Chapter 9: Using the First Law

Calculate q, w, ΔU, and ΔH for a reversible adiabatic expansion in a closed system for one mole of an ideal monatomic gas. The initial pressure is 10.0 bar, the initial temperature is 298.2 K, and the final pressure is 1.00 bar.

The principles underlying the First Law have a firm mathematical foundation. We should take advantage of the underlying structure of the mathematics to help us find the solutions for difficult problems. Calculus provides a cohesive structure and guidance for studying chemical processes. Thermodynamics is a very practical discipline. The success of thermodynamics should be judged by its ability to uncover useful insights into physical phenomena. The goal in this chapter is to gain experience in the manipulative techniques so that we can instead focus on the chemical phenomena. We often study processes for ideal gases. Using ideal gases acts as a point of comparison for non-ideal systems and allows us to concentrate on fundamental principles and not confounding details. Ideal gas approximations are surprisingly often sufficiently accurate for many purposes. The techniques developed in this chapter are generally useful and will help us build a theory of chemical reactivity.

9.1 State Functions Have Exact Differentials

The internal energy is the heat transfer at constant volume. This result suggests that the internal energy is best considered a function of the independent variables V and T. We symbolize this choice of independent variables by: U(V,T). For a closed system, with PV-work only, the total differential of the internal energy can be immediately written based on the general form in Eq. 7.11.13 as:

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \qquad \text{(closed, PV-work) (7.11.14) 9.1.1}$$

because the internal energy is a state function (see also Eq. 7.11.14). The definition of the constant volume heat capacity, Eq. 7.8.7, is $(\partial U/\partial T)_V = C_v$, which upon substitution into Eq. 9.1.1 gives:

$$dU = C_v\, dT + \left(\frac{\partial U}{\partial V}\right)_T dV \qquad \text{(closed, PV-work)} \qquad 9.1.2$$

The differential of the internal energy is exact, as discussed in Addendum Sec. 7.11. The differential is a function of the state of the system only. The differential of the internal energy can be integrated knowing only the initial and final states of the system, without information on the path of the process.

The enthalpy is the heat transfer at constant pressure, which suggests that the enthalpy is best considered a function of independent variables P and T, H(P,T). The total differential of the enthalpy for a closed system, with PV-work only, is also exact:

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \qquad \text{(closed, PV-work)} \qquad 9.1.3$$

Using the definition of the constant pressure heat capacity, Eq. 7.8.24, $(\partial H/\partial T)_P = C_p$, gives:

$$dH = C_p \, dT + \left(\frac{\partial H}{\partial P}\right)_T dP \qquad\qquad \text{(closed, PV-work)} \qquad 9.1.4$$

Eqs. 9.1.1-9.1.4 can be integrated for any general process, once the values for the partial derivatives are known. C_v, C_p, $(\partial U/\partial V)_T$, and $(\partial H/\partial P)_T$ are partial derivatives that characterize the system under study. In particular, $(\partial U/\partial V)_T$, and $(\partial H/\partial P)_T$ play comparable roles, for processes at constant V and P, respectively. One of the major goals of this chapter and successive chapters is to understand these important parameters. The distinction between state functions and path functions on the one hand and exact and inexact differentials on the other is particularly useful, in this regard.

Mixed Partials Are Equal: The Euler Criterion for Exactness: Exact differentials are easy to integrate; however, the path must be specified for inexact differentials. Given an expression in differential form, can you determine if the differential is exact? The general form for the total differential of a state function of two variables x and y is given by Eq. 7.11.13 as:

$$dF = \left(\frac{\partial F}{\partial x}\right)_y dx + \left(\frac{\partial F}{\partial y}\right)_x dy \qquad\qquad 9.1.5$$

The **Euler Criterion for exactness** is that the mixed partial derivatives are equal:

$$\left(\frac{\partial}{\partial y}\left(\frac{\partial F}{\partial x}\right)_y\right)_x = \left(\frac{\partial}{\partial x}\left(\frac{\partial F}{\partial y}\right)_x\right)_y \qquad\qquad \text{(exact)} \qquad 9.1.6$$

This relationship is also called Cauchy's criterion for integrability, or the cross derivative equality test. Several examples will help to clarify the test for exactness.

Example 9.1.1:

Determine if the following total differential is exact: $dV = \dfrac{nR}{P}\, dT - \dfrac{nRT}{P^2}\, dP$

Answer: The total differential of the volume is given by Eq. 7.11.11. Matching the terms in dP and dT identifies the coefficients:

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP \qquad\qquad (7.11.11)$$

$$\downarrow \qquad\qquad \downarrow$$

$$dV = \frac{nR}{P}\, dT \quad - \quad \frac{nRT}{P^2}\, dP$$

giving $\left(\dfrac{\partial V}{\partial T}\right)_P = \dfrac{nR}{P}$ and $\left(\dfrac{\partial V}{\partial P}\right)_T = \dfrac{-nRT}{P^2}$

The mixed partials are:

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

Completing the indicated derivatives gives:

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

The mixed partials are equal, so the differential is exact and V(P,T) is a state function. Thinking of this problem in another way, for an ideal gas V = nRT/P, and the total differential is given by Eq. 7.11.11 with the explicit derivatives $(\partial V/\partial T)_P = nR/P$ and $(\partial V/\partial P)_T = -nRT/P^2$. The total differential given in the original problem is the result of differentiation of the equation of state of the gas. The partial derivatives are both consistent with V = nRT/P.

Example 9.1.2:
Determine if the following total differential is exact: $dF = 3y^2\,dx + 6xy^2\,dy$

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:

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

The mixed partials are:

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

Completing the indicated derivatives gives:

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

The mixed partials are not equal, so the differential is inexact and F(x,y) is a path function. There is <u>no</u> possible function F(x,y) with the explicit derivatives $(\partial F/\partial x)_y = 3y^2$ and $(\partial F/\partial y)_x = 6xy^2$.

The identification of Eqs. 9.1.1-9.1.4 as exact differentials and U and H as state functions allows a wide variety of problems to be easily solved. In addition we can relate changes in internal energy to changes in enthalpy through the definition of the enthalpy and the differentials in Eqs. 7.8.19-7.8.21, dH = dU + d(PV) = dU + PdV + VdP. You may not have experience with differentials. The next two sections are designed to help you become more comfortable with differential expressions and to expand on the important concept of the path independence of state functions.

