

3 The Importance of State Functions: Internal Energy and Enthalpy

Problem numbers in italics indicate that the solution is included in the *Student Solutions Manual*.

Conceptual Problems

Q3.1 The heat capacity $C_{P,m}$ is less than $C_{V,m}$ for $\text{H}_2\text{O}(l)$ near 4°C . Explain this result.

$C_P < C_V$ is valid for a liquid if V decreases with T at constant P . Although unusual, this condition is satisfied for water between 4°C and the freezing point. This unusual behavior occurs because the density of water decreases with temperature in this range. Therefore, work is done by the surroundings on the system as water is heated at constant P between 4°C and 5°C because the molar volume decreases with temperature.

Q3.2 What is the physical basis for the experimental result that U is a function of V at constant T for a real gas? Under what conditions will U decrease as V increases?

U is a function of V for a real gas because of the interaction potential between gas molecules. U decreases as V increases if the density is such that the gas is dominated by the repulsive part of the potential.

Q3.3 Why didn't Joule change his experiment to make $C_{\text{surroundings}}/C_{\text{system approx}} = 0.001$ to increase the sensitivity of the apparatus?

The system is a gas and to make $C_{\text{surroundings}}/C_{\text{system approx}} = 0.001$ would require that the surroundings consist of a substance whose heat capacity is much less than that of a gas. There is no such substance.

Q3.4 Why does the relation $C_P > C_V$ always hold for a gas? Can $C_P < C_V$ be valid for a liquid?

This is the case because the volume of a real gas always increases with increasing T . Therefore, heating a real gas at constant P results in the system doing work on the surroundings.

Q3.5 Why can q_V be equated with a state function if q is not a state function?

If the path is defined, the value of q has a unique value even though q is not a state function.

Q3.6 Explain without using equations why $(\partial H/\partial P)_T$ is generally small for a real gas.

The variation of H with P is a measure of how the energy of a gas changes with the spacing between the molecules of the gas. Because the depth of the minimum in the potential in Figure 1.6 is generally very small, it takes very little energy to separate the atoms or molecules that make up the gas.

- Q3.7** Why is it reasonable to write $dH \approx C_p dT + V dP$ for a liquid or solid sample?
- This approximation is valid because $T \left(\frac{\partial U}{\partial V} \right)_T \ll V$ for a liquid or solid.
- Q3.8** Refer to Figure 1.10 and explain why $(\partial U / \partial V)_T$ is generally small for a real gas.
- The depth of the minimum in the potential is generally very small. Therefore, it takes very little energy to separate the atoms or molecules that make up the gas.
- Q3.9** Can a gas be liquefied through an isenthalpic expansion if $\mu_{J-T} = 0$?
- No. The gas would not be cooled if $\mu_{J-T} = 0$.
- Q3.10** Why is $q_V = \Delta U$ only for a constant volume process? Is this formula valid if work other than $P-V$ work is possible?
- Because $\Delta U = q + w$, $q_V = \Delta U$ only if w is zero. Therefore, the formula is not valid if work other than $P-V$ work is possible.
- Q3.11** Classify the following variables and functions as intensive or extensive: T, P, V, q, w, U, H .
- T and P are intensive variables because their value does not depend on the size of the system. The others are intensive because their value depends on the size of the system.
- Q3.12** Why are q and w not state functions?
- They are not state functions because their value depends on the path taken between initial and final states.
- Q3.13** Why is the equation $\Delta H = \int_{T_i}^{T_f} C_p(T) dT = n \int_{T_i}^{T_f} C_{p,m}(T) dT$ valid for an ideal gas even if P is not constant in the process? Is this equation also valid for a real gas? Why or why not?
- It is valid because for an ideal gas, H is a function of T only, and is not a function of V or P . The formula is not accurate for a real gas, because H is a weak function of V and P .
- Q3.14** What is the relationship between a state function and an exact differential?
- In order for a function $f(x, y)$ to be a state function, it must be possible to write the total differential df in the form $df = \left(\frac{\partial f}{\partial x} \right)_y dx + \left(\frac{\partial f}{\partial y} \right)_x dy$. If the form df as written exists, it is an exact differential.
- Q3.15** Is the following statement always, never, or sometimes valid? Explain your reasoning: ΔH is only defined for a constant pressure process.
- Never. ΔH can be calculated for a change between any two states that the system can be in.
- Q3.16** Is the following statement always, never, or sometimes valid? Explain your reasoning: A thermodynamic process is completely defined by the initial and final states of the system.
- Sometimes, namely when the process is defined by a state function. Otherwise the path also needs to be stated.
- Q3.17** Is the following statement always, never, or sometimes valid? Explain your reasoning: $q = 0$ for a cyclic process.
- Sometimes, namely for an adiabatic cycle or for a cycle consisting of a reversible isothermal expansion followed by a reversible isothermal compression back to the original state. Whenever the area in an indicator diagram for the cyclic process is not zero, q is not zero.
- Q3.18** The molar volume of $\text{H}_2\text{O}(l)$ decreases with increasing temperature near 4°C . Can you explain this behavior using a molecular level model?

The structure of liquid water is changing at a molecular level. At temperatures below 4°C, the hydrogen bonds in ice lead to a static structure with a lot of void space. When ice melts these clusters are slowly broken up but still persist up to about 4°C where they are broken up completely and water molecules move rapidly and randomly in the liquid with hydrogen bonds constantly forming and breaking. At that point the void space between the water molecules is minimized.

- Q3.19** Why was the following qualification made in Section 3.7? Note that Equation (3.47) is only applicable to a process in which there is no change in the phase of the system, such as vaporization or fusion, and in which there are no chemical reactions.

In these cases, either a phase change occurs or the composition of the system changes. In these cases, the enthalpy can change even though the temperature remains constant.

- Q3.20** Is the expression $\Delta U_V = \int_{T_1}^{T_2} C_V dT = n \int_{T_1}^{T_2} C_{V,m} dT$ only valid for an ideal gas if V is constant?

No. It is always valid for an ideal gas because for an ideal gas, there are no interactions between molecules and therefore U is independent of V .

