HOMEWORK 9 SOLUTIONS

Problem 1

Given: Initial and final values for temperature and specific volume.

Find: Estimate the change in pressure from the initial to final state.

Analysis:

The change in pressure, dP, can be expanded as: $dP = \left(\frac{\partial P}{\partial T}\right)_v dT + \left(\frac{\partial P}{\partial v}\right)_T dv$

For an ideal gas, $P = \frac{RT}{v}$ => $\left(\frac{\partial P}{\partial T}\right)_v = \left(\frac{R}{V}\right)_v$ and $\left(\frac{\partial P}{\partial v}\right)_T = -\left(\frac{RT}{v^2}\right)_T$

Therefore: $dP = \left(\frac{R}{v}\right)_v dT - \left(\frac{RT}{v^2}\right)_T dv$

where: $dT = T_2 - T_1 = 2K$ and $dv = v_2 - v_1 = 0.01\ m^3/kg$
$T = T_{avg} = 301K$ and $v = v_{avg} = 0.865\ m^3/kg$

Therefore, dP is:

$$0.287 kPa * m^3 / kg.K \left[\frac{2K}{0.865 m^3/kg} - \frac{301K * 0.01 m^3/kg}{(0.865 m^3/kg)^2} \right]$$

➔ **dP = -0.491 kPa**

Problem 2

Given: du = Tds – Pdv and the Maxwell relations

Find: An expression for $(\partial u/\partial P)_T$ that only has properties P, v, and T involved. Also, find $(\partial u/\partial P)_T$ for an ideal gas.

Analysis:

We start from: du = Tds – Pdv

To find an expression for $(\partial u/\partial P)_T$, divide the above relation by dP to get (consider T constant here across all terms):

$$\left(\frac{\partial u}{\partial P}\right)_T = T\left(\frac{\partial s}{\partial P}\right)_T - P\left(\frac{\partial v}{\partial P}\right)_T$$

Note: To be mathematically precise, we divided by ΔP and then for constant T we took the limit as ΔP→0. Similar approach is considered in similar derivations in other HW problems.

From the Maxwell Relations:

$\left(\frac{\partial s}{\partial P}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p$ Therefore (using the definitions of α and β from lecture notes),

$$\Rightarrow \underline{\left(\frac{\partial u}{\partial P}\right)_T = -T\left(\frac{\partial v}{\partial T}\right)_p - P\left(\frac{\partial v}{\partial P}\right)_T = -T\alpha v + P\beta v}$$

For an ideal gas, $P = \frac{RT}{v}$ => $\alpha = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p = \frac{1}{v}\left(\frac{R}{P}\right)_P = \frac{1}{T}$ and $\beta = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T = \frac{1}{v}\left(\frac{RT}{P^2}\right)_T = \frac{1}{P}$

Therefore, $\underline{\left(\frac{\partial u}{\partial P}\right)_T = -T\alpha v + P\beta v = -Tv\frac{1}{T} + Pv\frac{1}{P} = -v + v = 0}$

$$\Rightarrow \underline{\left(\frac{\partial u}{\partial P}\right)_T = 0}$$

This tells us that for an ideal gas, u is not a function of P – thus its only a function of T. We accepted this result up to now in the course but here a proof is finally provided!

Problem 3

Given: dh = Tds + vdP and the Maxwell relations

Find: An expression for $(\partial h/\partial v)_T$ that only has properties P, v, and T involved. Also, find and expression for $(\partial h/\partial T)_v$.