9.2 Differentials: A differential is a derivative "waiting to happen."

   In this section we will practice manipulating state functions from their definitions. The definition of enthalpy, $H \equiv U + PV$, is in a form that we will see often, and the manipulation of the definition of enthalpy will be analogous to problems that we will see later. $H \equiv U + PV$ is a simple statement; however, what we really want to know is how enthalpy changes for a process, ΔH. For example, how does enthalpy change when we change the temperature, or the pressure, or the volume of a system? Let's start with a cup of coffee on your desk and ask how the enthalpy changes with a change in temperature for a constant pressure process. Consider then that enthalpy is a function of temperature and pressure, $H(T,P)$, and find the derivative with respect to temperature from $H \equiv U + PV$:

$$\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + \left(\frac{\partial (PV)}{\partial T}\right)_P \qquad\qquad 9.2.1$$

and then using the product rule:

$$\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P + V\left(\frac{\partial P}{\partial T}\right)_P \qquad\qquad 9.2.2$$

For a constant pressure process the last derivative is zero since pressure is a constant. However, now let's change the problem, and ask what would happen if the volume was held constant instead of the pressure. Constant volume processes result from placing the sample in a rigid container, like a calorimeter bomb. For a change in temperature for a constant volume process, the pressure wouldn't remain constant, so Eq. 9.2.2 won't work anymore. For a constant volume process we could consider enthalpy as a function of temperature and volume, $H(T,V)$, and redo the derivative with respect to temperature:

$$\left(\frac{\partial H}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V + P\left(\frac{\partial V}{\partial T}\right)_V + V\left(\frac{\partial P}{\partial T}\right)_V \qquad\qquad 9.2.3$$

We could also ask how the enthalpy changes with pressure for a constant temperature process and redo the derivative again. The number of equations is starting to increase and it is getting difficult to focus on the underlying ideas. Instead, we could focus on the differential. Notice in Eqs. 9.2.2 and 9.2.3 that the "numerators" are the same. For an infinitesimal process for a closed system the differential is given as:

$$dH = dU + d(PV) \qquad\qquad (7.8.19)\ 9.2.4$$

or using the product rule for differentiation

$$dH = dU + P\,dV + V\,dP \qquad\qquad (7.8.20)\ 9.2.5$$

Notice that the "numerators" in Eq. 9.2.1 are the same as Eq. 9.2.4 and the "numerators" in Eqs. 9.2.2 and 9.2.3 are the same as the differential in Eq. 9.2.5. The power of differentials is that they are valid no matter which of T, V, or P is changing. Notice that we use the product rule for differentials in the same fashion as for normal derivatives, since a differential is really an intermediate step in finding the derivative. From the differential, we can form the derivatives for H directly, by essentially "dividing" by the infinitesimal for the desired independent variable. Of course, since these are partial derivatives, we also need to keep track of all the constant variables. This "division" process is frowned upon by mathematicians, but works generally none-the-less.

For example, dividing Eq. 9.2.5 by dT at constant P gives Eq. 9.2.2, which we derived directly without any tricks. Dividing Eq. 9.2.5 by dT at constant V gives Eq. 9.2.3. A problem we haven't tackled yet is the pressure dependence of the enthalpy at constant temperature. Using the differential, Eq. 9.2.5, and "dividing" by dP at constant T gives:

$$\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial U}{\partial P}\right)_T + P\left(\frac{\partial V}{\partial P}\right)_T + V\left(\frac{\partial P}{\partial P}\right)_T \qquad 9.2.6$$

In other words, you can think of a differential as a derivative "waiting to happen." The advantage of working with differentials is that differentials have properties that help to simplify many problems, regardless of the independent variable. One important property of the differential of a state function is that they are easy to integrate.

Example 9.2.1

(a). Find the differential for a new state function A defined as $A \equiv U - TS$. (b). From the differential find the derivative of A with respect to T at constant V.

Answer: (a). Using the product rule for differentiation: $dA = dU - T\,dS - S\,dT$.
(b). Then dividing by dT at constant V gives:

$$\left(\frac{\partial A}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V - T\left(\frac{\partial S}{\partial T}\right)_V - S\left(\frac{\partial T}{\partial T}\right)_V$$

Remember that $\left(\frac{\partial U}{\partial T}\right)_V = C_v$ and note that the derivative of T with respect to T is just one, so this equation simplifies to

$$\left(\frac{\partial A}{\partial T}\right)_V = C_v - T\left(\frac{\partial S}{\partial T}\right)_V - S$$

9.3 Integrating Differentials: A differential is an integral "waiting to happen."

A differential is a derivative "waiting to happen." But, a differential is also an integral "waiting to happen." This dual use gives differentials an important central role in helping us solve problems. The differential tells us the variable for the integration. For example, for a reversible expansion at constant pressure:

$$\int_{V_1}^{V_2} P\,dV = P(V_2 - V_1) \qquad\qquad \text{(cst. P)} \qquad 9.3.1$$

Without the dV, the integral is meaningless. For a general state function, F, the integral:

$$\int_{F_1}^{F_2} dF = F_2 - F_1 = \Delta F \qquad 9.3.2$$

can always be done, and always gives the change in that state function for the process, because dF is exact. Using enthalpy as an example, let's do some example integrals.

Enthalpy Change with Volume at Constant Pressure: Starting with Eq. 9.2.5, for a constant pressure process, $dP = 0$, and:

$$dH = dU + P\,dV \qquad\qquad \text{(closed, cst. P)} \ (7.8.21) \ 9.3.3$$

Since P is constant, for a change in volume from V_1 to V_2, this equation integrates to:

$$\int_{H_1}^{H_2}dH = \int_{U_1}^{U_2}dU + \int_{V_1}^{V_2}PdV \qquad\qquad \text{(closed, cst. P)} \qquad 9.3.4$$

$$\Delta H = \Delta U + P\Delta V \qquad\qquad \text{(closed, cst. P)}\,(7.8.17) \ 9.3.5$$

Enthalpy Change with Pressure for Constant Volume: Starting with Eq. 9.2.5, for a constant volume process, $dV = 0$, and:

$$dH = dU + V\,dP \qquad\qquad \text{(closed, cst. V)} \qquad 9.3.6$$

Since V is constant, for a change in pressure from P_1 to P_2, this equation integrates to:

$$\int_{H_1}^{H_2}dH = \int_{U_1}^{U_2}dU + \int_{P_1}^{P_2}VdP \qquad\qquad \text{(closed, cst. V)} \qquad 9.3.7$$

$$\Delta H = \Delta U + V\Delta P \qquad\qquad \text{(closed, cst. V)} \qquad 9.3.8$$

Note that in Chapter 7 we defined enthalpy to be useful for a constant pressure process, where $q_P = \Delta H$. This last example is a constant volume process. ΔH no longer gives the heat transfer, instead $q_v = \Delta U$, but we can still calculate the change in enthalpy.