Numerical Problems

- P3.1** Obtain an expression for the isothermal compressibility $\kappa = -1/V(\partial V/\partial P)_T$ for a van der Waals gas.

$$\kappa = -\frac{1}{V_m} \left(\frac{\partial V_m}{\partial P} \right)_T = -\frac{1}{V_m \left(\frac{\partial P}{\partial V_m} \right)_T} = -\frac{1}{V_m \left(\frac{\partial}{\partial V_m} \left[\frac{RT}{V_m - b} - \frac{a}{V_m^2} \right] \right)_T}$$

$$\kappa = -\frac{1}{V_m \left[\frac{2a}{V_m^3} - \frac{RT}{(V_m - b)^2} \right]}$$

- P3.2** Use the result of Problem P3.10 to show that $(\partial C_V/\partial V)_T$ for the van der Waals gas is zero.

We use the relationship

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

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

$$\left(\frac{\partial P}{\partial T} \right)_V = \frac{R}{V_m - b}$$

$$\left(\frac{\partial^2 P}{\partial T^2} \right)_V = \left(\frac{\partial}{\partial T} \frac{R}{V_m - b} \right)_V = 0$$

$$\text{therefore } \left(\frac{\partial C_V}{\partial V} \right)_T = T \left(\frac{\partial^2 P}{\partial T^2} \right)_V = T \times 0 = 0.$$

- P3.3** The molar heat capacity $C_{P,m}$ of $\text{SO}_2(\text{g})$ is described by the following equation over the range $300 \text{ K} < T < 1700 \text{ K}$:

$$\frac{C_{P,m}}{R} = 3.093 + 6.967 \times 10^{-3} \frac{T}{\text{K}} - 45.81 \times 10^{-7} \frac{T^2}{\text{K}^2} + 1.035 \times 10^{-9} \frac{T^3}{\text{K}^3}$$

In this equation, T is the absolute temperature in kelvin. The ratios T^n/K^n ensure that $C_{P,m}$ has the correct dimension. Assuming ideal gas behavior, calculate q , w , ΔU , and ΔH if 1.50 moles of $\text{SO}_2(\text{g})$ is heated from 22.5°C to 1140°C at a constant pressure of 1 bar. Explain the sign of w .

$$\begin{aligned}\Delta H = q &= n \int_{T_i}^{T_f} C_{P,m} dT = 1.50 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times \int_{295.65}^{1412.15} \left(3.093 + 6.977 \times 10^{-3} \frac{T}{\text{K}} - 45.81 \times 10^{-7} \frac{T^2}{\text{K}^2} + 1.035 \times 10^{-9} \frac{T^3}{\text{K}^3} \right) d\frac{T}{\text{K}} \\ &= 1.50 \text{ mol} \times 8.314 \text{ J mol}^{-1} \times \left[3.093 \frac{T}{\text{K}} + 0.0034835 \frac{T^2}{\text{K}^2} - 1.527 \times 10^{-6} \frac{T^3}{\text{K}^3} + 2.5875 \times 10^{-10} \frac{T^4}{\text{K}^4} \right]_{295.65}^{1412.15} \\ &= (4.311 \times 10^4 \text{ J mol}^{-1} + 8.308 \times 10^4 \text{ J mol}^{-1} - 5.325 \times 10^4 \text{ J mol}^{-1} + 1.284 \times 10^4 \text{ J mol}^{-1} \text{ K}^{-1}) \\ &= 8.58 \times 10^4 \text{ J} \\ \Delta U &= \Delta H - \Delta(PV) = \Delta H - nR\Delta T \\ &= 8.58 \times 10^4 \text{ J} - 1.50 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times (1413.15 \text{ K} - 295.65 \text{ K}) \\ &= 7.18 \times 10^4 \text{ J} \\ w &= \Delta U - q = 7.18 \times 10^4 \text{ J} - 8.58 \times 10^4 \text{ J} = -1.39 \times 10^4 \text{ J}\end{aligned}$$

Because the gas is heated, it expands. Therefore $\Delta V > 0$ and $w < 0$.

- P3.4** Use the relation $(\partial U/\partial V)_T = T(\partial P/\partial T)_V - P$ and the cyclic rule to obtain an expression for the internal pressure, $(\partial U/\partial V)_T$, in terms of P , β , T , and κ .

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

- P3.5** A mass of 34.05 g of $\text{H}_2\text{O}(\text{s})$ at 273 K is dropped into 185 g of $\text{H}_2\text{O}(\text{l})$ at 310. K in an insulated container at 1 bar of pressure. Calculate the temperature of the system once equilibrium has been reached. Assume that $C_{P,m}$ for $\text{H}_2\text{O}(\text{l})$ is constant at its values for 298 K throughout the temperature range of interest.

$$\begin{aligned}n_{\text{ice}}\Delta H_{\text{fusion}}^{\text{ice}} + n_{\text{ice}}C_{P,m}^{\text{H}_2\text{O}}(T_f - T_i^{\text{ice}}) + n_{\text{H}_2\text{O}}C_{P,m}^{\text{H}_2\text{O}}(T_f - T_i^{\text{H}_2\text{O}}) &= 0 \\ T_f &= \frac{n_{\text{ice}}C_{P,m}^{\text{ice}}T_i^{\text{ice}} + n_{\text{H}_2\text{O}}C_{P,m}^{\text{H}_2\text{O}}T_i^{\text{H}_2\text{O}} - n_{\text{ice}}\Delta H_{\text{fusion}}^{\text{ice}}}{n_{\text{ice}}C_{P,m}^{\text{ice}} + n_{\text{H}_2\text{O}}C_{P,m}^{\text{H}_2\text{O}}} \\ &= \frac{34.05 \text{ g ice}}{18.02 \text{ g ice mol}^{-1}} \times 75.3 \text{ J K}^{-1} \text{ mol}^{-1} \times 273 \text{ K} + \frac{185.0 \text{ g H}_2\text{O}}{18.02 \text{ g H}_2\text{O mol}^{-1}} \times 75.3 \text{ J K}^{-1} \text{ mol}^{-1} \times 310. \text{ K} \\ &\quad - \frac{34.05 \text{ g ice}}{18.02 \text{ g ice mol}^{-1}} \times 6010 \text{ J mol}^{-1} \\ &= \frac{34.05 \text{ g ice}}{18.02 \text{ g ice mol}^{-1}} \times 75.3 \text{ J K}^{-1} \text{ mol}^{-1} + \frac{185.0 \text{ g H}_2\text{O}}{18.02 \text{ g H}_2\text{O mol}^{-1}} \times 75.3 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

$$T_f = 292 \text{ K}$$

- P3.6** A vessel is filled completely with liquid water and sealed at 13.56°C and a pressure of 1.00 bar. What is the pressure if the temperature of the system is raised to 82.0°C ? Under these conditions, $\beta_{\text{water}} = 2.04 \times 10^{-4} \text{ K}^{-1}$, $\beta_{\text{vessel}} = 1.42 \times 10^{-4} \text{ K}^{-1}$, and $\kappa_{\text{water}} = 4.59 \times 10^{-3} \text{ bar}^{-1}$.

