

Chapter 9: Using the First Law

1. Write the total differential for V given as a function of the independent variables U and T.

Answer: Given $V(U,T)$ then from Addendum Sec. 7.11, Eq. 7.11.13:

$$dV = \left(\frac{\partial V}{\partial U}\right)_T dU + \left(\frac{\partial V}{\partial T}\right)_U dT$$

These partial derivatives are not so strange as they may first appear. The first can simply be inverted to give the fundamental derivative: $(\partial V/\partial U)_T = 1/(\partial U/\partial V)_T$. For the second, a process at constant energy corresponds to a process in an isolated system.

2. Write the total differential for the new function G with independent variables T and P.

Answer: Given $G(T,P)$ then from Addendum Sec. 7.11, Eq. 7.11.13:

$$dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP$$

We will use this equation often where G is the Gibbs Energy.

3. Determine if the following total differential is exact: $dF = 3y^2 dx + 6xy dy$

Answer: The general form of the total differential of $F(x,y)$ is given by Eq. 9.1.5. Matching the terms in dx and dy identifies the coefficients:

$$\left(\frac{\partial F}{\partial x}\right)_y = 3y^2 \quad \text{and} \quad \left(\frac{\partial F}{\partial y}\right)_x = 6xy$$

The mixed partials are:

$$\left(\frac{\partial}{\partial y}\left(\frac{\partial F}{\partial x}\right)_y\right)_x = \left(\frac{\partial(3y^2)}{\partial y}\right)_x \quad \text{and} \quad \left(\frac{\partial}{\partial x}\left(\frac{\partial F}{\partial y}\right)_x\right)_y = \left(\frac{\partial(6xy)}{\partial x}\right)_y$$

Completing the indicated derivatives gives:

$$\left(\frac{\partial}{\partial y}\left(\frac{\partial F}{\partial x}\right)_y\right)_x = 6y \quad \text{and} \quad \left(\frac{\partial}{\partial x}\left(\frac{\partial F}{\partial y}\right)_x\right)_y = 6y$$

The mixed partials are equal, so the differential is exact and $F(x,y)$ is a state function. Integrating either of these partial derivatives gives: $F = 3xy^2 + c$, where c is a constant. Compare the differential given in this problem with Example 9.1.2.

4. We showed that the differential in Example 9.1.1 is exact:

$$dV = \frac{nR}{P} dT - \frac{nRT}{P^2} dP \quad \text{with} \quad \left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{P} \quad \text{and} \quad \left(\frac{\partial V}{\partial P}\right)_T = \frac{-nRT}{P^2}$$

Separately integrate these partial derivatives to find V . Do indefinite integrals.

$$\text{Answer: From } \left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{P} \quad V = \int dV = \int \frac{nR}{P} dT = \frac{nRT}{P} + \text{constant}$$

$$\text{and from } \left(\frac{\partial V}{\partial P}\right)_T = \frac{-nRT}{P^2} \quad V = \int dV = \int \frac{-nRT}{P^2} dP = \frac{nRT}{P} + \text{constant}$$

Both coefficients in the differential are consistent with the same function of V , which is the ideal gas law to within a constant. In this sense the differential is “complete.” The same information about the original function is available from either partial derivative. Integrating either gives the original function. You couldn’t get the same result for an inexact differential. An inexact differential is incomplete without the specification of the path of integration.

5. Find the partial derivative of the enthalpy with respect to volume at constant temperature from $dH = dU + PdV + VdP$. Express the result in terms of C_v , C_p , α , κ_T , $(\partial U/\partial V)_T$, and $(\partial H/\partial P)_T$.

Answer: From $H \equiv U + PV$, $dH = dU + PdV + VdP$. Now, take the derivative with respect to V at constant T :

$$\left(\frac{\partial H}{\partial V}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T + P\left(\frac{\partial V}{\partial V}\right)_T + V\left(\frac{\partial P}{\partial V}\right)_T$$

Note that $\left(\frac{\partial U}{\partial V}\right)_T$ is internal pressure and since $\left(\frac{\partial V}{\partial V}\right)_T = 1$:

$$\left(\frac{\partial H}{\partial V}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T + P + V\left(\frac{\partial P}{\partial V}\right)_T$$

Also remember that $\left(\frac{\partial P}{\partial V}\right)_T = \frac{-1}{V\kappa_T}$ where κ_T is the isothermal compressibility.

$$\left(\frac{\partial H}{\partial V}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T + P - \frac{1}{\kappa_T}$$

This equation shows the relationship of the partial derivative to fundamental properties of the system.

6. Show that Eq. 9.4.12°, $dH = dU + nR dT$ or $\Delta H = \Delta U + nR\Delta T$, is consistent with $C_p = C_v + nR$, which is true for an ideal gas.

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Answer: Remember the definitions of the heat capacities: $\left(\frac{\partial U}{\partial T}\right)_V = C_v$ and $\left(\frac{\partial H}{\partial T}\right)_P = C_p$. To find $(\partial H/\partial T)_P$, “divide” $dH = dU + nRdT$ by dT at constant P :

$$\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + nR \left(\frac{\partial T}{\partial T}\right)_P \quad 1^\circ$$

Substituting the definition of C_p , and using $(\partial T/\partial T)_P = 1$ in Eq. 1° gives:

$$C_p = \left(\frac{\partial U}{\partial T}\right)_P + nR \quad 2^\circ$$

To find $(\partial U/\partial T)_P$, identify P as the “misplaced” variable and work through the total differential of dU , $U(V,T)$:

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \quad 3$$

Divide both sides of the equation by dT and specify constant P :

$$\left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \quad 4$$

(Remember that we derived this equation in our derivation of $C_p - C_v$, Eq. 9.4.5). Since $(\partial U/\partial V)_T = 0$ for an ideal gas, substitution into Eq. 4 and the definition of C_v gives:

$$\left(\frac{\partial U}{\partial T}\right)_P = C_v \quad 5^\circ$$

Then substitution of Eq. 5° into Eq. 2° gives:

$$C_p = C_v + nR \quad 6^\circ$$

Alternative Answer: Starting with $\Delta H = \Delta U + nR\Delta T$, remember that for an ideal gas for any process, $\Delta H = C_p \Delta T$ and $\Delta U = C_v \Delta T$. Substituting gives $C_p \Delta T = C_v \Delta T + nR\Delta T$. Division by ΔT gives $C_p = C_v + nR$.

7. Show that $\left(\frac{\partial H}{\partial V}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T$ for an ideal gas in a closed system.

