CHEM 444 HW#9

Answer key by Jiahao Chen
due December 1, 2004

Grading policy: One point is given for each numbered equation shown in the solution, or for written statements and/or equations to the same effect. The total score for this problem set is 35 points.

Important Note. For those who came to office hours, please note I made some mistakes in explaining the questions. I did not penalize you on this homework if you came for office hours since this is really my fault; this is noted by “CIL” on your homework (for credit-in-lieu). But for this homework, getting a perfect score will not necessarily imply that everything you have written is conceptually correct, and I gave some bonus points if you were smarter than your TA and did it the mathematically correct way.

1. For a reversible process show the relations:

(a) \( \bar{dq} = \left[ (\frac{\partial U}{\partial T})_P + P \left( \frac{\partial V}{\partial T} \right)_P \right] dT + \left[ (\frac{\partial U}{\partial P})_T + P \left( \frac{\partial V}{\partial P} \right)_T \right] dP \) [4 points]

(b) \( (\frac{\partial U}{\partial T})_P = C_P - PV \alpha \) [5 points]

(c) \( (\frac{\partial U}{\partial P})_T = PV \kappa_T - (C_P - C_V) \frac{\alpha}{\kappa} \) [8 points]

Solution.

(a) Begin with the first law of thermodynamics

\[ dU = dq - dw \]  

\[ \Rightarrow dq = dU + PdV \]  

Then consider \( U \) and \( V \) as functions of temperature \( T \) and pressure \( P \):

\[ dU = \left( \frac{\partial U}{\partial T} \right)_P dT + \left( \frac{\partial U}{\partial P} \right)_T dP \]  

\[ dV = \left( \frac{\partial V}{\partial T} \right)_P dT + \left( \frac{\partial V}{\partial P} \right)_T dP \]  

Collecting the terms,

\[ dq = \left[ \left( \frac{\partial U}{\partial T} \right)_P + P \left( \frac{\partial V}{\partial T} \right)_P \right] dT + \left[ \left( \frac{\partial U}{\partial P} \right)_T + P \left( \frac{\partial V}{\partial P} \right)_T \right] dP \]

(b) Consider the enthalpy function and ‘divide’ its differential form by \( dT \) at constant \( P \):

\[ \frac{H}{T} = U + PV \]  

\[ dH = dU + PdV + VdP \]  

\[ \Rightarrow \left( \frac{\partial H}{\partial T} \right)_P = \left( \frac{\partial U}{\partial T} \right)_P + P \left( \frac{\partial V}{\partial T} \right)_P + 0 \]
Identifying the derivatives completes the proof

\[ C_P = \left( \frac{\partial H}{\partial T} \right)_P \]
(8)

\[ \left( \frac{\partial V}{\partial T} \right)_P = V \cdot \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P = V \alpha \]
(9)

\[ \Rightarrow \left( \frac{\partial U}{\partial T} \right)_P = C_P - PV \alpha \]

(c) Consider the internal energy as a function of \( T \) and \( V \) and apply the previous result to get

\[ dU = \left( \frac{\partial U}{\partial T} \right)_P dT + \left( \frac{\partial U}{\partial P} \right)_T dP \]
(10)

\[ = (C_P - PV \alpha) dT + \left( \frac{\partial U}{\partial P} \right)_T dP \]
(11)

Then ‘divide’ by \(dT\) at constant \( V\) to get

\[ \left( \frac{\partial U}{\partial T} \right)_V = (C_P - PV \alpha) + \left( \frac{\partial U}{\partial P} \right)_T \left( \frac{\partial P}{\partial T} \right)_V \]
(12)

Identify

\[ C_V = \left( \frac{\partial U}{\partial T} \right)_V \]
(13)

and from the cyclic identity

\[ \left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial T}{\partial V} \right)_P \left( \frac{\partial V}{\partial P} \right)_T = -1 \]
(14)

the last unknown derivative can be found to be

\[ \left( \frac{\partial P}{\partial T} \right)_V = -\frac{1}{\left( \frac{\partial V}{\partial P} \right)_T \left( \frac{\partial P}{\partial T} \right)_P} = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T \alpha \]
(15)

\[ = \frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T = \frac{1}{\kappa_T} \alpha \]
(16)

So

\[ C_V = C_P + \left[ \left( \frac{\partial U}{\partial P} \right)_T - PV \kappa_T \right] \frac{\alpha}{\kappa_T} \]
(17)

which can be rearranged to obtain the desired identity.