$$\begin{aligned}\Delta P &= \int \frac{\beta_{\text{water}}}{\kappa} dT - \int \frac{1}{\kappa V} dV = \frac{\beta_{\text{water}} \Delta T}{\kappa} - \frac{1}{\kappa} \ln \frac{V_f}{V_i} \\ &= \frac{\beta_{\text{water}} \Delta T}{\kappa} - \frac{1}{\kappa} \ln \frac{V_i(1 + \beta_{\text{vessel}} \Delta T)}{V_i} = \frac{\beta_{\text{water}} \Delta T}{\kappa} - \frac{1}{\kappa} \frac{\beta_{\text{vessel}} \Delta T}{V_i} = \frac{(\beta_{\text{water}} - \beta_{\text{vessel}}) \Delta T}{\kappa} \\ &= \frac{(2.04 - 1.42) \times 10^{-4} (\text{C})^{-1}}{4.59 \times 10^{-5} (\text{bar})^{-1}} \times 68.44^\circ \text{C} = 92.4 \text{ bar} \\ P_f + \Delta P &= 93.4 \text{ bar}\end{aligned}$$

- P3.7** Integrate the expression $\beta = 1/V(\partial V/\partial T)_P$ assuming that β is independent of pressure. By doing so, obtain an expression for V as a function of T and β at constant P .

$$\begin{aligned}\beta &= \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \\ \frac{dV}{V} &= \beta dT \\ \int \frac{dV}{V} &= \int \beta dT \text{ or } \ln \frac{V_f}{V_i} = \beta(T_f - T_i)\end{aligned}$$

if β can be assumed constant in the temperature interval of interest.

- P3.8** A mass of 32.0 g of $\text{H}_2\text{O}(\text{g})$ at 373 K is flowed into 295 g of $\text{H}_2\text{O}(\text{l})$ at 310. K and 1 atm. Calculate the final temperature of the system once equilibrium has been reached. Assume that $C_{P,m}$ for $\text{H}_2\text{O}(\text{l})$ is constant at its values for 298 K throughout the temperature range of interest.

$$\begin{aligned}-n_{\text{steam}} \Delta H_{\text{vaporization}}^{\text{water}} + n_{\text{steam}} C_{P,m}^{\text{H}_2\text{O}}(T_f - T_i^{\text{steam}}) + n_{\text{H}_2\text{O}} C_{P,m}^{\text{H}_2\text{O}}(T_f - T_i^{\text{H}_2\text{O}}) &= 0 \\ T_f &= \frac{n_{\text{steam}} C_{P,m}^{\text{H}_2\text{O}} T_i^{\text{steam}} + n_{\text{H}_2\text{O}} C_{P,m}^{\text{H}_2\text{O}} T_i^{\text{H}_2\text{O}} + n_{\text{steam}} \Delta H_{\text{vaporization}}^{\text{water}}}{n_{\text{steam}} C_{P,m}^{\text{H}_2\text{O}} + n_{\text{H}_2\text{O}} C_{P,m}^{\text{H}_2\text{O}}} = \\ &= \frac{\frac{32.0 \text{ g steam}}{18.02 \text{ g steam mol}^{-1}} \times 75.3 \text{ J K}^{-1} \text{mol}^{-1} \times 373 \text{ K} + \frac{295 \text{ g H}_2\text{O}}{18.02 \text{ g H}_2\text{O mol}^{-1}} \times 75.3 \text{ J K}^{-1} \text{mol}^{-1} \times 310. \text{ K}}{\frac{32.0 \text{ g steam}}{18.02 \text{ g steam mol}^{-1}} + \frac{295 \text{ g H}_2\text{O}}{18.02 \text{ g H}_2\text{O mol}^{-1}}} + \frac{32.0 \text{ g steam}}{18.02 \text{ g steam mol}^{-1}} \times 40656 \text{ J mol}^{-1} \\ T_f &= 369 \text{ K}\end{aligned}$$

- P3.9** Because $(\partial H/\partial P)_T = -C_{P,m} \mu_{J-T}$, the change in enthalpy of a gas expanded at constant temperature can be calculated. To do so, the functional dependence of μ_{J-T} on P must be known. Treating Ar as a van der Waals gas, calculate ΔH when 1 mol of Ar is expanded from 325 bar to 1.75 bar at 375 K. Assume that μ_{J-T} is independent of pressure and is given by $\mu_{J-T} = [(2a/RT) - b]/C_{P,m}$, and $C_{P,m} = 5/2R$ for Ar. What value would ΔH have if the gas exhibited ideal gas behavior?

$$\begin{aligned}\Delta H_m &= - \int_{P_i}^{P_f} C_{P,m} \mu_{J-T} dP = -C_{P,m} \mu_{J-T} (P_f - P_i) \\ &= -C_{P,m} \times \frac{1}{C_{P,m}} \left(\frac{2 \times 0.1355 \text{ m}^6 \text{ Pa mol}^{-2}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 375 \text{ K}} - 0.03201 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1} \right) \\ &\quad \times (1.75 \times 10^5 \text{ Pa} - 325 \times 10^5 \text{ Pa}) \\ &= 1.78 \times 10^3 \text{ J}\end{aligned}$$

For an ideal gas, $\Delta H_m = 0$ because μ_{J-T} is zero for an ideal gas.

- P3.10** Derive the following expression for calculating the isothermal change in the constant volume heat capacity: $(\partial C_V / \partial V)_T = T(\partial^2 P / \partial T^2)_V$.