Answer: Using the results of Problem 5:

$$\left(\frac{\partial H}{\partial V}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T + P + V \left(\frac{\partial P}{\partial V}\right)_T$$

Note that for an ideal gas, $P = nRT/V$ and:

$$\left(\frac{\partial P}{\partial V}\right)_T = \frac{-nRT}{V^2}$$

Substitution gives:

$$\left(\frac{\partial H}{\partial V}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T + P + V\left(\frac{-nRT}{V^2}\right)$$

The V cancels in the last term to give $-nRT/V$, which is $-P$:

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

8. Show that $\left(\frac{\partial H}{\partial P}\right)_T = (-nRT/P^2)\left(\frac{\partial U}{\partial V}\right)_T$ for an ideal gas in a closed system.

Answer: Substituting the definition of enthalpy, $H \equiv U + PV$, into $(\partial H/\partial P)_T$ gives:

$$\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial U}{\partial P}\right)_T + \left(\frac{\partial(PV)}{\partial P}\right)_T$$

From the ideal gas law $PV = nRT$, with n a constant for a closed system:

$$\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial U}{\partial P}\right)_T + \left(\frac{\partial(nRT)}{\partial P}\right)_T$$

However, for an isothermal process T is constant and the second term is zero. We can use the chain rule to relate $(\partial U/\partial P)_T$ to $(\partial U/\partial V)_T$:

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

Using the ideal gas law in the form $V = nRT/P$ gives $(\partial V/\partial P)_T = -nRT/P^2$ and then substitution into the last equation gives:

$$\left(\frac{\partial H}{\partial P}\right)_T = (-nRT/P^2) \left(\frac{\partial U}{\partial V}\right)_T$$

9. Find ΔH in terms of ΔU for a gas that obeys the Virial-type equation of state at constant volume:

$$PV = nRT\left(1 + B\frac{n}{V}\right)$$

We will assume that B is a constant (the second Virial coefficient is actually temperature dependent). Use this result to find the change in enthalpy for heating one mole of water vapor starting at a pressure of 23.8 torr from an initial temperature of 298.2K to a final temperature of 373.2 K. Assume the volume is constant for the process. Assume $C_V = 6/2 nR$ and $B = -425 \text{ cm}^3 \text{ mol}^{-1}$ (roughly the value for water at 373 K).¹ Compare with Example 9.3.2.

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Answer: The plan is to use Eq. 9.3.10 and the Virial Equation in terms of the density:

$$PV = nRT\left(1 + B \frac{n}{V}\right) \quad 1$$

Since V is constant, substitution of Eq. 1 into Eq. 9.4.10 gives:

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + nR\Delta T + (n^2RB/V)\Delta T \quad 2$$

Next we need to find the volume of the gas. As a first approximation we can use the ideal gas law and the initial state to get the volume. Converting pressure units gives:

$$P = 23.8 \text{ torr} = 0.03132 \text{ atm} = 3.173 \times 10^3 \text{ Pa} \quad 3$$

and then:

$$V = 1.00 \text{ mol}(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.2 \text{ K})/3.173 \times 10^3 \text{ Pa} = 0.7814 \text{ m}^3 \quad 4^\circ$$

Is this ideal value close enough or do we need to use the Virial equation to get the volume? How big is the correction to the volume from the Virial equation? We can use a successive approximations approach. We can substitute the V from the ideal gas law into the right-hand side of Eq. 1 and then solve for the corrected volume. Solving for V with:

$$B = -425. \text{ cm}^3 \text{ mol}^{-1} = -0.425 \text{ L mol}^{-1} = -4.25 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1} \quad 5$$

$$V \approx nRT\left(1 + B \frac{n}{V}\right)/P \quad 6$$

$$\text{but } B \frac{n}{V} = -4.25 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1}(1 \text{ mol})/0.7814 \text{ m}^3 = 5.4 \times 10^{-4} \quad 7$$

is negligible compared to 1. So the ideal gas equation of state will do fine for calculating the volume.

Then as in Example 9.3.2:

$$\Delta U = C_v \Delta T = 6/2 nR \Delta T = 6/2 (1.00 \text{ mol})(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(373.2 - 298.2 \text{ K})$$

$$\Delta U = 1.871 \text{ kJ} \quad 8$$

Substitution of this value of the internal energy change into Eq 2. gives:

$$\begin{aligned} \Delta H &= 1.87 \text{ kJ} + (1.00 \text{ mol})(8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1})(373.2 - 298.2 \text{ K}) \\ &\quad + (1.00 \text{ mol})^2(8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1})(-4.25 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1})(373.2 - 298.2 \text{ K})/0.7814 \text{ m}^3 \\ \Delta H &= 1.871 \text{ kJ} + 0.624 \text{ kJ} - 0.000339 \text{ kJ} = 2.495 \text{ kJ} \end{aligned}$$

So for water vapor under these circumstances, the correction for non-ideality is negligible. We did assume that B was a constant, however. At 298.2 K, B is significantly more negative than the given value, which would make this correction larger. Eq. 2 is useful in geological circumstances where water vapor pressures are much higher and have a decisive effect on the types of minerals that are formed. Constant volume conditions are often appropriate for geological processes and computer simulations.

10. Show that:

$$\left(\frac{\partial H}{\partial T}\right)_V = C_v + nR + \frac{n^2RB}{V}$$

for a gas that obeys the Virial-type equation of state:

$$PV = nRT\left(1 + B \frac{n}{V}\right)$$

Assume that B is a constant (the second Virial coefficient is actually temperature dependent). Compare the result to the last problem.

Answer: Using the definition of the enthalpy: $H \equiv U + PV$:

$$\left(\frac{\partial H}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial(PV)}{\partial T}\right)_V$$

with $PV = nRT\left(1 + B \frac{n}{V}\right)$ gives:

$$\left(\frac{\partial(PV)}{\partial T}\right)_V = nR\left(1 + B \frac{n}{V}\right) = nR + \frac{n^2RB}{V}$$

Substitution back into $(\partial H/\partial T)_V$ gives the final result:

$$\left(\frac{\partial H}{\partial T}\right)_V = C_v + nR + \frac{n^2RB}{V}$$

since $(\partial U/\partial T)_V = C_v$. For a constant volume process and assuming B is a constant over the temperature range gives the integrated result:

$$\Delta H = C_v\Delta T + nR\Delta T + (n^2RB/V)\Delta T$$

as we saw in the last problem.

11. In Section 9.3 for the isothermal reversible expansion of an ideal gas, which is Path 1 in Figure 9.3.1, we integrated $dH = dU + d(PV)$ to prove that $\Delta H = \Delta U$. Integrate:

$$dH = dU + P dV + V dP \quad (9.2.5)$$

directly for an isothermal reversible process and show the result also gives $\Delta H = \Delta U$. In other words, assuming an ideal gas at constant temperature, substitute $P = nRT/V$ and $V = nRT/P$ and then integrate. Compare the integral to Eq. 9.3.10.