Analysis:

We start from: dh = Tds + vdP

To find an expression for $(\partial h/\partial v)_T$, divide this relation by dv to get (consider T constant):

$$\left(\frac{\partial h}{\partial v}\right)_T = T\left(\frac{\partial s}{\partial v}\right)_T + v\left(\frac{\partial P}{\partial v}\right)_T$$

From the Maxwell Relations:

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v$$ Therefore,

$$\rightarrow \underline{\left(\frac{\partial h}{\partial v}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_v + v\left(\frac{\partial P}{\partial v}\right)_T}$$

To find an expression for $(\partial h/\partial T)_v$, divide dh = Tds + vdP by dT to get (consider v constant):

$$\left(\frac{\partial h}{\partial T}\right)_T = T\left(\frac{\partial s}{\partial T}\right)_v + v\left(\frac{\partial P}{\partial T}\right)_v$$

From the definition of c_v → $c_v = (\partial u/\partial T)_v = T(\partial s/\partial T)_v$ we get:

$$\rightarrow \underline{\left(\frac{\partial h}{\partial T}\right)_T = c_v + v\left(\frac{\partial P}{\partial T}\right)_v}$$

Problem 4

Given: Definitions of c_v and c_p, and the fact that $c_p > c_v$

Find: Compare the slopes of constant P and constant v curves of a T-s diagram.

Analysis:

The slopes of constant v or constant P curves in a T-s diagram are T lines as a function of s with either v or P held constant. Therefore, the slopes of these lines are $(\partial T/\partial s)_v$ and $(\partial T/\partial s)_P$.

From the definitions of c_v and c_p:

$c_v = (\partial u/\partial T)_v = T\,(\partial s/\partial T)_v$ (for the derivation on the right we used: $du = Tds - Pdv$)
$c_p = (\partial h/\partial T)_P = T\,(\partial s/\partial T)_P$ (for the derivation on the right we used: $dh = Tds + vdP$)

we get using the inversion relation (e.g. $(\partial T/\partial s)_v = 1 / (\partial s/\partial T)_v$, etc.).

$(\partial T/\partial s)_v = T/c_v$ and
$(\partial T/\partial s)_P = T/c_p$

Since $c_p > c_v$ (recall the general relation $C_p - C_v = T\frac{\alpha^2 v}{\beta} > 0$), we can see that

$(\partial T/\partial s)_v > (\partial T/\partial s)_p$

➔ Therefore, we can conclude that the T(s) curves of constant volume are steeper than the T(s) curves of constant pressure.

Problem 5

Given: Definitions of c_v and c_p and the following relations:
dU=TdS-PdV, dH=TdS+VdP, dG=-SdT+VdP, dF=-SdT-PdV

Analysis:

(Part 1)

Using the equations above and the definition of C_v, show: $dS = \frac{C_V}{T} dT + \left(\frac{\partial P}{\partial T}\right)_V dV$

Expand $dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV.$

From the definition of c_v → $c_v = (\partial u/\partial T)_v = T\,(\partial s/\partial T)_v$

So that $(\partial s/\partial T)_v = c_v/T$.

Also, from the Maxwell relations, $(\partial s/\partial V)_T = (\partial P/\partial T)_V$.

Therefore, we get:

$$\rightarrow \underline{dS = \frac{C_V}{T} dT + \left(\frac{\partial P}{\partial T}\right)_V dV}$$

(Part 2)

Using the equations above and the definition of C_P and α, show $dS = \frac{C_P}{T} dT - \alpha V dP$

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

The second derivative above is equal to $-\left(\frac{\partial V}{\partial T}\right)_P = -\alpha V$ (using the Maxwell relation from the expression for dG given in the hints). From *dH=TdS+VdP* we see that for constant P, $dH|_P = T\, dS|_P$ from which we can write $\left(\frac{\partial H}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P$

→ with the definition of C_P we conclude that $T\left(\frac{\partial S}{\partial T}\right)_P = C_P$

$$\rightarrow \underline{dS = \frac{C_P}{T} dT - \alpha V dP}$$

(Part 3)

Start with the ``cyclic relation'' derived in class and the definitions of α and β to show that $\left(\frac{\partial P}{\partial T}\right)_V = \frac{\alpha}{\beta}$

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

We can re-write this equation using the inversion formula for partial derivatives as follows:

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

(Part 4)

Equate the results from Part 1 and 2 and use part 3 to show the following:

$$dV = \frac{C_p - C_v}{T}\frac{\beta}{\alpha}dT - \beta V dP$$

Start with

$$dS = \frac{C_V}{T}dT + \left(\frac{\partial P}{\partial T}\right)_V dV = \frac{C_P}{T}dT - \alpha V dP \rightarrow$$

$$\frac{C_p - C_v}{T}dT = \alpha V dP + \left(\frac{\partial P}{\partial T}\right)_V dV = \alpha V dP + \frac{\alpha}{\beta}dV$$

(using the result from part 3).