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

The order of differentiation can be reversed because U is a state function.

$$\text{Using the equation } \left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P$$

$$\begin{aligned} \left(\frac{\partial C_V}{\partial V}\right)_T &= \left(\frac{\partial}{\partial T} \left(T \left(\frac{\partial P}{\partial T}\right)_V - P\right)\right)_V \\ &= \left(\frac{\partial P}{\partial T}\right)_V + T \left(\frac{\partial^2 P}{\partial T^2}\right)_V - \left(\frac{\partial P}{\partial T}\right)_V = T \left(\frac{\partial^2 P}{\partial T^2}\right)_V \end{aligned}$$

- P3.11** An 75.0 g piece of gold at 650. K is dropped into 180. g of $\text{H}_2\text{O}(l)$ at 310. K in an insulated container at 1 bar pressure. Calculate the temperature of the system once equilibrium has been reached. Assume that $C_{P,m}$ for Au(s) and $\text{H}_2\text{O}(l)$ is constant at their values for 298 K throughout the temperature range of interest.

$$n_{\text{Au}} C_{P,m}^{\text{Au}} (T_f - T_i^{\text{Au}}) + n_{\text{H}_2\text{O}} C_{P,m}^{\text{H}_2\text{O}} (T_f - T_i^{\text{H}_2\text{O}}) = 0$$

$$\begin{aligned} T_f &= \frac{n_{\text{Au}} C_{P,m}^{\text{Au}} T_i^{\text{Au}} + n_{\text{H}_2\text{O}} C_{P,m}^{\text{H}_2\text{O}} T_i^{\text{H}_2\text{O}}}{n_{\text{Au}} C_{P,m}^{\text{Au}} + n_{\text{H}_2\text{O}} C_{P,m}^{\text{H}_2\text{O}}} \\ &= \frac{75.0 \text{ g Au}}{196.97 \text{ g Au mol}^{-1}} \times 25.42 \text{ J K}^{-1} \text{ mol}^{-1} \times 650. \text{ K} + \frac{180. \text{ g H}_2\text{O}}{18.02 \text{ g H}_2\text{O mol}^{-1}} \times 75.3 \text{ J K}^{-1} \text{ mol}^{-1} \times 310. \text{ K} \\ &= \frac{75.0 \text{ g Au}}{196.97 \text{ g Au mol}^{-1}} \times 25.42 \text{ J K}^{-1} \text{ mol}^{-1} + \frac{180. \text{ g H}_2\text{O}}{18.02 \text{ g H}_2\text{O mol}^{-1}} \times 75.3 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

$$T_f = 314 \text{ K}$$

- P3.12** Calculate w , q , ΔH , and ΔU for the process in which 1.75 mol of water undergoes the transition $\text{H}_2\text{O}(l, 373 \text{ K}) \rightarrow \text{H}_2\text{O}(g, 610. \text{ K})$ at 1 bar of pressure. The volume of liquid water at 373 K is $1.89 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$ and the molar volume of steam at 373 and 610. K is 3.03 and $5.06 \times 10^{-2} \text{ m}^3 \text{ mol}^{-1}$, respectively. For steam, $C_{P,m}$ can be considered constant over the temperature interval of interest at $33.58 \text{ J mol}^{-1} \text{ K}^{-1}$.

$$\begin{aligned} q &= \Delta H = n \Delta H_{\text{vaporization}} + n C_{P,m}^{\text{steam}} \Delta T \\ &= 1.75 \text{ mol} \times 40656 \text{ J} + 1.75 \text{ mol} \times 33.58 \text{ J mol}^{-1} \text{ K}^{-1} \times (610. \text{ K} - 373 \text{ K}) = 8.51 \times 10^4 \text{ J} \\ w &= -P_{\text{external}} \Delta V = -10^5 \text{ Pa} \times (1.75 \times 5.06 \times 10^{-2} \text{ m}^3 - 1.75 \times 1.89 \times 10^{-5} \text{ m}^3) \\ &= -8.85 \times 10^3 \text{ J} \\ \Delta U &= w + q = -8.85 \times 10^3 \text{ J} + 8.51 \times 10^4 \text{ J} = 7.62 \times 10^4 \text{ J} \end{aligned}$$

- P3.13** Equation (3.38), $C_P = C_V + TV(\beta^2/\kappa)$, links C_P and C_V with β and κ . Use this equation to evaluate $C_P - C_V$ for an ideal gas.

$$\begin{aligned} \beta &= \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{V} \frac{nR}{P}; \quad \kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T = \frac{nRT}{VP^2} = \frac{1}{P} \\ C_P - C_V &= TV \frac{\beta^2}{\kappa} = TV \left(\frac{1}{V} \frac{nR}{P}\right)^2 P = TV \frac{n^2 R^2}{V^2 P} = nR \end{aligned}$$

- P3.14** Use the result of Problem P3.10 to derive a formula for $(\partial C_V/\partial V)_T$ for a gas that obeys the Redlich-Kwong equation of state,

$$P = \frac{RT}{V_m - b} - \frac{a}{\sqrt{T} V_m(V_m + b)}$$

We use the relationship

$$\begin{aligned} \left(\frac{\partial C_V}{\partial V}\right)_T &= T \left(\frac{\partial^2 P}{\partial T^2}\right)_V \\ P &= \frac{RT}{V_m - b} - \frac{a}{\sqrt{T} V_m(V_m + b)} \\ \left(\frac{\partial P}{\partial T}\right)_V &= \frac{R}{V_m - b} + \frac{a}{2T^{3/2} V_m(V_m + b)} \\ \left(\frac{\partial^2 P}{\partial T^2}\right)_V &= \frac{-3a}{4T^{5/2} V_m(V_m + b)} \\ \left(\frac{\partial C_V}{\partial V}\right)_T &= -\frac{3a}{4T^{3/2} V_m(V_m + b)} \end{aligned}$$

- P3.15** The function $f(x, y)$ is given by $f(x, y) = xy \sin 5x + x^2 \sqrt{y} \ln y + 3e^{-2x^2} \cos y$. Determine

$$\left(\frac{\partial f}{\partial x}\right)_y, \left(\frac{\partial f}{\partial y}\right)_x, \left(\frac{\partial^2 f}{\partial x^2}\right)_y, \left(\frac{\partial^2 f}{\partial y^2}\right)_x, \left(\frac{\partial}{\partial y} \left(\frac{\partial f}{\partial x}\right)_y\right)_x$$

$$\text{and } \left(\frac{\partial}{\partial x} \left(\frac{\partial f}{\partial y}\right)_x\right)_y \cdot \text{Is } \left(\frac{\partial}{\partial y} \left(\frac{\partial f}{\partial x}\right)_y\right)_x = \left(\frac{\partial}{\partial x} \left(\frac{\partial f}{\partial y}\right)_x\right)_y ?$$