Answer: Integrating Eq. 9.2.5:

$$\int_{H_1}^{H_2} dH = \int_{U_1}^{U_2} dU + \int_{V_1}^{V_2} P dV + \int_{P_1}^{P_2} V dP \quad (\text{closed}) \quad 1$$

We need to be very careful about the P in PdV and the V in VdP . The P and V are not constant, as they are in Eq. 9.3.18. Assuming an ideal gas, at constant temperature $P = nRT/V$ and $V = nRT/P$. Substituting into Eq. 1 and integrating:

$$\Delta H = \Delta U + \int_{V_1}^{V_2} \frac{nRT}{V} dV + \int_{P_1}^{P_2} \frac{nRT}{P} dP \quad (\text{closed, ideal gas, cst. } T) \quad 2^\circ$$

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First note that since the process is isothermal, T is a constant, factors out of the integrals, and gives:

$$\Delta H = \Delta U + nRT \int_{V_1}^{V_2} \frac{1}{V} dV + nRT \int_{P_1}^{P_2} \frac{1}{P} dP \quad (\text{closed, ideal gas, cst. T}) \quad 3^\circ$$

and integrating gives:

$$\Delta H = \Delta U + nRT \ln\left(\frac{V_2}{V_1}\right) + nRT \ln\left(\frac{P_2}{P_1}\right) \quad (\text{closed, ideal gas, cst. T}) \quad 4^\circ$$

However, for an ideal gas,

$$\left(\frac{P_2}{P_1}\right) = \left(\frac{V_1}{V_2}\right) \quad 5^\circ$$

Substituting Eq. 5° into Eq. 4° gives

$$\Delta H = \Delta U + nRT \ln\left(\frac{V_2}{V_1}\right) + nRT \ln\left(\frac{V_1}{V_2}\right) = \Delta U + nRT \ln\left(\frac{V_2}{V_1}\right) - nRT \ln\left(\frac{V_2}{V_1}\right) \quad 6^\circ$$

The last two terms cancel giving:

$$\Delta H = \Delta U \quad (\text{closed, ideal gas, cst. T}) \quad 7^\circ$$

Once again we find that ΔH is independent of the path and integrating $dH = dU + d(PV)$ or $dH = dU + P dV + V dP$ is equivalent. The choice of the form of the differential to use is just dependent on convenience.

12. Given that: $\left(\frac{\partial H}{\partial P}\right)_T = 0$, show that $\left(\frac{\partial H}{\partial V}\right)_T = 0$.

Answer: Since the enthalpy is usually considered a function of the independent variables P and T , the “misplaced” variable is the derivative with respect to V . Using the chain rule:

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

Using the given partial derivative $(\partial H/\partial P)_T = 0$:

$$\left(\frac{\partial H}{\partial V}\right)_T = 0$$

13. We will prove in a later chapter that the internal pressure for a Van der Waals gas is given by:

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

Find $C_p - C_v$ for a Van der Waals gas.

Answer: From Eq. 9.4.7:

$$C_p - C_v = \left[\left(\frac{\partial U}{\partial V} \right)_T + P \right] \left(\frac{\partial V}{\partial T} \right)_P \quad 1$$

For a Van der Waals gas: $P = \frac{nRT}{(V - nb)} - \frac{an^2}{V^2}$, which upon substitution into Eq. 1 gives:

$$C_p - C_v = \left[\frac{an^2}{V^2} + \frac{nRT}{(V - nb)} - \frac{an^2}{V^2} \right] \left(\frac{\partial V}{\partial T} \right)_P = \frac{nRT}{(V - nb)} \left(\frac{\partial V}{\partial T} \right)_P \quad 2$$

The remaining partial derivative is difficult to find directly. Notice however that the inverse is easier. Solving the Van der Waals equation for T:

$$T = \frac{1}{nR} \left(P + \frac{an^2}{V^2} \right) (V - nb) \quad 3$$

Using the product rule:

$$\left(\frac{\partial T}{\partial V} \right)_P = \frac{1}{nR} \left[\left(P + \frac{an^2}{V^2} \right) + (V - nb) \left(\frac{-2an^2}{V^3} \right) \right] \quad 4$$

We will do a bit of algebra below, but it is sufficient for our purposes to simply divide Eq. 2 by Eq. 4 to get the final result:

$$C_p - C_v = nR \frac{\frac{nRT}{(V - nb)}}{\left[\left(P + \frac{an^2}{V^2} \right) + (V - nb) \left(\frac{-2an^2}{V^3} \right) \right]} \quad 5$$

In the denominator we can substitute for the first term:

$$\left(P + \frac{an^2}{V^2} \right) = \frac{nRT}{(V - nb)} \quad 6$$

to give:

$$C_p - C_v = nR \frac{\frac{nRT}{(V - nb)}}{\left[\left(\frac{nRT}{(V - nb)} \right) + (V - nb) \left(\frac{-2an^2}{V^3} \right) \right]} = nR \frac{1}{\left[1 + \frac{(V - nb)^2}{nRT} \left(\frac{-2an^2}{V^3} \right) \right]} \quad 7$$

Notice that when $a = 0$, that this last equation reduces to $C_p - C_v = nR$, which is the correct result for an ideal gas.

14. For CO_2 , $\mu_{JT} = 1.11 \text{ K bar}^{-1}$ and $C_{p,m}$ for CO_2 is $37.11 \text{ J K}^{-1} \text{ mol}^{-1}$. Calculate the change in enthalpy per mole of CO_2 for an isothermal process for a change in pressure of 1.00 bar. Assume that both μ_{JT} and C_p are constant over the pressure range.

Answer: The process corresponds to the partial derivative $(\partial H/\partial P)_T$. The value of this partial derivative is given by the Joule-Thompson coefficient:

$$\mu_{JT} = -\frac{1}{C_p} \left(\frac{\partial H}{\partial P} \right)_T \quad \text{or equivalently} \quad \left(\frac{\partial H}{\partial P} \right)_T = -\mu_{JT} C_p$$

Integration assuming a constant μ_{JT} and C_p gives:

$$\Delta H = -\mu_{JT} C_p \Delta P$$

Substitution of the values for this problem gives:

$$\Delta H = -1.11 \text{ K bar}^{-1} (37.11 \text{ J K}^{-1} \text{ mol}^{-1}) (1.00 \text{ bar}) = -41.2 \text{ J mol}^{-1}$$

For an ideal gas, the change would be zero since the process is isothermal.

15. Determine the “misplaced” variable for $(\partial H/\partial V)_T$ and express the result in terms of C_v , C_p , α , κ_T , $(\partial U/\partial V)_T$, and $(\partial H/\partial P)_T$.