Rearranging gives:

➔ $$\underline{dV = \frac{C_p - C_v}{T}\frac{\beta}{\alpha}dT - \beta V dP}$$

(Part 5)

In class we derive in expression of dV in terms of dT and dP using the definitions of α and β (Hint: to arrive at this equation, start from $dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP$).

Equate the simplification of this expression with the result in part 4 above to show that:

$$C_p - C_v = T\frac{\alpha^2 v}{\beta}$$

Recall that $dV = \alpha V dT - \beta V dP$

Thus equating the first term multiplying dT with that from part 4, we conclude:

$$\frac{C_p - C_v}{T}\frac{\beta}{\alpha} = \alpha V$$ or the final result:

➔ $$\underline{C_p - C_v = TV\frac{\alpha^2}{\beta}}$$

(Part 6)

Consider an ideal gas (PV=RT). Derive simplified expressions for α and β (in terms of P,T or V) and simplify the equation in Part 5 to a familiar form for ideal gases.

For ideal gases, PV=RT and the following hold:

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{V}\frac{R}{P} = \frac{R}{RT} = \frac{1}{T}$$

$$\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = -\frac{1}{V}\left(-\frac{RT}{P^2}\right) = \frac{RT}{P(PV)} = \frac{1}{P}$$

Substituting these results into Part 5, we conclude:

$$C_p - C_v = TV\frac{\alpha^2}{\beta} = TV\frac{\frac{1}{T^2}}{\frac{1}{P}} = TV\frac{P}{T^2} = \frac{PV}{T} = \frac{RT}{T} = R$$

➔ $\underline{\mathbf{c_p - c_v = R}}$

Problem 6

Solution:

For the most straightforward solution visit your class notes – Prof. Z did this in class Using the expressions in terms of P and T. Below is another solution procedure that does not follow the general methodology. Its your pick!

Since T is one of the independent variables we can write that

$$\left(\frac{\partial V}{\partial U}\right)_T = \frac{\left(\frac{\partial V}{\partial P}\right)_T}{\left(\frac{\partial U}{\partial P}\right)_T} \qquad (1)$$

Solving for the resulting relations, we use equations for dU and dV

$$dV = V\alpha dT - V\beta dP \qquad (2)$$

The equation for dS is given as: dS= c_P/T dT – α v dP (the Maxwell equation used here is $\left(\frac{\partial \mathrm{S}}{\partial \mathrm{P}}\right)_\mathrm{T} = -\left(\frac{\partial \mathrm{V}}{\partial \mathrm{T}}\right)_\mathrm{P} = -\alpha \mathrm{V}$ derived from dG = -S dT + V dP)

From the above equation using TdS = dU+ P dV, we derive the following:

$$dU = (C_P - PV\alpha)dT + V(P\beta - T\alpha)dP \qquad (3)$$

At constant T, the coefficients of dP are (from eqs 2 and 3, respectively):

$$\left(\frac{\partial V}{\partial P}\right)_T = -V\beta \qquad (4)$$

$$\left(\frac{\partial U}{\partial P}\right)_T = V(P\beta - T\alpha) \qquad (5)$$

Substituting 4 and 5 into 1 and reducing we find that

$$\boxed{\left(\frac{\partial V}{\partial U}\right)_T = -\frac{\beta}{(P\beta - T\alpha)}}$$

Problem 7

The correct answers are a,b,c.

Obviously (a) $dU = TdS - PdV$ is correct – the first and second law combined in their most fundamental way.