Obtain an expression for the total differential df .

$$\begin{aligned} \left(\frac{\partial f}{\partial x}\right)_y &= 5xy \cos 5x + y \sin 5x - 12xe^{-2x^2} \cos y + 2x\sqrt{y} \ln y \\ \left(\frac{\partial f}{\partial y}\right)_x &= x \sin 5x + \frac{x^2}{\sqrt{y}} + \frac{x^2 \ln y}{2\sqrt{y}} - 3e^{-2x^2} \sin y \\ \left(\frac{\partial^2 f}{\partial x^2}\right)_y &= 10y \cos 5x - 25xy \sin 5x - 12e^{-2x^2} \cos y + 48e^{-2x^2} x^2 \cos y + 2\sqrt{y} \ln y \\ \left(\frac{\partial^2 f}{\partial y^2}\right)_x &= -3e^{-2x^2} \cos y - \frac{x^2 \ln y}{4y^2} \\ \left(\frac{\partial}{\partial x} \left(\frac{\partial f}{\partial y}\right)_x\right)_y &= \frac{2x}{\sqrt{y}} + \frac{x \ln y}{\sqrt{y}} + \sin 5x + 5x \cos 5x + 12e^{-2x^2} x \sin y \\ \left(\frac{\partial}{\partial y} \left(\frac{\partial f}{\partial x}\right)_y\right)_x &= 5x \cos 5x + 12e^{-2x^2} x \sin y + \frac{2x}{\sqrt{y}} + \frac{x \ln y}{\sqrt{y}} + \sin 5x = \left(\frac{\partial}{\partial x} \left(\frac{\partial f}{\partial y}\right)_x\right)_y \\ df &= \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy = (5xy \cos 5x + y \sin 5x - 12xe^{-2x^2} \cos y + 2x\sqrt{y} \ln y) dx \\ &\quad + \left(x \sin 5x + \frac{x^2}{\sqrt{y}} + \frac{x^2 \ln y}{2\sqrt{y}} - 3e^{-2x^2} \sin y\right) dy \end{aligned}$$

- P3.16** The Joule coefficient is defined by $(\partial T/\partial V)_U = (1/C_V)[P - T(\partial P/\partial T)_V]$. Calculate the Joule coefficient for an ideal gas and for a van der Waals gas.

For an ideal gas

$$\left(\frac{\partial T}{\partial V}\right)_U = \frac{1}{C_{V,m}} \left[P - T \left(\frac{\partial}{\partial T} \frac{nRT}{V} \right)_V \right] = \frac{1}{C_{V,m}} \left[P - \frac{nRT}{V} \right] = 0$$

For a van der Waals gas,

$$\left(\frac{\partial T}{\partial V}\right)_U = \frac{1}{C_{V,m}} \left[P - T \left(\frac{\partial}{\partial T} \left[\frac{RT}{V_m - b} - \frac{a}{V_m^2} \right] \right)_V \right] = \frac{1}{C_{V,m}} \left[P - \frac{RT}{(V_m - b)} \right] = -\frac{1}{C_V} \frac{a}{V_m^2}$$

- P3.17** Using the result of Equation (3.8), $(\partial P/\partial T)_V = \beta/\kappa$, express β as a function of κ and V_m for an ideal gas, and β as a function of b , κ , and V_m for a van der Waals gas.

For the ideal gas,

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V_m} = \frac{\beta}{\kappa}; \quad \beta = \frac{\kappa R}{V_m}$$

For the van der Waals gas,

$$\left(\frac{\partial}{\partial T} \left[\frac{RT}{V_m - b} - \frac{a}{V_m^2} \right] \right)_V = \frac{R}{(V_m - b)}; \quad \beta = \frac{\kappa R}{V_m - b}$$

- P3.18** Show that the expression $(\partial U/\partial V)_T = T(\partial P/\partial T)_V - P$ can be written in the form

$$\begin{aligned} \left(\frac{\partial U}{\partial V}\right)_T &= T^2 \left(\frac{\partial \left[\frac{P}{T} \right]}{\partial T} \right)_V = - \left(\frac{\partial \left[\frac{P}{T} \right]}{\partial \left[\frac{1}{T} \right]} \right)_V \\ \left(\frac{\partial U}{\partial V}\right)_T &= T \left(\frac{\partial P}{\partial T} \right)_V - P \\ \left(\frac{\partial [P/T]}{\partial T}\right)_V &= P \left(\frac{\partial [1/T]}{\partial T} \right)_V + \frac{1}{T} \left(\frac{\partial P}{\partial T} \right)_V \\ &= -\frac{P}{T^2} + \frac{1}{T} \left(\frac{\partial P}{\partial T} \right)_V \\ \left(\frac{\partial P}{\partial T}\right)_V &= T \left(\left(\frac{\partial [P/T]}{\partial T} \right)_V + \frac{P}{T^2} \right) \\ \left(\frac{\partial U}{\partial V}\right)_T &= T^2 \left(\left(\frac{\partial [P/T]}{\partial T} \right)_V + \frac{P}{T^2} \right) - P \\ &= T^2 \left(\frac{\partial [P/T]}{\partial T} \right)_V + P - P = T^2 \left(\frac{\partial [P/T]}{\partial T} \right)_V \end{aligned}$$

We now change the differentiation to the variable $1/T$.

$$\begin{aligned} \left(\frac{\partial [P/T]}{\partial T}\right)_V &= \left(\frac{\partial [P/T]}{\partial [1/T]}\right)_V \left(\frac{\partial [1/T]}{\partial T}\right)_V = -\frac{1}{T^2} \left(\frac{\partial [P/T]}{\partial [1/T]}\right)_V \\ \left(\frac{\partial U}{\partial V}\right)_T &= T^2 \left(\frac{\partial [P/T]}{\partial T}\right)_V = T^2 \left(-\frac{1}{T^2} \frac{\partial [P/T]}{\partial [1/T]} \right)_V = - \left(\frac{\partial [P/T]}{\partial [1/T]}\right)_V \end{aligned}$$

P3.19 Derive an expression for the internal pressure of a gas that obeys the Bethelot equation of state,

$$P = \frac{RT}{V_m - b} - \frac{a}{TV_m^2}.$$

The internal pressure of a gas is given by Equation (3.19)

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

Using the Bethelot equation of state

$$\begin{aligned}\left(\frac{\partial P}{\partial T}\right)_V &= \frac{R}{V_m - b} + \frac{a}{T^2 V_m^2} \\ \left(\frac{\partial U}{\partial V}\right)_T &= \frac{RT}{V_m - b} + \frac{a}{TV_m^2} - \left(\frac{RT}{V_m - b} - \frac{a}{TV_m^2}\right) = \frac{2a}{TV_m^2}\end{aligned}$$

P3.20 Because U is a state function, $(\partial/\partial V)(\partial U/\partial T)_T = (\partial/\partial T)(\partial U/\partial V)_T$. Using this relationship, show that $(\partial C_V/\partial V)_T = 0$ for an ideal gas.

