Practice questions

1. For a general substance the pressure dependence of the enthalpy is

$$\left(\frac{\partial H}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P + V = -TV\alpha + V,$$

where $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$.

   (a) Using $PV = nRT$, verify directly that $\left(\frac{\partial H}{\partial P}\right)_T = 0$ for an ideal gas.

   (b) Show that $\alpha = 1/T$ for an ideal gas, and use this to obtain the same result.

2. The Gibbs equation relates the fundamental thermodynamic state functions U, S and V,

$$dU = T\,dS - P\,dV.$$

Starting from this expression, show that

$$\left(\frac{\partial S}{\partial V}\right)_U = \frac{P}{T}.$$

Hint: Solve for dS, then write the total differential of S as a function of U and V and compare the two expressions term by term.

3. For a van der Waals gas the equation of state is

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT,$$

where a and b are constants. Using the thermodynamic equation of state,

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P,$$

show that

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{an^2}{V^2}.$$

   (a) Which van der Waals constant does *not* appear in your result, and why?

   (b) What value does $(\partial U/\partial V)_T$ take for an ideal gas?

4. The thermal expansion coefficient and the isothermal compressibility are defined by

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P, \qquad \kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T.$$

Starting from the Gibbs equation for dU, show that

$$\left(\frac{\partial U}{\partial P}\right)_T = -TV\alpha + PV\kappa.$$

Hints:

- You may use the Maxwell relation $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$.

5. The thermal expansion coefficient is defined by $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$. Starting from the Gibbs equation,

$$dU = T\,dS - P\,dV,$$

show that

$$\left(\frac{\partial U}{\partial T}\right)_P = C_P - PV\alpha.$$

6. A certain gas obeys the equation of state

$$PV_m = RT\,(1 + bP)\,,$$

where b is a constant. Prove that for this gas

(a) $\left(\dfrac{\partial U}{\partial V}\right)_T = bP^2$

(b) $C_{P,m} - C_{V,m} = R\,(1 + bP)^2$

Hints:

- Write V_m explicitly as a function of T and P before differentiating.
- You may use the cyclic relation $\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial V}{\partial T}\right)_P \Big/ \left(\frac{\partial V}{\partial P}\right)_T$, and the thermodynamic equation of state $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$.
- For part (b), $C_P - C_V = \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\left(\frac{\partial V}{\partial T}\right)_P$.
- Check that your answer gives the ideal-gas result when $b = 0$.

7. Verify the **Gibbs–Helmholtz equation**,

$$\left[\frac{\partial\,(G/T)}{\partial T}\right]_P = -\frac{H}{T^2}.$$

Hints:

- Treat G/T as a product (or quotient) and differentiate both factors.
- From $dG = -S\,dT + V\,dP$ you may use $\left(\frac{\partial G}{\partial T}\right)_P = -S$.
- Recall the definition $G = H - TS$.

8. The Gibbs equations for the internal energy and the enthalpy are

$$dU = T\,dS - P\,dV, \qquad dH = T\,dS + V\,dP.$$

Starting from these, derive

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V, \qquad C_P = T\left(\frac{\partial S}{\partial T}\right)_P.$$

Hints:

- Use the definitions $C_V = \left(\frac{\partial U}{\partial T}\right)_V$ and $C_P = \left(\frac{\partial H}{\partial T}\right)_P$.
- Differentiate each Gibbs equation with respect to T, holding the variable that is kept constant in the corresponding heat capacity. One term drops out in each case.

Cont.

9. Consider the multivariate function

$$f(x,y) = x^2 e^{xy} + \ln\left(\frac{x}{y}\right).$$

(a) Compute $\dfrac{\partial f}{\partial x}$ and $\dfrac{\partial f}{\partial y}$.

(b) Verify explicitly that $\dfrac{\partial^2 f}{\partial x\,\partial y} = \dfrac{\partial^2 f}{\partial y\,\partial x}$.

(c) Write the Hessian matrix of f.

10. The Helmholtz energy A is a state function of T and V, with total differential

$$dA = -S\,dT - P\,dV.$$

(a) Identify $\left(\frac{\partial A}{\partial T}\right)_V$ and $\left(\frac{\partial A}{\partial V}\right)_T$.

(b) By equating the mixed second partial derivatives of A, derive the Maxwell relation

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V.$$

(c) Evaluate $\left(\frac{\partial S}{\partial V}\right)_T$ for a van der Waals gas, $P = \frac{nRT}{V-nb} - \frac{an^2}{V^2}$, and compare it with the ideal-gas result.

Hint: Because A is a state function, $\dfrac{\partial^2 A}{\partial V\,\partial T} = \dfrac{\partial^2 A}{\partial T\,\partial V}$.

11. A differential $M\,dT + N\,dV$ is **exact** (that is, it is the differential of a state function) only if

$$\left(\frac{\partial M}{\partial V}\right)_T = \left(\frac{\partial N}{\partial T}\right)_V.$$

For one mole of an ideal gas the internal energy depends only on temperature, so $dU = C_V\,dT$ and the first law gives

$$\delta q = C_V\,dT + \frac{RT}{V}\,dV.$$

(a) Apply the test to δq and show that it is **not** exact.

(b) Now divide by T to form $dS = \delta q/T$, apply the same test, and show that dS **is** exact.

(c) Explain what this tells you about q and S as thermodynamic quantities.

Hint: For an ideal gas C_V depends only on T.

12. The internal energy of a closed system, as a state function of T and V, has the total differential

$$dU = C_V\,dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right]dV.$$

(a) For a van der Waals gas, $P = \frac{nRT}{V-nb} - \frac{an^2}{V^2}$, show that $\left(\frac{\partial U}{\partial V}\right)_T = \frac{an^2}{V^2}$.

(b) By equating the mixed second partial derivatives of U, show that in general

$$\left(\frac{\partial C_V}{\partial V}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V.$$

(c) Evaluate this for the van der Waals gas. What does your answer say about how C_V depends on volume?

Cont.

(d) Repeat part (c) for a Berthelot gas, $P = \frac{nRT}{V-nb} - \frac{an^2}{TV^2}$.

Hint: In part (b), differentiate the coefficient of dV with respect to T; two terms cancel.

13. The entropy of a closed system, as a state function of T and P, has the total differential

$$dS = \frac{C_P}{T}\,dT - \left(\frac{\partial V}{\partial T}\right)_P dP.$$

Consider a gas obeying

$$\bar{V} = \frac{RT}{P} - \frac{a}{RT}P + b,$$

where a and b are constants.

(a) Determine $\left(\frac{\partial \bar{S}}{\partial P}\right)_T$ for this gas.

(b) By equating the mixed second partial derivatives of $\bar{S}$, show that

$$\left(\frac{\partial \bar{C}_P}{\partial P}\right)_T = -T\left(\frac{\partial^2 \bar{V}}{\partial T^2}\right)_P,$$

and evaluate it for this equation of state.

Hint: Compare your answer to part (b) with the result obtained from the total differential of $\bar{H}$. The two routes must agree.

The End.