Example 9.3.1

Calculate the change in enthalpy for a constant volume process where the pressure for one mole of an ideal gas is increased from 1.00 bar to 2.00 bar starting at an initial temperature of 298.2 K. Assume that the gas is diatomic with $C_v = \frac{5}{2}\,nRT$, from Equipartition without vibration.

Answer: The volume of the gas can be obtained from the ideal gas law and starting conditions:

$$V = nRT/P \ = 1.000 \text{ mol } (8.314 \text{ J mol}^{-1}\text{ K}^{-1})(298.2 \text{ K})/(1.00\text{x}10^5\text{ Pa}) = 0.02479 \text{ m}^3$$

The final temperature can be obtained from the final state:

$$T = PV/nR = 2.00 \text{ x}10^5\text{ Pa } (0.02479 \text{ m}^3)/1.00 \text{ mol}/8.314 \text{ J mol}^{-1}\text{ K}^{-1} = 596.4 \text{ K}$$

which should not be surprising. Since the pressure increased by a factor of two, the temperature should increase by a factor of two. The internal energy change is:

$$\Delta U = C_v\Delta T = 5/2 \ (1.000 \text{ mol})(8.314 \text{ J mol}^{-1}\text{ K}^{-1}) \ (596.4 - 298.2 \text{ K}) = 6198. \text{ J}$$

Then using Eq. 9.3.8:

$$\Delta H = \Delta U + V\Delta P = 6198. \text{ J} + 0.02479 \text{ m}^3 \ (2.00\text{x}10^5 - 1.00\text{x}10^5 \text{ Pa}) =$$
$$= \ 6198. \text{ J} + 2479. \text{ J} = 8677. \text{ J} = 8.677 \text{ kJ}$$

To help verify the result, we could also have done this problem using $C_p = C_v + nR = 7/2 \ nR$ and then using $\Delta H = C_p\Delta T = 7/2 \ (1.000 \text{ mol})(8.314 \text{ J mol}^{-1}\text{ K}^{-1}) \ (596.4 - 298.2 \text{ K}) = 8.677 \text{ kJ}$ giving the same result.

General Processes for Changing P and V: Now we need to work with $dH = dU + d(PV)$ or all three terms in $dH = dU + PdV + VdP$, since P and V both change. Consider a process from V_1, P_1 to V_2, P_2 in a closed system. The easiest way to proceed is to integrate Eq. 9.2.4 directly:

$$\int_{H_1}^{H_2}dH = \int_{U_1}^{U_2}dU + \int_{P_1V_1}^{P_2V_2}d(PV) \qquad \text{(closed)} \qquad 9.3.9$$

$$\Delta H = \Delta U + (P_2V_2 - P_1V_1) = \Delta U + \Delta(PV) \qquad \text{(closed)} \quad (7.8.16) \quad 9.3.10$$

This equation is true for any closed system. For the specific case of an ideal gas we can calculate $\Delta(PV)$ from the ideal gas law, Eq. 7.8.28°:

$$\Delta(PV) = P_2V_2 - P_1V_1 = (nRT_2) - (nRT_1) = nR\Delta T \qquad \text{(closed, ideal gas)} \qquad 9.3.11°$$

Substituting this final result into Eq. 9.3.10 gives Eq. 7.8.29°:

$$\Delta H = \Delta U + nR\Delta T \qquad \text{(closed, ideal gas)} \quad (7.8.29°) \quad 9.3.12°$$

This equation holds for any general closed process for an ideal gas.

Isothermal Processes: Now, let's assume we have an isothermal process in a closed system, Figure 9.3.1. Both P and V change. Since enthalpy is a state function, the change in enthalpy will be independent of the path. Therefore, we can choose any convenient path in doing the integral. We will do the problem with two different paths to give us practice in working with differentials and also to verify that H is a state function. This general process will be invaluable as we introduce additional state functions.
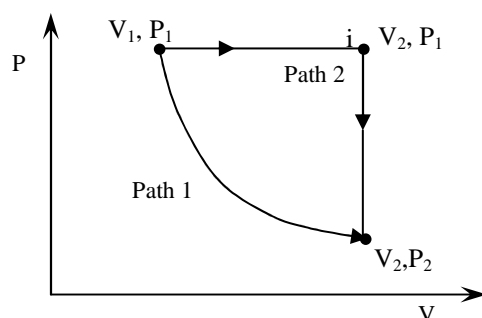

Figure 9.3.1: An isothermal process from V_1, P_1 to V_2, P_2 can be done by two different paths. Path 1 is an isothermal reversible process, and Path 2 is a constant pressure step followed by a constant volume step. ΔH is a state function and is independent of the path.

Path 1: Isothermal Reversible Expansion: Consider an isothermal reversible process from V_1, P_1 to V_2, P_2 in a closed system, path 1 in Figure 9.3.1. Both Eqs. 9.3.10 and 9.3.12° apply, $\Delta H = \Delta U + \Delta(PV)$, where P and V both change along path 1. For this specific isothermal expansion, $\Delta T = 0$, which then gives:

$$\Delta H = \Delta U \qquad \text{(closed, ideal gas, cst. T)} \qquad 9.3.13°$$

The result is that for a closed system for an isothermal process for an ideal gas, the internal energy and enthalpy changes are the same.