Equation (b) $dS = \frac{C_p}{T}dT - V\alpha dP$ also is correct. Indeed, we have $dS = \frac{\partial S}{\partial T}|_P \, dT + \frac{\partial S}{\partial P}|_T \, dP$ or $TdS = T\frac{\partial S}{\partial T}|_P \, dT + T\frac{\partial S}{\partial P}|_T \, dP$ (*)

However, using dH=TdS+VdP→$dH|_P = TdS|_P = c_P dT$→ $T\frac{\partial S}{\partial T}|_P = c_P$

And from the Maxwell relations: $\frac{\partial S}{\partial P}|_T = -\frac{\partial V}{\partial T}|_P = -\alpha V$

Plugging in the last 2 equations in Eq.. (*) gives: $TdS = C_P dT - T\alpha VdP \Rightarrow dS = \frac{C_P}{T}dT - \alpha VdP$ -- thus equation (b) is also correct.

Equation (c) can now be seen in sequence to also be correct: From dH=TdS+VdP, substitute dS from equation (2) to see that.

Equation (d) looks weird and is wrong! The correct relation between dF and dT and dP was shown in class to be dF=-SdT—PdV (you only exchange S with T from U).

Problem 8

The answer is (d). This cyclic relation shown in class and recitation is true for any P-V-T relation. Note that choice (c) as given is not correct as it is not giving you a P-V-T relation. We will be sure to correct this in future HWs and exams!

Problem 9

(Part 1)

$$\mathrm{dU} = \mathrm{T}\left[\left(\frac{\partial \mathrm{S}}{\partial \mathrm{T}}\right)_{\mathrm{V}} \mathrm{dT} + \left(\frac{\partial \mathrm{S}}{\partial \mathrm{V}}\right)_{\mathrm{T}} \mathrm{dV}\right] - \mathrm{PdV} = \mathrm{T}\left(\frac{\partial \mathrm{S}}{\partial \mathrm{T}}\right)_{\mathrm{V}} \mathrm{dT} + \left[\mathrm{T}\left(\frac{\partial \mathrm{S}}{\partial \mathrm{V}}\right)_{\mathrm{T}} - \mathrm{P}\right]\mathrm{dV}$$

or using the definitions of $\mathrm{C_V}$ and the given Maxwell equation:

$$\mathrm{dU} = \mathrm{C_V dT} + \left[\mathrm{T}\left(\frac{\partial \mathrm{P}}{\partial \mathrm{T}}\right)_{\mathrm{V}} - \mathrm{P}\right]\mathrm{dV}$$

(Part 2)

Applying the test for exactness of the differential in Equation (1) above, we see that

$$\left(\frac{\partial \mathrm{C_v}}{\partial \mathrm{v}}\right)_{\mathrm{T}} = \left(\frac{\partial\left(\mathrm{T}\left(\frac{\partial \mathrm{P}}{\partial \mathrm{T}}\right)_{\mathrm{V}} - \mathrm{P}\right)}{\partial \mathrm{T}}\right)_{\mathrm{v}} \Rightarrow \left(\frac{\partial \mathrm{C_v}}{\partial \mathrm{v}}\right)_{\mathrm{T}} = \mathrm{T}\left(\frac{\partial^2 \mathrm{P}}{\partial \mathrm{T}^2}\right)_{\mathrm{v}} + \left(\frac{\partial \mathrm{P}}{\partial \mathrm{T}}\right)_{\mathrm{V}} - \left(\frac{\partial \mathrm{P}}{\partial \mathrm{T}}\right)_{\mathrm{V}}.$$

or $\left(\frac{\partial C_v}{\partial v}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_v$. Hence proved.

(Part 3)

We know from Equation (1) that dU = $C_v dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right]dV$

For an ideal gas, $PV = RT$ and $\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V}$; Further from Equation (2) we know that

$\left(\frac{\partial C_v}{\partial v}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V$ => for an ideal gas => $\left(\frac{\partial C_v}{\partial v}\right)_T = 0$. Thus C_v is independent of *V*.

Thus C_v is only dependent on T.
Then

$$dU = C_v dT + \left[T\left(\frac{\partial P}{\partial T}\right)_v - P\right]dv = C_v dT + \left[T\frac{R}{V} - P\right]dV = C_v dT + \left[\cancel{P - P}\right]dV$$

Therefore dU = $C_v dT$ and U is a function of temperature T alone.