theta}{\beta} dP + \left(\frac{\partial U}{\partial V}\right)_P dV.$$

We now plug this in the first law,

$$\begin{aligned} đQ &= dU + PdV \\ &= C_V \frac{\kappa_\theta}{\beta} dP + \left[\left(\frac{\partial U}{\partial V}\right)_P + P\right] dV \end{aligned} \quad (1)$$

At constant pressure, i.e. $dP = 0$, we have,

$$đQ_P = \left[\left(\frac{\partial U}{\partial V}\right)_P + P\right] dV_P$$

where the subscript denotes constant P. Dividing both sides by $d\theta_P$, we get,

$$\begin{aligned}
\frac{đQ_P}{d\theta_P} &= \left[\left(\frac{\partial U}{\partial V}\right)_P + P\right] \left(\frac{\partial V}{\partial \theta}\right)_P \\
\Rightarrow C_P &= \left[\left(\frac{\partial U}{\partial V}\right)_P + P\right] \left(\frac{\partial V}{\partial \theta}\right)_P \\
\Rightarrow \frac{C_P}{V\left[\frac{1}{V}\left(\frac{\partial V}{\partial \theta}\right)_P\right]} &= \left(\frac{\partial U}{\partial V}\right)_P + P \\
\Rightarrow \frac{C_P}{V\beta} &= \left(\frac{\partial U}{\partial V}\right)_P + P.
\end{aligned}$$

Inserting this back in first law expression (1), we get,

$$đQ = C_V \frac{\kappa_\theta}{\beta} dP + \frac{C_P}{V\beta} dV. \tag{2}$$

(4 points for this part)

Next we consider an adiabatic process. In such a case, $đQ = 0$, and the first law expression (2) becomes,

$$0 = C_V \frac{\kappa_\theta}{\beta} dP_s + \frac{C_P}{V\beta} dV_s,$$

where the subscript s denotes adiabatic conditions. Rearranging this expression we get,

$$\frac{C_P}{C_V} = \frac{\kappa_\theta dP_s}{(-dV_s/V)} = \frac{\kappa_\theta}{\underbrace{-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S}_{=\kappa_S}} = \frac{\kappa_\theta}{\kappa_S}.$$

(2 points for this part)

3\.

(a) Show that for a hydrostatic system,

$$\left(\frac{\partial H}{\partial V}\right)_P = \frac{C_P}{\beta V}$$

(2 points)

Solution:
Recall that the first law in terms of enthalpy change is,

$$đQ = dU + PdV = dH - VdP.$$

Holding pressure fixed, i.e. $dP = 0$ and dividing both sides by $d\theta$, one has,

$$C_P = \frac{đQ_P}{d\theta_P} = \left(\frac{\partial H}{\partial \theta}\right)_P.$$

Now, considering the enthalpy to be a function of temperature and pressure, i.e. $H = H(\theta, P)$, the infinitesimal change in enthalpy is given by,

$$\begin{aligned} dH &= \left(\frac{\partial H}{\partial \theta}\right)_P d\theta + \left(\frac{\partial H}{\partial P}\right)_\theta dP \\ &= C_P d\theta + \left(\frac{\partial H}{\partial P}\right)_\theta dP. \end{aligned}$$

Now in this expression, again we hold P fixed, i.e. $dP = 0$ and divide both sides by dV, to get,

$$\begin{aligned} \left(\frac{\partial H}{\partial V}\right)_P &= C_P \left(\frac{\partial \theta}{\partial V}\right)_P \\ &= \frac{C_P}{V\left[\underbrace{\frac{1}{V}\left(\frac{\partial V}{\partial \theta}\right)_P}_{=\beta}\right]} \\ &= \frac{C_P}{\beta V}. \end{aligned}$$

4\. A unit mole of a gas obeys the van der Waals equation of state:

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

and its molar internal energy is given by ,

$$u = c\,\theta - \frac{a}{v}$$

where $a, b, c,$ and R are constants. Calculate the molar heat capacities c_v and c_P.