Path 2: Constant Pressure Then Constant Volume: Let's choose a different path and integrate $dH = dU + PdV + VdP$. Choose a two-step process, Figure 9.3.1 path 2. The first step is a constant pressure process at P_1, followed by the second step at constant volume at V_2. Let the intermediate state be signified by U_i or H_i. For the first step ΔH_1 is calculated from:

$$\int_{H_1}^{H_i} dH = \int_{U_1}^{U_i} dU + \int_{V_1}^{V_2} P_1 dV \qquad \text{(closed, cst. P)} \qquad 9.3.14$$

The integrand for this volume integral, P_1, is a constant and factors out:

$$\Delta H_1 = \Delta U_1 + P_1(V_2 - V_1) \qquad \text{(closed, cst. P)} \qquad 9.3.15$$

For the second constant volume step, ΔH_2 is given by:

$$\int_{H_i}^{H_2} dH = \int_{U_i}^{U_2} dU + \int_{P_1}^{P_2} V_2 dP \qquad \text{(closed, cst. V)} \qquad 9.3.16$$

$$\Delta H_2 = \Delta U_2 + V_2(P_2 - P_1) \qquad \text{(closed, cst. V)} \qquad 9.3.17$$

The overall change is the sum of the two steps, $\Delta U = \Delta U_1 + \Delta U_2$, and then adding Eqs. 9.3.15 and 9.3.17 to get the overall change for the process gives:

$$\Delta H = \Delta U + P_1(V_2 - V_1) + V_2(P_2 - P_1) \qquad \text{(closed)} \qquad 9.3.18$$

or more succinctly:

$$\Delta H = \Delta U + P_1 \Delta V + V_2 \Delta P \qquad \text{(closed)} \qquad 9.3.19$$

This result looks very different from Eq. 9.3.10. However, notice that multiplying out the terms in Eq. 9.3.18 gives:

$$\Delta H = \Delta U + P_1 V_2 - P_1 V_1 + P_2 V_2 - P_1 V_2 \qquad \text{(closed)} \qquad 9.3.20$$

and cancelling the $P_1 V_2$ terms gives:

$$\Delta H = \Delta U + P_2 V_2 - P_1 V_1 = \Delta U + \Delta(PV) \qquad \text{(closed)} \qquad 9.3.21$$

This last equation gives the same result as path 1, Eq. 9.3.10. The enthalpy change is independent of the path as we expected; the direct and two-part path give the same result.

Example 9.3.2:
Calculate the change in enthalpy for heating of one mole of water vapor from an initial temperature of 298.2K to a final temperature of 373.2 K at constant volume. Water vapor even at pressures near its equilibrium vapor pressure at room temperature is amazingly close to an ideal gas. Assume that the water vapor is an ideal gas and that $C_v = \frac{6}{2} nR$, which is appropriate for water (translation and rotation only for a non-linear molecule).

Answer: Use Eq. 9.3.12°. Then the internal energy change for any process at constant volume is:

$$\Delta U = C_v \Delta T = \frac{6}{2} nR \, \Delta T = 6/2 \, (1.00 \text{ mol })(8.314 \text{ J mol}^{-1}\text{K}^{-1})(373.2 - 298.2\text{K}) = 1.87 \text{ kJ}$$

Now from Eq. 9.3.12°, $\Delta H = \Delta U + nR(T_2 - T_1)$:

$\Delta H = 1.87 \text{ kJ} + (1.00 \text{ mol})(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(1 \text{ kJ}/1000\text{J})(373.2\text{-}298.2\text{K})$
$\Delta H = 1.87 \text{ kJ} + 0.624 \text{ kJ} = 2.49 \text{ kJ}$

In summary, what did we learn from these four simple problems? First, we practiced integrating differentials. Second, we showed that ΔH was independent of the path we chose. Third, these examples show how to do the integrals properly; now we can avail ourselves of some short cuts. Short cuts are good, if you are careful to make sure they are valid! For example, starting with the differential $dH = dU + d(PV)$ the infinitesimals can be rigorously converted to finite differences, $\Delta H = \Delta U + \Delta(PV)$, as proven by Eq. 9.3.10. In other words we are safe to change the "d" into a "Δ." However, for the differential $dH = dU + P \, dV + V \, dP$, we need to be more careful. For a constant pressure process at pressure P, $dP = 0$, and Eq. 9.2.5 simplifies to Eq. 9.3.3, $dH = dU + P \, dV$, and the integrated result is Eq. 9.3.5: $\Delta H = \Delta U + P\Delta V$. Once again for the constant pressure process we can just change the "d" into a finite "Δ." If the pressure isn't constant, Eq. 9.2.5 must be integrated for the specific process. In general,

> an infinitesimal can be integrated directly to a finite difference if the integrand is a constant.

We shouldn't dwell on incorrect solutions. But, one in particular is instructive. Starting with a general process with $dH = dU + PdV + VdP$, it would be incorrect to write

$$\Delta H \stackrel{?}{=} \Delta U + P\Delta V + V\Delta P \qquad \text{(incorrect!!)}$$

since both the pressure and volume can change. Instead, we showed that, from Eq. 9.3.19:

$$\Delta H = \Delta U + P_1\Delta V + V_2\Delta P \qquad\qquad \text{(closed)} \qquad (9.3.19)$$

Even though we derived Eq 9.3.19 for a two step process, the equation is valid in general since H is a state function and is independent of the path.

Example 9.3.3
Calculate the change in enthalpy, using Eq. 9.2.5, for an isothermal process using a two-step path. The first step is a constant volume process from V_1, P_1 to V_1, P_2 and the second step is a constant pressure process from V_1, P_2 to V_2, P_2. Draw this process on a graph such as in Figure 9.3.1.

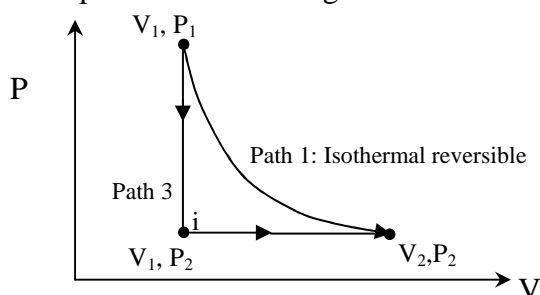*Answer*:   The path is shown in Figure 9.3.2.

Figure 9.3.2: A constant volume first step and a constant pressure second step.

For the first step the integral is:

$$\int_{H_1}^{H_i} dH = \int_{U_1}^{U_i} dU + \int_{P_1}^{P_2} V_1 dP \qquad\qquad 9.3.22$$

$$\Delta H_1 = \Delta U_1 + V_1(P_2 - P_1) \qquad\qquad 9.3.23$$

and the second, constant pressure step gives:

$$\int_{H_i}^{H_2} dH = \int_{U_i}^{U_2} dU + \int_{V_1}^{V_2} P_2 dV \qquad\qquad 9.3.24$$

$$\Delta H_2 = \Delta U_2 + P_2(V_2 - V_1) \qquad\qquad 9.3.25$$

Adding Eqs. 9.3.23 and 9.3.25 gives:

$$\Delta H = \Delta U + V_1(P_2 - P_1) + P_2(V_2 - V_1) \qquad\qquad 9.3.26$$

which should also be compared with Eq. 9.3.19. Multiplying and cancelling terms gives:

$$\Delta H = \Delta U + P_2V_1 - P_1V_1 + P_2V_2 - P_2V_1 = \Delta U + \Delta(PV) \qquad\qquad 9.3.27$$

as before.