Answer: The partial derivative that is required is $(\partial H/\partial V)_T$. Substituting the definition of enthalpy, $H \equiv U + PV$, gives using the product rule:

$$\left(\frac{\partial H}{\partial V} \right)_T = \left(\frac{\partial (U + PV)}{\partial V} \right)_T = \left(\frac{\partial U}{\partial V} \right)_T + P \left(\frac{\partial V}{\partial V} \right)_T + V \left(\frac{\partial P}{\partial V} \right)_T \quad 1$$

Given that $(\partial V/\partial V)_T = 1$ and from Eq. 7.6.14:

$$\left(\frac{\partial V}{\partial P} \right)_T = -V \kappa_T \quad \text{or the inverse:} \quad \left(\frac{\partial P}{\partial V} \right)_T = \frac{-1}{V \kappa_T} \quad 2$$

Substituting Eq. 2 into Eq. 1 gives:

$$\left(\frac{\partial H}{\partial V} \right)_T = \left(\frac{\partial U}{\partial V} \right)_T + P - \frac{1}{\kappa_T}$$

Everything on the right-hand side is in the form of a fundamental partial derivative or can be obtained from the equation of state of the substance. Compare this problem to Problem 5.

16. Show that for an ideal gas C_v is not a function of the volume of the system and that C_p is not a function of the pressure of a system. In other words show that, for a closed system:

$$\left(\frac{\partial C_v}{\partial V} \right)_T = 0 \quad \left(\frac{\partial C_p}{\partial P} \right)_T = 0$$

Answer: (a). The definition of the constant volume heat capacity is:

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

Substitution into the partial derivative with respect to V, above, gives:

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

The order of differentiation can be reversed because U is a state function. The fact that mixed partials are equal is the basis of the Euler criterion for exactness for state functions. For an ideal gas, $(\partial U/\partial V)_T = 0$, giving:

$$\left(\frac{\partial C_v}{\partial V} \right)_T = 0$$

In other words C_v is not a function of volume for an ideal gas.

(b). The definition of the constant pressure heat capacity is:

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

Substitution into the partial derivative with respect to V, above, gives:

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

The order of differentiation can be reversed because H is a state function. For an ideal gas, $(\partial H/\partial P)_T = 0$, giving:

$$\left(\frac{\partial C_p}{\partial P} \right)_T = 0$$

In other words C_p is not a function of pressure for an ideal gas.

17. Show that $\left(\frac{\partial H}{\partial T} \right)_V = C_p + \left(\frac{\partial H}{\partial P} \right)_T \left(\frac{\alpha}{\kappa_T} \right)$.

Answer: We can get a hint of how to proceed by substituting in the definition of C_p and also that $\alpha/\kappa_T = (\partial P/\partial T)_V$. Correspondingly we need to show that:

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

Since we normally consider $H(P, T)$ and not $H(V, T)$, we can consider the “misplaced” variable the constant V specification. Notice that given $H(P, T)$ the total differential of H is:

$$dH = \left(\frac{\partial H}{\partial T} \right)_P dT + \left(\frac{\partial H}{\partial P} \right)_T dP$$

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Notice that the partials in this total differential also occur in the relationship we are trying to derive. Simply “dividing” this last equation by dT and specifying constant V for any new partial derivative gives:

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

Using the definition of the constant pressure heat capacity, $C_p = (\partial H/\partial T)_P$, and the result from Eq. 7.6.21, that is $\alpha/\kappa_T = (\partial P/\partial T)_V$, gives:

$$\left(\frac{\partial H}{\partial T}\right)_V = C_p + \left(\frac{\partial H}{\partial P}\right)_T \left(\frac{\alpha}{\kappa_T}\right)$$

Notice that it is often helpful to “work backwards” from the original statement of the problem. Working “backwards” can help give you hints on how to proceed. Just remember to present the full derivation in the “forward” direction as we did here.

18. The Joule-Thomson coefficient is $\mu_{JT} = (\partial T/\partial P)_H$. Show that the corresponding coefficient for constant internal energy processes is given by:

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

Answer: Starting with $(\partial T/\partial V)_U$, the “misplaced” variable is the constant internal energy. Since U is held constant, we can set the total differential of U equal to zero. As normal we consider $U(V,T)$, in other words the independent variables for U are V and T :

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT = 0$$

Subtracting the volume dependent term from both side sof the equality:

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

“Dividing” both sides of the equation by dV and applying constant U :

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

Using the definition of the constant volume heat capacity: $C_v = \left(\frac{\partial U}{\partial T}\right)_V$

gives the final result:

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

This result is an example of the Euler chain relationship.

19. Rewrite Figure 9.7.1 for the partial derivatives:

$$\left(\frac{\partial U}{\partial T}\right)_P \quad \left(\frac{\partial T}{\partial U}\right)_V \quad \left(\frac{\partial U}{\partial P}\right)_T \quad \left(\frac{\partial U}{\partial T}\right)_P \quad \left(\frac{\partial T}{\partial V}\right)_U$$

Answer: The partial derivative conversions are shown below:

$\left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P - P \left(\frac{\partial V}{\partial T}\right)_P = C_p + PV\alpha$ $U = H - PV$	$\left(\frac{\partial T}{\partial U}\right)_V = \frac{1}{\left(\frac{\partial U}{\partial T}\right)_V} = \frac{1}{C_v}$						
$H \equiv U + PV$ definition <i>misplaced numerator</i>	invert <i>misplaced numerator</i>						
<table border="1" style="margin: auto; border-collapse: collapse;"> <tr> <td style="padding: 5px;">$\left(\frac{\partial U}{\partial T}\right)_P$</td> <td style="padding: 5px;">$\left(\frac{\partial T}{\partial U}\right)_V$</td> </tr> <tr> <td style="padding: 5px;">$\left(\frac{\partial U}{\partial P}\right)_T$</td> <td style="padding: 5px;">$\left(\frac{\partial U}{\partial T}\right)_P$</td> </tr> <tr> <td style="padding: 5px;">$\left(\frac{\partial U}{\partial P}\right)_T$</td> <td style="padding: 5px;">$\left(\frac{\partial T}{\partial V}\right)_U$</td> </tr> </table>		$\left(\frac{\partial U}{\partial T}\right)_P$	$\left(\frac{\partial T}{\partial U}\right)_V$	$\left(\frac{\partial U}{\partial P}\right)_T$	$\left(\frac{\partial U}{\partial T}\right)_P$	$\left(\frac{\partial U}{\partial P}\right)_T$	$\left(\frac{\partial T}{\partial V}\right)_U$
$\left(\frac{\partial U}{\partial T}\right)_P$	$\left(\frac{\partial T}{\partial U}\right)_V$						
$\left(\frac{\partial U}{\partial P}\right)_T$	$\left(\frac{\partial U}{\partial T}\right)_P$						
$\left(\frac{\partial U}{\partial P}\right)_T$	$\left(\frac{\partial T}{\partial V}\right)_U$						
<i>misplaced denominator</i> chain rule	<i>misplaced constant variable</i> total differential, dU	<i>misplaced constant variable</i> total differential, dU=0					
$\left(\frac{\partial U}{\partial P}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T$ $\left(\frac{\partial U}{\partial P}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T (-V\kappa_T)$	$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$ $\left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial U}{\partial T}\right)_V$ $= \left(\frac{\partial U}{\partial V}\right)_T V\alpha + C_v$	$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT = 0$ $\left(\frac{\partial T}{\partial V}\right)_U = \frac{-\left(\frac{\partial U}{\partial V}\right)_T}{\left(\frac{\partial U}{\partial T}\right)_V} = \frac{-\left(\frac{\partial U}{\partial V}\right)_T}{C_v}$					

Figure P.1: Partial Derivative Conversion. Partial derivative manipulations to convert unknown partial derivatives to those involving C_v , C_p , α , κ_T , $(\partial U/\partial V)_T$, and $(\partial H/\partial P)_T$.