For an ideal gas, by definition, $\left(\frac{\partial U}{\partial V}\right)_T = 0$. Because the order of differentiation can be changed for a state function,

$$\left(\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial T}\right)_T\right)_T = \left(\frac{\partial C_V}{\partial V}\right)_T = \left(\frac{\partial}{\partial T}\left(\frac{\partial U}{\partial V}\right)_T\right)_T = 0$$

P3.21 Starting with the van der Waals equation of state, find an expression for the total differential dP in terms of dV and dT . By calculating the mixed partial derivatives $(\partial(\partial P/\partial V)_T/\partial T)_V$ and $(\partial(\partial P/\partial T)_V/\partial V)_T$, determine if dP is an exact differential.

$$\begin{aligned}\left(\frac{\partial}{\partial V}\left[\frac{RT}{V_m - b} - \frac{a}{V_m^2}\right]\right)_T &= \frac{2a}{V_m^3} - \frac{RT}{(V_m - b)^2} \\ \left(\frac{\partial}{\partial T}\left[\frac{RT}{V_m - b} - \frac{a}{V_m^2}\right]\right)_V &= \frac{R}{V_m - b} \\ dP &= \left(\frac{2a}{V_m^3} - \frac{RT}{(V_m - b)^2}\right)dV + \frac{R}{V_m - b}dT \\ \left(\frac{\partial}{\partial T}\left(\frac{\partial P}{\partial V}\right)_T\right)_V &= \left(\frac{\partial}{\partial T}\left[\frac{2a}{V_m^3} - \frac{RT}{(V_m - b)^2}\right]\right)_V = -\frac{R}{(V_m - b)^2} \\ \left(\frac{\partial}{\partial V}\left(\frac{\partial P}{\partial T}\right)_V\right)_T &= \left(\frac{\partial}{\partial V}\left[\frac{R}{V_m - b}\right]\right)_T = -\frac{R}{(V_m - b)^2}\end{aligned}$$

Therefore, dP is an exact differential.

P3.22 Use $(\partial U/\partial V)_T = (\beta T - \kappa P)/\kappa$ to calculate $(\partial U/\partial V)_T$ for an ideal gas.

$$\begin{aligned}\beta &= \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{V}\frac{nR}{P}; \quad \kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \frac{nRT}{VP^2} = \frac{1}{P} \\ \left(\frac{\partial U}{\partial V}\right)_T &= \frac{\beta T - \kappa P}{\kappa} = \frac{\frac{1}{V}\frac{nRT}{P} - 1}{\frac{1}{P}} = P(1 - 1) = 0\end{aligned}$$

P3.23 Derive the following relation,

$$\left(\frac{\partial U}{\partial V_m}\right)_T = \frac{3a}{2\sqrt{TV_m}(V_m + b)}$$

for the internal pressure of a gas that obeys the Redlich-Kwong equation of state,

$$P = \frac{RT}{V_m - b} - \frac{a}{\sqrt{T} V_m(V_m + b)}$$

The internal pressure of a gas is given by Equation (3.19)

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

Using the Redlich-Kwong equation of state,

$$\begin{aligned} \left(\frac{\partial P}{\partial T}\right)_V &= \frac{R}{V_m - b} + \frac{1}{2T^{3/2}V_m(V_m + b)} \frac{a}{\sqrt{T}} \\ \left(\frac{\partial U}{\partial V}\right)_T &= T\left(\frac{\partial P}{\partial T}\right)_V - P = \frac{RT}{V_m - b} + \frac{1}{2\sqrt{T}V_m(V_m + b)} \frac{a}{\sqrt{T}} - \left(\frac{RT}{V_m - b} - \frac{a}{\sqrt{T}V_m(V_m + b)}\right) \\ &= \frac{1}{2\sqrt{T}V_m(V_m + b)} \frac{a}{\sqrt{T}} + \frac{a}{\sqrt{T}V_m(V_m + b)} = \frac{3a}{2\sqrt{T}V_m(V_m + b)} \end{aligned}$$

P3.24 A differential $dz = f(x, y) dx + g(x, y) dy$ is exact if the integral $\int f(x, y) dx + \int g(x, y) dy$ is independent of the path. Demonstrate that the differential $dz = 2xy dx + x^2 dy$ is exact by integrating dz along the paths (1, 1) \rightarrow (1, 8) \rightarrow (6, 8) and (1, 1) \rightarrow (1, 3) \rightarrow (4, 3) \rightarrow (4, 8) \rightarrow (6, 8). The first number in each set of parentheses is the x coordinate, and the second number is the y coordinate.

$$\int dz = \int 2xy dx + \int x^2 dy$$

Path 1

$$\int dz = 2 \int_1^6 8x dx + 1 \int_1^8 dy = 280 + 7 = 287$$

Path 2

$$\begin{aligned} \int dz &= \int_1^3 dy + \int_1^4 6x dx + \int_3^8 16 dy + \int_4^6 16x dx \\ &= 2 + 45 + 80 + 160 = 287 \end{aligned}$$

P3.25 Show that $d\rho/\rho = -\beta dT + \kappa dP$, where ρ is the density $\rho = m/V$. Assume that the mass, m , is constant.