Example 9.3.4

Given that $A \equiv U - TS$ is a state function, find the differential in terms of the definition. Can you always integrate the definition to give $\Delta A = \Delta U - \Delta(TS)$? Can you always integrate to give $\Delta A = \Delta U - T\Delta S$?

Answer: The differentials are $dA = dU - d(TS)$ and $dA = dU - TdS - SdT$. $\Delta A = \Delta U - \Delta(TS)$ is always true, however, $\Delta A = \Delta U - T\Delta S$ is only true for an isothermal process. For example, for a constant S process $dA = dU - SdT$, which integrates to $\Delta A = \Delta U - S\Delta T$.

This section shows that the internal energy and enthalpy changes for processes are directly related by $H \equiv U + PV$, after some straight-forward manipulations. Are C_v and C_p similarly related and are $(\partial U/\partial V)_T$, and $(\partial H/\partial P)_T$ related?

9.4 The Constant Volume and Constant Pressure Heat Capacities are Related

The constant volume and constant pressure heat capacities are fundamental properties of a substance:

$$C_v = \left(\frac{\partial U}{\partial T}\right)_V \qquad\qquad C_p = \left(\frac{\partial H}{\partial T}\right)_P \qquad\qquad (7.8.7, 7.8.24)$$

Are C_v and C_p independent or are they related? The constant pressure and constant volume heat capacities are related through the definition of the enthalpy. Substituting $H \equiv U + PV$ into the expression for C_p gives:

$$C_p = \left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial (U + PV)}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P \qquad 9.4.1$$

The difference between the constant pressure and constant volume heat capacities is given by:

$$C_p - C_v = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V \qquad 9.4.2$$

We have not yet encountered the first partial derivative, $(\partial U/\partial T)_P$. We can relate this new partial derivative to the constant volume heat capacity using the total differential of the internal energy with V and T taken as the independent variables:

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \qquad 9.4.3$$

"Dividing" both sides of the equation by dT at constant P gives the partial derivative we are looking for:

$$\left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V \frac{dT}{dT} + \left(\frac{\partial U}{\partial V}\right)_T \frac{dV}{dT} \qquad \text{(cst. P)} \qquad 9.4.4$$

where dT/dT is equal to one and the new derivative is at constant pressure:

$$\left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \qquad 9.4.5$$

This last equation determines the change in internal energy for a constant pressure process. The equation is useful in its own right, but for our present problem, substituting Eq. 9.4.5 into Eq. 9.4.2 gives:

$$C_p - C_v = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V \qquad 9.4.6$$

The $(\partial U/\partial T)_v$ terms cancel giving:

$$C_p - C_v = \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\left(\frac{\partial V}{\partial T}\right)_P \qquad 9.4.7$$

This important equation relates the constant pressure and constant volume heat capacities and is valid for any system. This expression also provides useful insight into the meaning of $(\partial U/\partial V)_T$. When adding two numbers, the units must be the same; the units for $(\partial U/\partial V)_T$ must then be the units of pressure. The measured pressure of the system is P; so what pressure does $(\partial U/\partial V)_T$ correspond to?

   Consider the expansion of a gas as the temperature is increased. The derivative, $(\partial V/\partial T)_P$, determines the increase in volume of the system. The mechanical work done by the gas during the expansion is $w = -P\,dV = -P\,(\partial V/\partial T)_P\,dT$. This second term in the sum in Eq. 9.4.7 therefore accounts for the mechanical work of expansion. The first term, $(\partial U/\partial V)_T\,dV = (\partial U/\partial V)_T\,(\partial V/\partial T)_P\,dT$, is the increase in the internal energy necessary to overcome the intermolecular forces between the gas molecules as the volume increases. As the gas expands, the distances between the molecules increase, which increases the potential energy of the molecular attractions. The molecular attractions are less favorable, higher in energy. The

separation of the molecules then requires the conversion of some random thermal energy into intermolecular potential energy, increasing the constant pressure heat capacity. The partial derivative $(\partial U/\partial V)_T$ is called the **internal pressure**. The stronger the intermolecular forces, the larger the internal pressure. Liquids and solids have large internal pressures. Since an ideal gas has no intermolecular forces, the internal pressure for an ideal gas is zero:

$$\left(\frac{\partial U}{\partial V}\right)_T = 0 \qquad\qquad \text{(ideal gas)} \qquad 9.4.8°$$

For an Ideal Gas, $C_p - C_v = nR$: We can now determine the heat capacity difference for an ideal gas. For an ideal gas $V = nRT/P$ and $(\partial V/\partial T)_P = nR/P$. Since $(\partial U/\partial V)_T = 0$, for an ideal gas, Eq. 9.4.7 reduces to:

$$C_p - C_v = P\left(\frac{\partial V}{\partial T}\right)_P = P\,(nR/P) = nR \qquad\qquad \text{(ideal gas)} \qquad 9.4.9°$$

For example, for a monatomic gas, using Equipartition, $C_v = {}^3/_2\,nR$, and $C_p = C_v + nR = {}^5/_2\,nR$. For a diatomic gas, Table 8.8.1, neglecting the vibration, $C_v = {}^5/_2\,nR$ and $C_p = C_v + nR = {}^7/_2\,nR$. The ratio of C_p to C_v can be measured using several experimental techniques (see Sec. 9.8):

$$\gamma \equiv \frac{C_p}{C_v} \qquad\qquad 9.4.10$$

This **heat capacity ratio** is also useful on theoretical grounds. The ratio arises naturally when constant pressure and constant volume processes are compared. Assuming the ideal heat capacity relationship, $C_p - C_v = nR$, for a monatomic ideal gas, $\gamma = C_p/C_v = ({}^5/_2\,nR)/({}^3/_2\,nR) \approx {}^5/_3$. For a diatomic ideal gas, neglecting vibrations, $\gamma = ({}^7/_2\,nR)/({}^5/_2\,nR) \approx {}^7/_5 = 1.40$. For example, N_2 has nearly the ideal ratio at 20°C with $\gamma = 1.403$, but near the boiling point $\gamma = 1.470$ because of increased effects of intermolecular forces at the higher density.[1]