20. One mole of an ideal diatomic gas at 200. K is compressed in a reversible adiabatic process until its temperature reaches 300. K. Given that $C_{v,m} = \frac{5}{2}R$, calculate q , w , ΔU , and ΔH .

Answer: For a reversible adiabatic expansion of an ideal gas $q = 0$, which gives $\Delta U = w$. In addition, $\Delta U = C_v \Delta T$ and $\Delta H = C_p \Delta T$ for any process in an ideal gas:

$$\Delta U = C_v \Delta T = \frac{5}{2} nR \Delta T = \frac{5}{2} (1 \text{ mol})(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(300. - 200. \text{ K}) = 2078. \text{ J}$$

$$\Delta U = 2.08 \text{ kJ} = w$$

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With $C_p - C_v = nR$, $C_p = 7/2 nR$:

$$\Delta H = C_p \Delta T = 7/2 nR \Delta T = 7/2 (1 \text{ mol})(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(300. - 200. \text{ K}) = 2910. \text{ J}$$

$$\Delta H = 2.91 \text{ kJ}$$

21. Calculate q , w , ΔU , and ΔH for a reversible isothermal expansion of 10.0 mol of an ideal diatomic gas. The initial pressure is 5.00 bar, and the temperature is 298.2 K. The final pressure is 1.00 bar. Assume $C_v = 5/2 nR$ (equipartition neglecting vibration).

Answer: The plan is to use $\Delta T=0$, $q = -w$, $\Delta U = \Delta H = 0$ for an isothermal expansion of an ideal gas. For a reversible isothermal expansion in an ideal gas, $w = -nRT \ln(V_2/V_1)$.

Using $P_2 V_2 = P_1 V_1$ to relate the work to the pressure change gives Eq. 9.8.25°:

$$w = -nRT \ln(V_2/V_1) = -nRT \ln(P_1/P_2) = nRT \ln(P_2/P_1)$$

$$w = 10.0 \text{ mol}(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(1 \text{ kJ}/1000 \text{ J})(298.15 \text{ K}) \ln(1.00/5.00) = -39.9 \text{ kJ}$$

$$q = -w = 39.9 \text{ kJ}$$

22. Calculate q , w , ΔU , and ΔH for an isothermal expansion of 10.0 mol of an ideal diatomic gas against a constant external pressure of 1.00 bar. The final pressure of the gas is equal to the external pressure, $P_2 = P_{\text{ext}}$. The initial pressure is 5.00 bar, and the temperature is 298.2 K. Assume $C_v = 5/2 nR$ (equipartition neglecting vibration).

Answer: The plan is to use $\Delta T=0$, $q = -w$, $\Delta U = \Delta H = 0$ for an isothermal expansion of an ideal gas. For an irreversible expansion, $w = -P_{\text{ext}}\Delta V$.

The initial and final volumes are calculated from the ideal gas equation of state:

$$V_1 = (10.0 \text{ mol})(0.083145 \text{ L bar K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})/(5.0 \text{ bar}) = 49.58 \text{ L}$$

$$V_2 = (10.0 \text{ mol})(0.083145 \text{ L bar K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})/(1.00 \text{ bar}) = 247.9 \text{ L}$$

The work done is: $w = -P_{\text{ext}}\Delta V$:

$$w = -(1.00 \text{ bar})(1 \times 10^5 \text{ Pa}/1 \text{ bar})(247.9 - 49.58 \text{ L})(1 \text{ m}^3/1000 \text{ L}) = -19.8 \text{ kJ}$$

$$q = -w = 19.8 \text{ kJ}$$

Notice that the magnitude of the work done is significantly less than the reversible case in the last problem, because the gas is expanding against a constant external pressure.

23. The volume of 1.00 mol of an ideal diatomic gas exactly doubles in a reversible adiabatic expansion. The initial pressure is 5.00 bar and the initial temperature is 298.2 K. Calculate q , w , ΔU , and ΔH . Use the constant volume heat capacity for water vapor, $C_v = 25.3 \text{ J K}^{-1} \text{ mol}^{-1}$.

Answer: The plan is to use Eq. 9.8.13° to find the final temperature, and then for an adiabatic expansion of an ideal gas, $q = 0$, $\Delta U = w$, $\Delta U = C_v \Delta T$, $\Delta H = C_p \Delta T$.

Using the heat capacity for water $C_v/nR = 25.3 \text{ J K}^{-1} \text{ mol}^{-1}/8.314 \text{ J K}^{-1} \text{ mol}^{-1} = 3.04$. From Eq. 9.8.13°:

$$\left(\frac{T_2}{T_1}\right)^{C_v/nR} = \left(\frac{V_1}{V_2}\right) \quad \text{giving} \quad T_2 = T_1 \left(\frac{V_1}{V_2}\right)^{1/3.04}$$

$$T_2 = 298.15 \text{ K} (1/2)^{0.3286} = 298.15 \text{ K}(0.7963) = 237.4 \text{ K}$$

$$w = \Delta U = C_v \Delta T = (1.00 \text{ mol})(25.3 \text{ J K}^{-1} \text{ mol}^{-1})(237.4 - 298.15 \text{ K}) = -1537. \text{ J}$$

$$w = \Delta U = -1.54 \text{ kJ}$$

Assuming ideal gas behavior $C_p = C_v + nR = 25.3 + 8.314 \text{ J K}^{-1} \text{ mol}^{-1} = 33.6 \text{ J K}^{-1} \text{ mol}^{-1}$:

$$\Delta H = C_p \Delta T = (1.000 \text{ mol})(33.6 \text{ J K}^{-1} \text{ mol}^{-1}) (237.4 - 298.15 \text{ K}) = -2041. \text{ J}$$

$$= -2.04 \text{ kJ}$$

The temperature difference is -60.8 K, so you might expect only 2 significant figures in the result. But a quick propagation of errors treatment allows 3 significant figures for ΔU , with $\Delta T = -60.79 \pm 0.18 \text{ K}$ based on 3 significant figures in the heat capacity. On a test, however, when you don't have time to do an error analysis, it would be safest to report only 2 significant figures in the final ΔU and ΔH . The heat capacity limits the number of significant figures to no more than three.