$$\frac{d\rho}{\rho} = \frac{d(m/V)}{m/V} = Vd(1/V). \text{ Because } \frac{d(1/V)}{dV} = -\frac{1}{V^2}, \quad Vd(1/V) = -\frac{dV}{V}$$

$$Vd(1/V) = -\frac{1}{V} \left[\left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP \right] = -\frac{1}{V} [V\beta dT - V\kappa dP]$$

$$\frac{d\rho}{\rho} = -\beta dT + \kappa dP$$

P3.26 For a gas that obeys the equation of state

$$V_m = \frac{RT}{P} + B(T)$$

derive the result

$$\left(\frac{\partial H}{\partial P}\right)_T = B(T) - T \frac{dB(T)}{dT}$$

Equation (3.44) states that

$$\left(\frac{\partial H_m}{\partial P}\right)_T = V_m - T \left(\frac{\partial V_m}{\partial T}\right)_P$$

$$\text{For } V_m = \frac{RT}{P} + B(T)$$

$$\begin{aligned} \left(\frac{\partial V_m}{\partial T}\right)_P &= \frac{R}{P} + \frac{dB}{dT} \\ \left(\frac{\partial H_m}{\partial P}\right)_T &= \frac{RT}{P} + B(T) - T\left(\frac{R}{P} + \frac{dB}{dT}\right) = \frac{RT}{P} + B(T) - \frac{RT}{P} - T\frac{dB(T)}{dT} \\ &= B(T) - T\frac{dB(T)}{dT} \end{aligned}$$

P3.27 Because V is a state function, $(\partial(\partial V/\partial T)_P/\partial P)_T = (\partial(\partial V/\partial P)_T/\partial T)_P$. Using this relationship, show that the isothermal compressibility and isobaric expansion coefficient are related by $(\partial\beta/\partial P)_T = -(\partial\kappa/\partial T)_P$.

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

$$\text{Because } \beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \text{ and } \kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

$$\left(\frac{\partial[V\beta]}{\partial P}\right)_T = -\left(\frac{\partial[V\kappa]}{\partial T}\right)_P \text{ or } \left(\frac{\partial\beta}{\partial P}\right)_T = -\left(\frac{\partial\kappa}{\partial T}\right)_P$$

P3.28 Use the relation

$$C_{P,m} - C_{V,m} = T\left(\frac{\partial V_m}{\partial T}\right)_P\left(\frac{\partial P}{\partial T}\right)_V$$

the cyclic rule and the van der Waals equation of state, to derive an equation for $C_{P,m} - C_{V,m}$ in terms of V_m , T , and the gas constants R , a , and b .

We use the cyclic rule to evaluate $\left(\frac{\partial V_m}{\partial T}\right)_P$.

$$\begin{aligned} \left(\frac{\partial V_m}{\partial T}\right)_P\left(\frac{\partial T}{\partial P}\right)_V\left(\frac{\partial P}{\partial V_m}\right)_T &= -1 \\ \left(\frac{\partial V_m}{\partial T}\right)_P &= -\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V_m}{\partial P}\right)_T \end{aligned}$$

$$C_{P,m} - C_{V,m} = T\left(\frac{\partial V_m}{\partial T}\right)_P\left(\frac{\partial P}{\partial T}\right)_V = -T\left[\left(\frac{\partial P}{\partial T}\right)_V\right]^2\left(\frac{\partial V_m}{\partial P}\right)_T = -T\frac{\left[\left(\frac{\partial P}{\partial T}\right)_V\right]^2}{\left(\frac{\partial V_m}{\partial P}\right)_T}$$

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V_m - b}$$

$$\left(\frac{\partial V_m}{\partial P}\right)_T = \frac{-RT}{(V_m - b)^2} + \frac{2a}{V_m^3} = \frac{-RTV_m^3 + 2a(V_m - b)}{V_m^3(V_m - b)^2}$$

$$C_{P,m} - C_{V,m} = -T\frac{\left(\frac{R}{V_m - b}\right)^2}{\frac{-RT}{(V_m - b)^2} + \frac{2a}{V_m^3}} = -T\frac{R}{-T + \frac{2a(V_m - b)^2}{RV_m^3}} = \frac{R}{1 - \frac{2a(V_m - b)^2}{RTV_m^3}}$$

In the ideal gas limit, $a = 0$, and $C_{P,m} - C_{V,m} = R$.

P3.29 For the equation of state $V_m = RT/P + B(T)$, show that

$$\left(\frac{\partial C_{P,m}}{\partial P}\right)_T = -T \frac{d^2 B(T)}{dT^2}$$

[Hint: Use Equation (3.44) and the property of state functions with respect to the order of differentiation in mixed second derivatives.]

Using Equation (3.44),

$$\left(\frac{\partial}{\partial T} \left(\frac{\partial H_m}{\partial P}\right)_T\right)_P = \left(\frac{\partial}{\partial P} \left(\frac{\partial H_m}{\partial T}\right)_P\right)_T = \left(\frac{\partial C_{P,m}}{\partial P}\right)_T$$

Equation (3.44) states that

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

Therefore,

$$\begin{aligned} \left(\frac{\partial C_{P,m}}{\partial P}\right)_T &= \left(\frac{\partial}{\partial T} \left(V_m - T \left(\frac{\partial V_m}{\partial T}\right)_P \right)\right)_P \\ &= \left(\frac{\partial}{\partial T} \left(RT/P + B(T) - T \left(\frac{\partial [RT/P + B(T)]}{\partial T}\right)_P \right)\right)_P \\ &= \left(\frac{\partial}{\partial T} \left(RT/P + B(T) - T \left(\frac{R}{P} + \frac{dB(T)}{dT}\right)_P \right)\right)_P \\ &= \left(\frac{R}{P} + \frac{dB(T)}{dT} - \frac{R}{P} - \frac{dB(T)}{dT} + T \frac{d^2 B(T)}{dT^2}\right)_P \\ &= T \frac{d^2 B(T)}{dT^2} \end{aligned}$$

P3.30 Starting with $\beta = (1/V)(\partial V/\partial T)_P$, show that $\beta = -(1/\rho)(\partial \rho/\partial T)_P$, where ρ is the density

$$\begin{aligned} \beta &= \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P = \frac{\rho}{m} \left(\frac{\partial [m/\rho]}{\partial T}\right)_P = \rho \left(\frac{\partial [1/\rho]}{\partial T}\right)_P = \rho \left(\frac{\partial \rho}{\partial T}\right)_P \left(\frac{[1/\rho]}{\partial \rho}\right)_P \\ &= -\frac{1}{\rho^2} \rho \left(\frac{\partial \rho}{\partial T}\right)_P = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T}\right)_P \end{aligned}$$