   To calculate $C_p - C_v$ for real gases, liquids, and solids, the value of $(\partial U/\partial V)_T$ must be known. The experimental determination of $(\partial U/\partial V)_T$ is discussed in Section 9.6. However, returning to Eq. 9.4.7, the mechanical derivative $(\partial V/\partial T)_P$ is given by the coefficient of thermal expansion, Eq. 7.6.8, with $(\partial V/\partial T)_P = V\alpha$. The coefficient of thermal expansion for a liquid or a solid is quite small, suggesting that $C_p \approx C_v$. We often use this approximation in the absence of experimental information. However, even though α is small for a liquid or a solid, $(\partial U/\partial V)_T$ can be quite large and the constant pressure and constant volume heat capacities for liquids and solids can differ by more than 40%.[2] Clearly, we need to know more about the internal pressure, $(\partial U/\partial V)_T$.

9.5 The Internal Pressure of An Ideal Gas Is Zero, $(\partial U/\partial V)_T = 0$

The conclusion that $(\partial U/\partial V)_T = 0$ for an ideal gas provides an important simplification. The total differential of the internal energy, Eq. 9.1.2, simplifies to:

$$dU = C_v\,dT + \underbrace{\left(\frac{\partial U}{\partial V}\right)_T}_{0} dV = C_v\,dT \qquad\qquad \text{(closed, PV-work, ideal gas)} \quad 9.5.1°$$

The corresponding partial derivative for the enthalpy, from Eq. 9.1.3, can be related to $(\partial U/\partial V)_T$ using the definition of the enthalpy, $H \equiv U + PV$:

$$\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial(U + PV)}{\partial P}\right)_T = \left(\frac{\partial U}{\partial P}\right)_T + \left(\frac{\partial(PV)}{\partial P}\right)_T \qquad 9.5.2$$

Since $PV = nRT$ for an ideal gas, the last term is zero. The derivative $(\partial U/\partial P)_T$, in Eq. 9.5.2, can be related to the internal pressure using the chain rule:

$$\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T^{\;0} \left(\frac{\partial V}{\partial P}\right)_T = 0 \qquad \text{(closed, ideal gas)} \quad 9.5.3°$$

For an ideal gas, both $(\partial H/\partial P)_T = 0$ and $(\partial U/\partial V)_T = 0$. The total differential of the enthalpy then reduces to:

$$dH = C_p\, dT + \left(\frac{\partial H}{\partial P}\right)_T^{\;0} dP = C_p dT \qquad \text{(closed, PV-work, ideal gas)} \quad 9.5.4°$$

In other words, the internal energy and enthalpy of an ideal gas depend only on temperature. For the special case of an ideal gas, $dU = C_v dT$ and $dH = C_p\, dT$ apply to <u>all processes</u> in a closed system, including constant volume, constant pressure, adiabatic, and of course isothermal where $dU = dH = 0$.

We will do several example problems using these relationships in Sec. 9.8. However, for real gases, we still need to know $(\partial H/\partial P)_T$ and $(\partial U/\partial V)_T$. These important partial derivatives can be measured experimentally using the Joule-Thomson expansion.

9.6 The Joule-Thompson Expansion Determines the Internal Pressure for a Real Gas

The total differentials of U and H determine the results of gas phase processes, Eqs. 9.1.1-9.1.4. For a general process, the important partial derivatives $(\partial U/\partial V)_T$ and $(\partial H/\partial P)_T$ need to be determined. These derivatives are important fundamental properties of a substance. The Joule-Thomson expansion measures $(\partial H/\partial P)_T$ by expanding a gas through a porous barrier and measuring the temperature change.
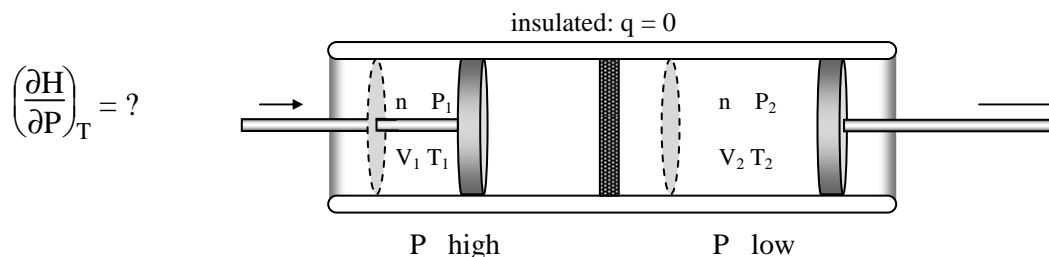

Figure 9.6.1: Joule-Thomson expansion through a porous frit. The pressures on both sides of the frit are constant; high pressure on the left and low pressure on the right. The initial position of the pistons is shown by the outlined disks.

The Joule-Thomson expansion, Figure 9.6.1, is done in an insulated cylinder, giving an adiabatic expansion, $q = 0$. The two halves of the expansion cylinder are separated by a porous disk, or

other flow restriction. The pressure on the left is held at a high constant value by a piston that advances, forcing gas through the porous barrier. The gas expands into the right-hand chamber where a second piston advances maintaining a constant lower pressure. In actual practice the right-hand, low pressure portion of the cylinder is often at atmospheric pressure. During the expansion, the gas may heat or cool, depending on the initial temperature of the gas. Let the number of moles of gas that passes through the porous barrier be n, with the initial state on the left-hand side given by P_1, V_1, and T_1. After expansion of n moles of gas through the flow restriction, the state is given by P_2, V_2, and T_2. Work is done on the gas as the gas is compressed on the high-pressure side as given by $w_{left} = P_1V_1$. The gas does work, $w_{right} = -P_2V_2$, as it expands through the porous disk on the low-pressure side. The total work is the sum of the work on both sides:

$$w = P_1V_1 - P_2V_2 \qquad \text{(cst. } P_1 \& P_2) \qquad 9.6.1$$

Since the expansion is adiabatic the internal energy change is given by the work:

$$\Delta U = U_2 - U_1 = q + w = w \qquad \text{(adiabatic)} \qquad 9.6.2$$

Substituting Eq. 9.6.1 for the work into Eq. 9.6.2 gives:

$$U_2 - U_1 = P_1V_1 - P_2V_2 \qquad 9.6.3$$

Rearranging this last expression by grouping the parameters for the final state on the left and the initial state on the right gives:

$$U_2 + P_2V_2 = U_1 + P_1V_1 \qquad 9.6.4$$

The definition of the enthalpy is $H \equiv U + PV$. Substitution of this definition for the initial and final state in Eq. 9.6.4 shows that the enthalpy of the gas is constant during a Joule-Thomson expansion:

$$H_2 = H_1 \qquad \text{(adiabatic, cst. } P_1 \& P_2) \qquad 9.6.5$$

The Joule-Thomson expansion is a particularly unusual expansion, since the expansion is at constant enthalpy. The temperatures of the gas are measured before and after the expansion, and the Joule-Thomson expansion coefficient is defined as:

$$\mu_{JT} \equiv \left(\frac{\partial T}{\partial P}\right)_H = \frac{T_2 - T_1}{P_2 - P_1} \quad \text{limit } \Delta P \to 0 \qquad 9.6.6$$

If the gas cools $\mu_{JT} > 0$ and if the gas heats up $\mu_{JT} < 0$. The cooling effect is the basis for refrigeration and air-conditioners. However, we began this section by asking if the value for the partial derivatives $(\partial U/\partial V)_T$ or $(\partial H/\partial P)_T$ might be measured experimentally. The relationship of these important partial derivatives to the Joule-Thomson coefficient is not obvious. Notice that μ_{JT} is in a very unusual form, since the enthalpy is the variable that is held constant. We can recast $(\partial T/\partial P)_H$ into a more useful form by focusing on the total differential of the enthalpy:

$$dH = \left(\frac{\partial H}{\partial P}\right)_T dP + \left(\frac{\partial H}{\partial T}\right)_P dT = 0 \qquad 9.6.7$$

where dH = 0, because the enthalpy is held constant for the partial derivative. $(\partial T/\partial P)_H$ can then be constructed by dividing both sides of Eq. 9.6.7 by dP at constant H:

$$\left(\frac{\partial H}{\partial P}\right)_T + \left(\frac{\partial H}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_H = 0 \qquad \qquad 9.6.8$$

This last equation is then solved for $(\partial T/\partial P)_H$:

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{-\left(\dfrac{\partial H}{\partial P}\right)_T}{\left(\dfrac{\partial H}{\partial T}\right)_P} \qquad \qquad 9.6.9$$

Notice that this last equation is just the result of applying the Euler Chain relationship, Eq. 7.11.20, to $(\partial T/\partial P)_H$. Eq. 9.6.9 shows that experimental measurements of μ_{JT} determine the value of $(\partial H/\partial P)_T$:

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H = -\frac{1}{C_p}\left(\frac{\partial H}{\partial P}\right)_T \qquad \qquad \left(\frac{\partial H}{\partial P}\right)_T = -C_p\,\mu_{JT} \qquad \qquad 9.6.10$$

$(\partial H/\partial P)_T$ can then be used to calculate $(\partial U/\partial V)_T$, see Example 9.7.2.

The Joule-Thomson coefficient can be positive or negative. Each gas is characterized by an inversion temperature, T_I, Table 9.5.1. If the initial temperature is greater than the inversion temperature, then the temperature of the gas increases upon a Joule-Thomson expansion. If the initial temperature is less than the inversion temperature, the gas cools upon expansion.

Table 9.5.1: Joule-Thomson inversion temperatures, where $\mu_{JT} = 0$

Gas	T_I (K)
O_2	764
N_2	621
H_2	202
He	40

Along with considerable theoretical utility, the Joule-Thomson expansion is important for home and auto air conditioners, kitchen refrigerators, and laboratory cold traps, where the gas is usually a fluorinated hydrocarbon or butane. Expansion of gaseous carbon dioxide from the vapor space above liquid carbon dioxide in a high pressure cylinder can be used in cooling. A carbon dioxide based fire-extinguisher produces a cold stream of CO_2 that smothers and cools flammable substances. The Joule-Thomson expansion is also used in the production of cryogenic liquids.

Cryogenic Liquids are Produced Using the Joule-Thompson Expansion: Liquid oxygen, nitrogen, hydrogen, and helium are commonly used industrial cryogenic liquids that are produced by Joule-Thomson gas liquefiers, Figure 9.6.2. A compressor is used to establish a flow of high pressure gas. The gas at high pressure is forced through a small orifice, cooling the gas by a Joule-Thomson expansion. After passing through the flow-restriction, the cooled gas returns to the compressor through the outer portion of a concentric tube with the high-pressure gas flowing in the opposite direction. The counter flow of the cool gas lowers the temperature of

the gas on the high pressure side. When the temperature after the expansion drops below the boiling point of the substance, liquid forms, which is collected in a reservoir that can be emptied periodically. After return, the gas passes though the compressor to begin the process again. The compression of the gas increases the temperature, so the high-pressure stream is passed through a heat exchanger to cool the gas. The operation of your home refrigerator is essentially identical. The heat exchange coils for home refrigerators and window air conditioners are visible on the back of the appliance.

The normal boiling point of liquid helium is 4.2 K. Liquid helium is used to keep the solenoids for high field NMR and MRI magnets below the super-conducting transition temperature. To produce liquid helium, the gas must first be cooled below its inversion temperature, 40 K. The most common and economical cryogenic liquid is liquid nitrogen. The normal boiling point of liquid nitrogen is 77 K, which is not sufficient to cool helium below its inversion temperature. The temperature of a liquid may be decreased by attaching a vacuum pump to the vapor space above the liquid. The rapid evaporation of the liquid requires energy, $\Delta_{vap}H$, thus lowering the temperature of the liquid. To cool the helium before the Joule-Thomson expansion, a vacuum pump is used to lower the temperature of a bath of liquid nitrogen that is placed around the heat exchanger.
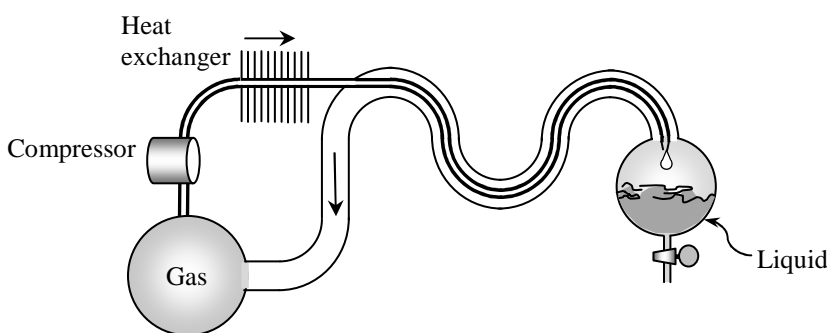

Figure 9.5.2: Joule-Thomson gas liquefier. The gas must initially be below its inversion temperature.