24. Calculate q , w , ΔU , and ΔH for a reversible adiabatic expansion of an ideal diatomic gas. The initial volume is 50.0 L, the initial pressure is 5.00 bar, and the initial temperature is 298.2 K. The final volume is 157.8 L. Assume $C_v = 5/2 nR$ (equipartition neglecting vibration).

Answer: The plan is to use Eq. 9.8.13° to find the final temperature, and then for an adiabatic expansion of an ideal gas, $q = 0$, $\Delta U = w$, $\Delta U = C_v \Delta T$, $\Delta H = C_p \Delta T$.

The number of moles of gas is calculated from the ideal gas equation of state:

$$n = PV/RT = 5.00 \text{ bar } 50.0 \text{ L}/0.083145 \text{ J K}^{-1} \text{ mol}^{-1}/298.15 \text{ K} = 10.08 \text{ mol}$$

Using the equipartition predicted heat capacity, neglecting vibrations, $C_v = 5/2 nR$, gives $C_v/nR = 5/2$. From Eq. 9.8.13°:

$$\left(\frac{T_2}{T_1}\right)^{C_v/nR} = \left(\frac{V_1}{V_2}\right) \quad \text{giving} \quad T_2 = T_1 \left(\frac{V_1}{V_2}\right)^{2/5}$$

$$T_2 = 298.15 \text{ K} \left(\frac{50.0}{157.8}\right)^{2/5} = 298.15 \text{ K}(0.6315) = 188.3 \text{ K}$$

$$w = \Delta U = C_v \Delta T = 5/2 (10.08 \text{ mol})(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(188.3 - 298.15 \text{ K})$$

$$= -23.0 \text{ kJ}$$

Assuming ideal gas behavior $C_p = C_v + nR = 7/2 nR$:

$$\Delta H = C_p \Delta T = 7/2 (10.08 \text{ mol})(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(188.3 - 298.15 \text{ K}) = -32.2 \text{ kJ}$$

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25. Calculate the initial and final volume, q , w , ΔU , and ΔH for a reversible adiabatic expansion of 2.000 mol of an ideal monatomic gas. The initial pressure is 10.00 bar and the initial temperature is 298.2 K. The final pressure is 1.000 bar. Use the heat capacities predicted by equipartition. Verify that Eqs. 9.8.19° and 9.8.21°, $P_2 V_2^\gamma = P_1 V_1^\gamma$, give the same result.

Answer: For an adiabatic expansion of an ideal gas, $q = 0$, $\Delta U = w$, $\Delta U = C_v \Delta T$, $\Delta H = C_p \Delta T$. For a monatomic gas $C_v = 3/2 nR$ and $C_p = C_v + nR = 5/2 nR$. Using Eq. 9.8.19° to determine the final temperature:

$$\left(\frac{T_2}{T_1}\right)^{C_{p/nR}} = \left(\frac{P_2}{P_1}\right) \quad \text{and} \quad T_2 = T_1 (P_2/P_1)^{2/5} = 298.15 \text{ K}(1.000/10.00)^{2/5}$$

$$T_2 = 118.70 \text{ K}$$

$$\Delta U = C_v (T_2 - T_1) = 3/2 (1.000 \text{ mol})(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(118.70 - 298.15 \text{ K})$$

$$\Delta U = -2238. \text{ J}$$

$$\Delta H = C_p (T_2 - T_1) = 5/2 (1.000 \text{ mol})(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(118.70 - 298.15 \text{ K})$$

$$\Delta H = -3730. \text{ J}$$

The initial and final volumes are determined from the ideal gas equation of state:

$$V_1 = (1.000 \text{ mol})(0.083145 \text{ L bar K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})/(10.00 \text{ bar}) = 2.4790 \text{ L}$$

$$V_2 = (1.000 \text{ mol})(0.083145 \text{ L bar K}^{-1} \text{ mol}^{-1})(118.70 \text{ K})/(1.000 \text{ bar}) = 9.8689 \text{ L}$$

Alternatively, for the final volume, $\gamma = C_p/C_v = 5/3$ and using $P_2 V_2^\gamma = P_1 V_1^\gamma$:

$$V_2 = V_1(P_1/P_2)^{1/\gamma} = 2.4790 \text{ L}(10.00/1.000)^{3/5} = 9.8689 \text{ L}$$

26. Calculate the initial and final volume, q , w , ΔU , and ΔH for a reversible adiabatic expansion of an ideal diatomic gas. The initial pressure is 5.000 bar and the initial temperature is 298.2 K for 10.00 moles. The final pressure is 1.000 bar. Assume $C_v = 5/2 nR$ (equipartition neglecting vibration).

Answer: The plan is to use Eq. 9.8.19° to calculate the change in temperature for the reversible adiabatic expansion. Then, for an adiabatic expansion of an ideal gas, $q = 0$, $\Delta U = w$, $\Delta U = C_v \Delta T$, $\Delta H = C_p \Delta T$.

Assuming ideal gas behavior $C_p = C_v + nR = 7/2 nR$. For a reversible expansion, the change in temperature is given by Eq. 9.8.19°:

$$\left(\frac{T_2}{T_1}\right)^{C_{p/nR}} = \left(\frac{P_2}{P_1}\right) \quad \text{and} \quad T_2 = T_1 (P_2/P_1)^{2/7} = 298.15 \text{ K}(1.000/5.000)^{2/7}$$

$$T_2 = 188.25 \text{ K}$$

$$\Delta U = C_v (T_2 - T_1) = 5/2 (10.000 \text{ mol})(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(188.25 - 298.15 \text{ K})$$

$$w = \Delta U = -22.844 \text{ kJ}$$

$$\Delta H = C_p (T_2 - T_1) = 7/2 (10.000 \text{ mol})(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(188.25 - 298.15 \text{ K})$$

$$\Delta H = -31.982 \text{ kJ}$$

The initial and final volumes are determined from the ideal gas equation of state:

$$V_1 = (10.000 \text{ mol})(0.083145 \text{ L bar K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})/(5.000 \text{ bar}) = 49.579 \text{ L}$$

$$V_2 = (10.000 \text{ mol})(0.083145 \text{ L bar K}^{-1} \text{ mol}^{-1})(154.43 \text{ K})/(1.000 \text{ bar}) = 128.40 \text{ L}$$

Alternatively, for the final volume, using $P_2 V_2^\gamma = P_1 V_1^\gamma$:

$$V_2 = V_1(P_1/P_2)^{1/\gamma} = 49.579 \text{ L}(5.000/1.000)^{5/7} = 156.52 \text{ L}$$

Notice that the magnitude of the work done is significantly less than the corresponding isothermal expansion in Problem 21, since the temperature drops, causing the pressure to decrease, decreasing the pressure against which the gas expands.