(5 + 5 = 10 points)

Solution :

$$\begin{aligned} c_v \equiv \left(\frac{\partial q}{\partial \theta}\right)_v &= \left(\frac{\partial u}{\partial \theta}\right)_v \\ &= \left[\frac{\partial}{\partial \theta}\left(c\,\theta - \frac{a}{v}\right)\right]_v \\ &= c. \end{aligned}$$

(5 points for this part)

Next,

$$c_P \equiv \left(\frac{\partial q}{\partial \theta}\right)_P = c_v + \left[\left(\frac{\partial u}{\partial v}\right)_\theta + P\right]\left(\frac{\partial v}{\partial \theta}\right)_P \tag{3}$$

From the internal energy expression, we compute,

$$\left(\frac{\partial u}{\partial v}\right)_\theta = \frac{a}{v^2}$$

and from the vdW equation of state we compute (recall calculation of β from last HW),

$$\left(\frac{\partial v}{\partial \theta}\right)_P = \frac{Rv^3(v-b)}{R\theta v^3 - 2a\,(v-b)^2}.$$

So gathering all contributions,

$$c_P = c + \left(\frac{a}{v^2} + P\right)\frac{Rv^3(v-b)}{R\theta v^3 - 2a\,(v-b)^2} = c + \frac{R}{1 - \frac{2a\,(v-b)^2}{R\theta v^3}}.$$

One can check that in the ideal gas limit, i.e. when $a = b = 0$, these indeed reproduce the well known result, $c_P - c_v = R$.
(5 points for this part)

5.

For a paramagnetic solid obeying Curie's law as the equation of state, show that

$$C_M = \left(\frac{\partial U}{\partial \theta}\right)_M,$$

and,

$$C_B = \left(\frac{\partial U}{\partial \theta}\right)_B + \frac{M^2}{C_c}.$$

Here C_c denotes the Curie constant, not some heat capacity.

(2 + 3 = 5 points)

Solution:
The first law of thermodynamics gives,

$$đQ = dU - BdM$$

Now the internal energy, U can be thought of as function of two of the three thermodynamic coordinates, B, M, θ. Let's take it to be a function of M and B, i.e. $U = U(B, M)$. Then we can expand the first law,

$$\begin{aligned}
đQ &= dU - B\,dM \\
&= \left(\frac{\partial U}{\partial B}\right)_M dB + \left(\frac{\partial U}{\partial M}\right)_B dM - B\,dM \\
&= \left(\frac{\partial U}{\partial B}\right)_M dB + \left[\left(\frac{\partial U}{\partial M}\right)_B - B\right] dM
\end{aligned}$$

At constant magentization, i.e. when $dM = 0$, this becomes

$$đQ_M = \left(\frac{\partial U}{\partial B}\right)_M dB_M,$$

where the subscript implies constant M. Dividing both sides by $d\theta_M$ and we get,

$$C_M \equiv \left(\frac{dQ}{d\theta}\right)_M = \left(\frac{\partial U}{\cancel{\partial B}}\right)_M \left(\frac{\cancel{\partial B}}{\partial \theta}\right)_M = \left(\frac{\partial U}{\partial \theta}\right)_M.$$

(**2 points for this**)

Next, we set B constant, i.e. $dB = 0$. In such a case the first law becomes,

$$đQ_B = \left[\left(\frac{\partial U}{\partial M} \right)_B - B \right] dM_B,$$

Divinding both sides by $d\theta_B$ we then get,

$$\begin{aligned} C_B \equiv \left(\frac{dQ}{d\theta} \right)_B &= \left[\left(\frac{\partial U}{\partial M} \right)_B - B \right] \left(\frac{\partial M}{\partial \theta} \right)_B \\ &= \left(\frac{\partial U}{\cancel{\partial M}} \right)_B \left(\frac{\cancel{\partial M}}{\partial \theta} \right)_B - B \left(\frac{\partial M}{\partial \theta} \right)_B \\ &= \left(\frac{\partial U}{\partial \theta} \right)_B - \underline{B \left(\frac{\partial M}{\partial \theta} \right)_B}. \end{aligned}$$

Next we use Curie's law, $M = C_C \frac{B}{\theta}$, to compute the underlined quantity,

$$B \left(\frac{\partial M}{\partial \theta} \right)_B = B \frac{\partial}{\partial \theta} \left(C_C \frac{B}{\theta} \right) = -C_C \frac{B^2}{\theta^2} = -\frac{1}{C_C} \left(C_C \frac{B}{\theta} \right)^2 = -\frac{M^2}{C_C},$$

and substitute this back to get,

$$C_B = \left(\frac{\partial U}{\partial \theta} \right)_B + \frac{M^2}{C_C}.$$

(**3 points for this part**)