**Note.** Since \( d_q \) is an inexact differential,

\[ d_q \neq \left( \frac{\partial q}{\partial T} \right)_P dT + \left( \frac{\partial q}{\partial P} \right)_T dP \]

since the following mixed differentials are unequal

\[ \frac{\partial^2 q}{\partial T \partial P} \neq \frac{\partial^2 q}{\partial P \partial T} \]

and the differential equation cannot be integrated. This is the distinguishing feature of an inexact differential. So what we discussed during office hours was wrong. The mathematically correct way to do this entire question is to work from thermodynamic potentials such as enthalpy and entropy since these are state functions.
2. For a single-component fluid show that

\[ \frac{1}{V} \left( \frac{\partial \mu}{\partial V} \right)_T = \left( \frac{\partial P}{\partial V} \right)_T \]  

(18)

Next, assume that the fluid obeys the van der Waals equation of state. Find the chemical potential of the gas to within an arbitrary function of \( T \) along, i.e., express it in the form

\[ \mu (T, V) = g (T, V) + f (T) \]  

(19)

where \( f (T) \) is an “integration constant”, and determine \( g (T, V) \). [8 points]

**Solution.** Begin with the differential form for the molar Gibbs free energy (which is just the chemical potential):

\[ d\mu = dG = -S dT + V dP \]  

(20)

Dividing by \( dV \) at constant \( T \) immediately gives the result

\[ \left( \frac{\partial \mu}{\partial V} \right)_T = V \left( \frac{\partial P}{\partial V} \right)_T \]  

(21)

which can be rearranged to get the desired equation. Applying the van der Waals equation of state then gives

\[ \left( \frac{\partial \mu}{\partial V} \right)_T = V \left( \frac{RT}{V - b} - \frac{a}{V^2} \right)_T \]  

(22)

\[ = \frac{RTV}{(V - b)^2} + \frac{2a}{V^2} \]  

(23)

\[ \begin{align*}
= & \frac{RT \left( V - b + b \right)}{(V - b)^2} + \frac{2a}{V^2} \\
= & \frac{RT \left( V - b \right)}{(V - b)^2} + \frac{2a}{V^2}
\end{align*} \]  

(24)

\[ \begin{align*}
= & \frac{RT}{V - b} - \frac{RTb}{(V - b)^2} + \frac{2a}{V^2}
\end{align*} \]  

(25)

Directly integrating (note the indefinite integral) then gives

\[ \mu = \int -\frac{RT}{V - b} - \frac{RTb}{(V - b)^2} + \frac{2a}{V^2} dV \]  

(26)

\[ = -RT \ln (V - b) + \frac{RTb}{V - b} - \frac{2a}{V} + f (T) \]  

(27)

where the constant of integration is possibly a function of temperature since \( \mu = \mu (T, V) \). Explicitly,

\[ g (T, V) = -RT \ln (V - b) + \frac{RTb}{V - b} - \frac{2a}{V} \]

3. A system obeys the van der Waals equation of state. One mole of this system is expanded isothermally at temperature \( T \) from an initial volume \( V_1 \) to a final volume \( V_2 \). Find the heat transfer to the system in this expansion. [10 points]
Solution. Consider changes in the entropy $S = S(T,V)$ [1 point]:

$$dS = (\frac{\partial S}{\partial T})_V dT + (\frac{\partial S}{\partial V})_T dV \quad (28)$$

but since the process is isothermal

$$dT = 0 \quad (29)$$

and the remaining derivative can be evaluated from the Maxwell relation arising from

$$dA = -SdT - PdV \quad (30)$$

$$\Rightarrow (\frac{\partial S}{\partial V})_T = (\frac{\partial P}{\partial T})_V \quad (31)$$

So

$$dS = (\frac{\partial P}{\partial T})_V dV \quad (32)$$

and since by definition

$$d\bar{q} = TdS = T \left(\frac{\partial P}{\partial T}\right)_V dV \quad (33)$$

$$= \frac{RT}{V-b} dV \quad (34)$$

for a van der Waals gas, so

$$\bar{q} = \int_{V_1}^{V_2} \frac{RT}{V-b} dV \quad (35)$$

$$= RT \ln \frac{V_2-b}{V_1-b} \quad (36)$$

Note. $dU = 0$ only for an ideal gas. Energy is required to break bonds in the expansion of a non-ideal gas. Therefore $dU \neq 0$ for model gases that are non-ideal, such as a van der Waals gas.