27. Calculate the final pressure, initial and final volume, q , ΔU , and ΔH for a reversible adiabatic expansion of an ideal diatomic gas that does -10.00 kJ of work in the process. The initial pressure is 10.00 bar and the initial temperature is 298.2 K for 10.00 moles . Assume $C_v = 5/2 nR$ (equipartition neglecting vibration).

Answer: The plan is to calculate the final temperature from $w = \Delta U = C_v \Delta T$, and from the final temperature the final pressure is calculated from Eq. 9.8.19°.

For an adiabatic expansion of an ideal gas, $q = 0$, $\Delta U = w$, $\Delta U = C_v \Delta T$, $\Delta H = C_p \Delta T$. Solving for the change in temperature from the work specified:

$$w = \Delta U = C_v \Delta T = -10000. \text{ J}$$

giving:

$$-10000. \text{ J} = 5/2 (10.00 \text{ mol})(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(T_2 - 298.15 \text{ K})$$

$$T_2 = 250.04 \text{ K}$$

$$\Delta H = C_p (T_2 - T_1) = 7/2 (10.000 \text{ mol})(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(250.04 - 298.15 \text{ K})$$

$$\Delta H = -14.00 \text{ kJ}$$

Assuming ideal gas behavior $C_p = C_v + nR = 7/2 nR$. For a reversible expansion, the change in temperature and pressure are related by Eq. 9.8.19°:

$$\left(\frac{T_2}{T_1}\right)^{C_p/nR} = \left(\frac{P_2}{P_1}\right) \quad \text{and} \quad P_2 = P_1 (T_2/T_1)^{7/2} = 10.0 \text{ bar}(250.04 \text{ K} / 298.15 \text{ K})^{7/2}$$

$$P_2 = 5.4015 \text{ bar}$$

The initial and final volumes are determined from the ideal gas equation of state:

$$V_1 = (10.000 \text{ mol})(0.083145 \text{ L bar K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})/(10.00 \text{ bar}) = 24.790 \text{ L}$$

$$V_2 = (10.000 \text{ mol})(0.083145 \text{ L bar K}^{-1} \text{ mol}^{-1})(250.04 \text{ K})/(5.4015 \text{ bar}) = 38.488 \text{ L}$$

Alternatively, for the final volume, using $P_2 V_2^\gamma = P_1 V_1^\gamma$:

$$V_2 = V_1(P_1/P_2)^{1/\gamma} = 24.790 \text{ L}(10.00/5.4015)^{5/7} = 38.488 \text{ L}$$

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The temperature drops less in this problem as compared to Example 9.8.1c, the magnitude of the work done per mole is less, and $w = \Delta U = C_v \Delta T$. The work comes at the expense of the internal energy, since less work is done the internal energy change is less.

28. Calculate the initial and final volume, q , w , ΔU , and ΔH for an adiabatic expansion of an ideal diatomic gas against a constant external pressure, with the final pressure of the gas equal to the external pressure, $P_2 = P_{\text{ext}}$. The initial pressure is 5.000 bar and the initial temperature is 298.2 K for 10.00 moles. The external pressure is 1.000 bar. Use the heat capacities predicted by equipartition, neglecting vibration.

Answer: For an adiabatic expansion of an ideal gas, $q = 0$, $\Delta U = w$, $\Delta U = C_v \Delta T$, $\Delta H = C_p \Delta T$. For an adiabatic irreversible expansion against a constant external pressure of P_{ext} :

$$\Delta U = C_v (T_2 - T_1) \quad \Delta U = w = -P_{\text{ext}} (V_2 - V_1) \quad 1$$

Solve these two expressions simultaneously for T_2 gives:

$$C_v (T_2 - T_1) = -P_{\text{ext}} (V_2 - V_1) \quad 2$$

For the final state to be in equilibrium with the surroundings, $P_2 = P_{\text{ext}}$. Then for an ideal gas $V_2 = nRT_2/P_2 = nRT_2/P_{\text{ext}}$:

$$C_v (T_2 - T_1) = -P_{\text{ext}} \left(\frac{nRT_2}{P_{\text{ext}}} - \frac{nRT_1}{P_1} \right) \quad 3$$

Divide both sides of the equation by nR :

$$\frac{C_v}{nR} (T_2 - T_1) = -P_{\text{ext}} \left(\frac{T_2}{P_{\text{ext}}} - \frac{T_1}{P_1} \right) = -T_2 + \frac{P_{\text{ext}}}{P_1} T_1 \quad 4$$

Collecting terms in T_2 and T_1 :

$$\left(\frac{C_v}{nR} + 1 \right) T_2 = \frac{C_v}{nR} T_1 + \frac{P_{\text{ext}}}{P_1} T_1 \quad 5$$

Solving for T_2 :

$$T_2 = \frac{\left(\frac{C_v}{nR} + \frac{P_{\text{ext}}}{P_1} \right)}{\left(\frac{C_v}{nR} + 1 \right)} T_1 \quad 6$$

For a diatomic gas, neglecting vibrations, $C_v/nR = 5/2$:

$$T_2 = \frac{\left(\frac{5}{2} + \frac{1.000 \text{ bar}}{5.000 \text{ bar}} \right)}{\left(\frac{5}{2} + 1 \right)} 298.2 \text{ K} \quad 7$$

$$T_2 = 230.00 \text{ K}$$

$$\Delta U = C_v (T_2 - T_1) = \frac{5}{2} (10.000 \text{ mol})(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(230.00 - 298.15 \text{ K})$$

$$= -14.17 \text{ kJ}$$

Using $C_p = C_v + nR = \frac{5}{2} nR + nR = \frac{7}{2} nR$:

$$\begin{aligned} \Delta H &= C_p (T_2 - T_1) = \frac{7}{2} (10.000 \text{ mol})(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(230.00 - 298.15 \text{ K}) \\ &= -19.83 \text{ kJ} \end{aligned}$$

The initial and final volumes are determined from the ideal gas equation of state:

$$\begin{aligned} V_1 &= (10.000 \text{ mol})(0.083145 \text{ L bar K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})/(5.000 \text{ bar}) = 49.579 \text{ L} \\ V_2 &= (10.000 \text{ mol})(0.083145 \text{ L bar K}^{-1} \text{ mol}^{-1})(230.00 \text{ K})/(1.000 \text{ bar}) = 191.23 \text{ L} \end{aligned}$$

The work is given by $w = \Delta U = -14.17 \text{ kJ}$, or checking for consistency:

$$\begin{aligned} w &= -P_{\text{ext}} \Delta V = - (1.000 \text{ bar})(1 \times 10^5 \text{ Pa}/1 \text{ bar})(191.23 - 49.579 \text{ L})(1 \text{ m}^3/1000 \text{ L}) \\ &= -14.17 \text{ kJ} \end{aligned}$$

The magnitude of the work is less than the reversible expansion, Problem 26, as expected, since the gas is expanding against a constant external pressure. The magnitude of the work is much less than Problem 21, because in addition to being irreversible, the temperature also decreases.