P3.31 This problem will give you practice in using the cyclic rule. Use the ideal gas law to obtain the three functions $P = f(V, T)$, $V = g(P, T)$, and $T = h(P, V)$. Show that the cyclic rule $(\partial P/\partial V)_T (\partial V/\partial T)_P (\partial T/\partial P)_V = -1$ is obeyed.

$$\begin{aligned} P &= \frac{nRT}{V}; \quad V = \frac{nRT}{P}; \quad T = \frac{PV}{nR} \\ \left(\frac{\partial P}{\partial V}\right)_T &= -\frac{nRT}{V^2}; \quad \left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{P}; \quad \left(\frac{\partial T}{\partial P}\right)_V = \frac{V}{nR} \\ \left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V &= \left(-\frac{nRT}{V^2}\right) \left(\frac{nR}{P}\right) \left(\frac{V}{nR}\right) = \frac{-nRT}{PV} = -1 \end{aligned}$$

P3.32 Regard the enthalpy as a function of T and P . Use the cyclic rule to obtain the expression

$$\begin{aligned} C_P &= -\left(\frac{\partial H}{\partial P}\right)_T \left/\left(\frac{\partial T}{\partial P}\right)_H\right. \\ \left(\frac{\partial H}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_H \left(\frac{\partial T}{\partial H}\right)_P &= -1 \end{aligned}$$

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

- P3.33** Using the chain rule for differentiation, show that the isobaric expansion coefficient expressed in terms of density is given by $\beta = -(1/\rho)(\partial\rho/\partial T)_P$.

$$\begin{aligned}\beta &= \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P = \frac{\rho}{m} \left(\frac{\partial[m/\rho]}{\partial T}\right)_P = \rho \left(\frac{\partial[1/\rho]}{\partial T}\right)_P = \rho \left(\frac{\partial\rho}{\partial T}\right)_P \left(\frac{[1/\rho]}{\partial\rho}\right)_P \\ &= -\frac{1}{\rho^2} \rho \left(\frac{\partial\rho}{\partial T}\right)_P = -\frac{1}{\rho} \left(\frac{\partial\rho}{\partial T}\right)_P\end{aligned}$$

- P3.34** Derive the equation $(\partial P/\partial V)_T = -1/(\kappa V)$ from basic equations and definitions.

$$\begin{aligned}\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V &= -1 \\ \left(\frac{\partial P}{\partial V}\right)_T &= -\frac{\left(\frac{\partial P}{\partial T}\right)_V}{\left(\frac{\partial V}{\partial T}\right)_P} = \frac{\beta/\kappa}{\beta V} \quad \text{from Equation (3.9)} \\ \left(\frac{\partial P}{\partial V}\right)_T &= -\frac{1}{\kappa V}\end{aligned}$$

- P3.35** Derive the equation $(\partial H/\partial T)_V = C_V + V\beta/\kappa$ from basic equations and definitions.

$$(\partial H/\partial T)_V = (\partial[U + PV]/\partial T)_V = (\partial U/\partial T)_V + V(\partial P/\partial T)_V$$

$$\text{From Equation (3.8), } (\partial P/\partial T)_V = \frac{\beta}{\kappa}$$

$$(\partial H/\partial T)_V = C_V + V\beta/\kappa$$

- P3.36** For an ideal gas, $\left(\frac{\partial U}{\partial V}\right)_T$ and $\left(\frac{\partial H}{\partial P}\right)_T = 0$. Prove that C_V is independent of volume and C_P is independent of pressure.

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

$$\left(\frac{\partial C_V}{\partial V}\right)_T = \left(\frac{\partial}{\partial V} \left(\frac{\partial U}{\partial T}\right)_V\right)_T = \left(\frac{\partial}{\partial T} \left(\frac{\partial U}{\partial V}\right)_T\right)_V \quad \text{because } U \text{ is a state function.}$$

$$\text{Because } \left(\frac{\partial U}{\partial V}\right)_T = 0 \text{ for an ideal gas, } \left(\frac{\partial C_V}{\partial V}\right)_T = 0$$

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

$$\left(\frac{\partial C_P}{\partial P}\right)_T = \left(\frac{\partial}{\partial P} \left(\frac{\partial H}{\partial T}\right)_P\right)_T = \left(\frac{\partial}{\partial T} \left(\frac{\partial H}{\partial P}\right)_T\right)_P \quad \text{because } H \text{ is a state function.}$$

$$\text{Because } \left(\frac{\partial H}{\partial P}\right)_T = 0 \text{ for an ideal gas, } \left(\frac{\partial C_P}{\partial P}\right)_T = 0.$$

P3.37 Prove that $C_V = -\left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_U$.

$$\left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_U \left(\frac{\partial V}{\partial U}\right)_T = -1 \text{ from the cyclic rule}$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{-1}{\left(\frac{\partial T}{\partial V}\right)_U \left(\frac{\partial V}{\partial U}\right)_T} = -\left(\frac{\partial V}{\partial T}\right)_U \left(\frac{\partial U}{\partial V}\right)_T$$

P3.38 Show that $\left(\frac{\partial C_V}{\partial V}\right)_T = T \left(\frac{\partial^2 P}{\partial T^2}\right)_V$.

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

because U is a state function.

$$= \left(\frac{\partial}{\partial T} \left(T \left(\frac{\partial P}{\partial T}\right)_V - P \right)\right)_V$$

Using Equation (3.19),

$$= \left(\frac{\partial P}{\partial T}\right)_V + T \left(\frac{\partial^2 P}{\partial T^2}\right)_V - \left(\frac{\partial P}{\partial T}\right)_V = T \left(\frac{\partial^2 P}{\partial T^2}\right)_V$$

P3.39 Show that $\left(\frac{\partial C_V}{\partial V}\right)_T = 0$ for an ideal and for a van der Waals gas.

Using the result of P3.10,

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

For an ideal gas,

$$T \left(\frac{\partial^2 P}{\partial T^2}\right)_V = T \left(\frac{\partial^2 nRT}{\partial T^2}\right)_V = 0$$

For a van der Waals gas,

$$T \left(\frac{\partial^2 P}{\partial T^2}\right)_V = T \left(\frac{\partial^2 \left[\frac{nRT}{V-nb} + \frac{n^2 a}{V^2} \right]}{\partial T^2}\right)_V = 0$$