29. Consider an adiabatic expansion against a constant external pressure, P_{ext} , with the final pressure of the gas equal to the external pressure. The initial pressure is 10.00 bar and the initial temperature is 298.2 K for 10.00 moles of an ideal diatomic gas. Calculate the external pressure that is required for -10.00 kJ of work to be done by the gas. Calculate the final temperature, volume, q , ΔU , and ΔH . Use the heat capacities predicted by equipartition, neglecting vibration.

Answer: For an adiabatic expansion of an ideal gas, $q = 0$, $\Delta U = w$, $\Delta U = C_v \Delta T$, $\Delta H = C_p \Delta T$. For an adiabatic irreversible expansion against a constant external pressure of P_{ext} :

$$\Delta U = C_v (T_2 - T_1) \quad \Delta U = w = -P_{\text{ext}} (V_2 - V_1) \quad 1$$

Solve these two expressions simultaneously for P_{ext} to give:

$$C_v (T_2 - T_1) = -P_{\text{ext}} (V_2 - V_1) \quad 2$$

For the final state to be in equilibrium with the surroundings, $P_2 = P_{\text{ext}}$. Then for an ideal gas $V_2 = nRT_2/P_2 = nRT_2/P_{\text{ext}}$:

$$C_v (T_2 - T_1) = -P_{\text{ext}} \left(\frac{nRT_2}{P_{\text{ext}}} - \frac{nRT_1}{P_1} \right) \quad 3$$

Divide both sides of the equation by nR :

$$\frac{C_v}{nR} (T_2 - T_1) = -P_{\text{ext}} \left(\frac{T_2}{P_{\text{ext}}} - \frac{T_1}{P_1} \right) = -T_2 + \frac{P_{\text{ext}}}{P_1} T_1 \quad 4$$

Collecting terms in T_2 and T_1 :

$$\left(\frac{C_v}{nR} + 1 \right) T_2 = \frac{C_v}{nR} T_1 + \frac{P_{\text{ext}}}{P_1} T_1 \quad 5$$

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Solving Eq. 5 for $P_{\text{ext}} = P_2$:

$$\left(\frac{C_v}{nR} + 1\right) \frac{T_2}{T_1} - \frac{C_v}{nR} = \frac{P_{\text{ext}}}{P_1} \quad 6$$

$$P_{\text{ext}} = P_1 \left[\left(\frac{C_v}{nR} + 1\right) \frac{T_2}{T_1} - \frac{C_v}{nR} \right] \quad 7$$

For a diatomic gas, neglecting vibrations, $C_v/nR = 5/2$. Solving for the final temperature from the work gives:

$$\begin{aligned} w &= \Delta U = C_v (T_2 - T_1) \\ -10000. \text{ J} &= \frac{5}{2} (10.00 \text{ mol})(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(T_2 - 298.15 \text{ K}) \\ T_2 &= 250.04 \text{ K} \end{aligned}$$

The constant pressure for the expansion from Eq. 7 is:

$$\begin{aligned} P_{\text{ext}} &= P_1 \left[\left(\frac{5}{2} + 1\right) \frac{250.04 \text{ K}}{298.15 \text{ K}} - \frac{5}{2} \right] \\ P_{\text{ext}} &= 4.3525 \text{ bar} \end{aligned}$$

The initial and final volumes are determined from the ideal gas equation of state:

$$\begin{aligned} V_1 &= (10.000 \text{ mol})(0.083145 \text{ L bar K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})/(10.00 \text{ bar}) = 24.790 \text{ L} \\ V_2 &= (10.000 \text{ mol})(0.083145 \text{ L bar K}^{-1} \text{ mol}^{-1})(250.04 \text{ K})/(4.3525 \text{ bar}) = 47.765 \text{ L} \end{aligned}$$

Using $C_p = C_v + nR = 5/2 nR + nR = 7/2 nR$:

$$\begin{aligned} \Delta U &= w = -10000. \text{ J} = -10.00 \text{ kJ} \\ \Delta H &= C_p (T_2 - T_1) = \frac{7}{2} (10.000 \text{ mol}) (8.314 \text{ J K}^{-1} \text{ mol}^{-1})(250.04 - 298.15 \text{ K}) \\ &= -14.00 \text{ kJ} \end{aligned}$$

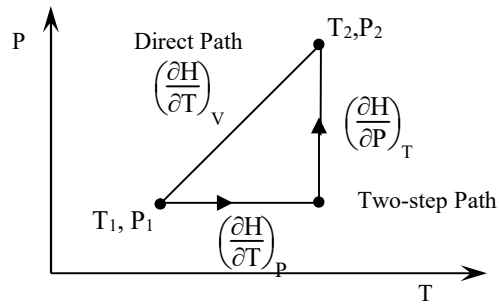
Notice that the change in temperature for this problem is the same as in Problem 27, since $w = \Delta U = C_v \Delta T$ for an adiabatic process, reversible or irreversible.

30. The relationships of the variables that are being held constant for the partial derivative transformation in Eq. 9.4.5 are sketched Figure 9.10.1. (a). Sketch the corresponding relationships for the transformation:

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

(b). Rewrite this expression in terms of the fundamental properties, C_v , C_p , α , κ_T , and μ_{JT} , and integrate the resulting expression assuming that the temperature range is sufficiently narrow that the system properties are constant.

Answer: The change in state for the constant volume path may simply be accomplished using a constant temperature path followed by a constant pressure path.



The direct path is shown as a straight line because, assuming an ideal gas with $P = nRT/V$:

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V} \quad \text{gives a linear relationship at cst. } V: \quad dP = \frac{nR}{V} dT$$

(b). The two-step path is a more convenient way of accomplishing the same change in state, since the values of the partial derivatives are available from experiment; which are tabulated in the form of Joule-Thomson coefficients and constant pressure heat capacities. Using Eq. 9.6.10, Eq. 7.6.16, and the constant pressure heat capacity, Eq. 7.8.24:

$$\left(\frac{\partial H}{\partial T}\right)_V = \left(\frac{\partial H}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V + \left(\frac{\partial H}{\partial T}\right)_P = -C_p \mu_{JT} \left(\frac{\alpha}{\kappa_T}\right) + C_p$$

If these system properties are all constant then the infinitesimals may be replaced by finite differences (Sec. 9.3):

$$\frac{\Delta H}{\Delta T} = -C_p \mu_{JT} \left(\frac{\alpha}{\kappa_T}\right) + C_p$$