We now have the information needed to calculate the change in internal energy and enthalpy for any process in any closed system, by using Eqs. 9.1.1-9.1.3. The system is characterized by the values of the partial derivatives: C_v, C_p, α, κ_T, $(\partial U/\partial V)_T$, and $(\partial H/\partial P)_T$. We can also relate C_v to C_p and $(\partial U/\partial V)_T$ to $(\partial H/\partial P)_T$. These results are quite an accomplishment. Along the way however, we have worked through many derivations, which might be a bit bewildering at first. The focus is on providing the background necessary for you to derive these relationships on your own. You might wonder if some general guidance for approaching thermodynamic problems can be provided.

9.7 Partial Derivative Conversion: A General Procedure

Thermodynamic problems can often be recast in terms of a partial derivative, which is then integrated for a given process. For example: "calculate the change in internal energy for one mole of an ideal diatomic gas that is heated from 298.2 K to 310.2 K at a constant pressure of 1.00 bar," is determined by the partial derivative $(\partial U/\partial T)_P$, Figure 9.7.1. Each problem must

specify the process, the result desired, and the system. In this example, the process is a change in temperature at constant pressure, the result is the change in internal energy, and the system is an ideal diatomic gas. Next the value of the derivative must be found and then integrated for the specified process.

Calculate the change in internal energy for *one mole of an ideal diatomic gas*

system

$$\left(\frac{\partial U}{\partial T}\right)_P = \ ?$$

the process

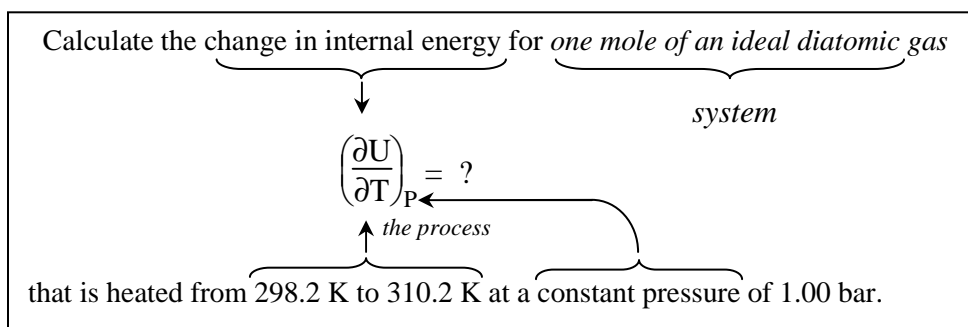that is heated from 298.2 K to 310.2 K at a constant pressure of 1.00 bar.

Figure 9.7.1: Many thermodynamics problems reduce to integrating a specific partial derivative. Each problem must specify the process, the result desired, and the system.

This example would be easy if the process were at constant volume, for then $(\partial U/\partial T)_V = C_v$ and $\Delta U = C_v \Delta T$. However, the example problem is at constant pressure. How do you proceed if the partial derivative is not in a form that is easy to integrate? There is a general procedure for reducing a partial derivative to a relationship that is written in terms of values that are readily available through experiment. The procedure uses the six partial derivative relationships discussed in Addendum 7.11: *Partial Derivative Transformations*. The goal is to recast a given partial derivative into terms that are related to C_v, C_p, α, κ_T, $(\partial U/\partial V)_T$, and $(\partial H/\partial P)_T$. These values are available from data tables or the equation of state for the substance. The first step is to determine the "misplaced variable." In our example problem with $(\partial U/\partial T)_P$, the misplaced variable is the variable that is held constant, P, since U is normally considered a function of V and T, not P and T. Consider the following five possibilities for the "misplaced variable," which are also summarized in Figure 9.7.2:

(1). *Misplaced Numerator*: For $(\partial H/\partial T)_V$, the specified independent variables are V and T. One choice for the misplaced variable is then H, since the independent variables for H are usually considered to be P and T, H(P,T). The given partial may be reduced to a relationship involving the internal energy, which is usually considered a function of V and T, U(V,T). Whenever you need to relate a function of H to a function of U, the definition $H \equiv U + PV$ is useful. Substitution of $H \equiv U + PV$ into the partial derivative gives:

$$\left(\frac{\partial H}{\partial T}\right)_V = \left(\frac{\partial (U + PV)}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial P}{\partial T}\right)_V V = C_v + \frac{\alpha}{\kappa_T} V \qquad 9.7.1$$

where the last substitutions use Eqs. 7.8.7 and 7.6.16 to recast the results into parameters that are commonly tabulated or available from the equation of state.

(2). *Misplaced Numerator*: For $(\partial T/\partial H)_P$, the misplaced variable is the T, since the numerators in all the standard partial derivatives involve either a potential energy function, U or H in this case, or V, as in α, κ_T. The set of variables is consistent with H(P,T). The given partial

may be transformed using <u>inversion</u>, Eq. 7.11.17, and the definition of the heat capacity, Eq. 7.8.24: $(\partial T/\partial H)_P = 1/(\partial H/\partial T)_P = 1/C_p$.

(3). *Misplaced Denominator*: For $(\partial H/\partial V)_T$, the misplaced variable is the V, since the independent variables for H are usually considered to be P and T, H(P,T). The <u>chain rule</u>, Eq. 7.11.18, may be used to express the desired partial derivative in terms of $(\partial H/\partial P)_T$:

$$\left(\frac{\partial H}{\partial V}\right)_T = \left(\frac{\partial H}{\partial P}\right)_T \left(\frac{\partial P}{\partial V}\right)_T = \left(\frac{\partial H}{\partial P}\right)_T \left(\frac{1}{-V\kappa_T}\right) \qquad 9.7.2$$

where the last substitution used the definition of κ_T from Eqs. 7.6.9. Notice that the chain rule was useful, because the constant variable didn't need to be changed.
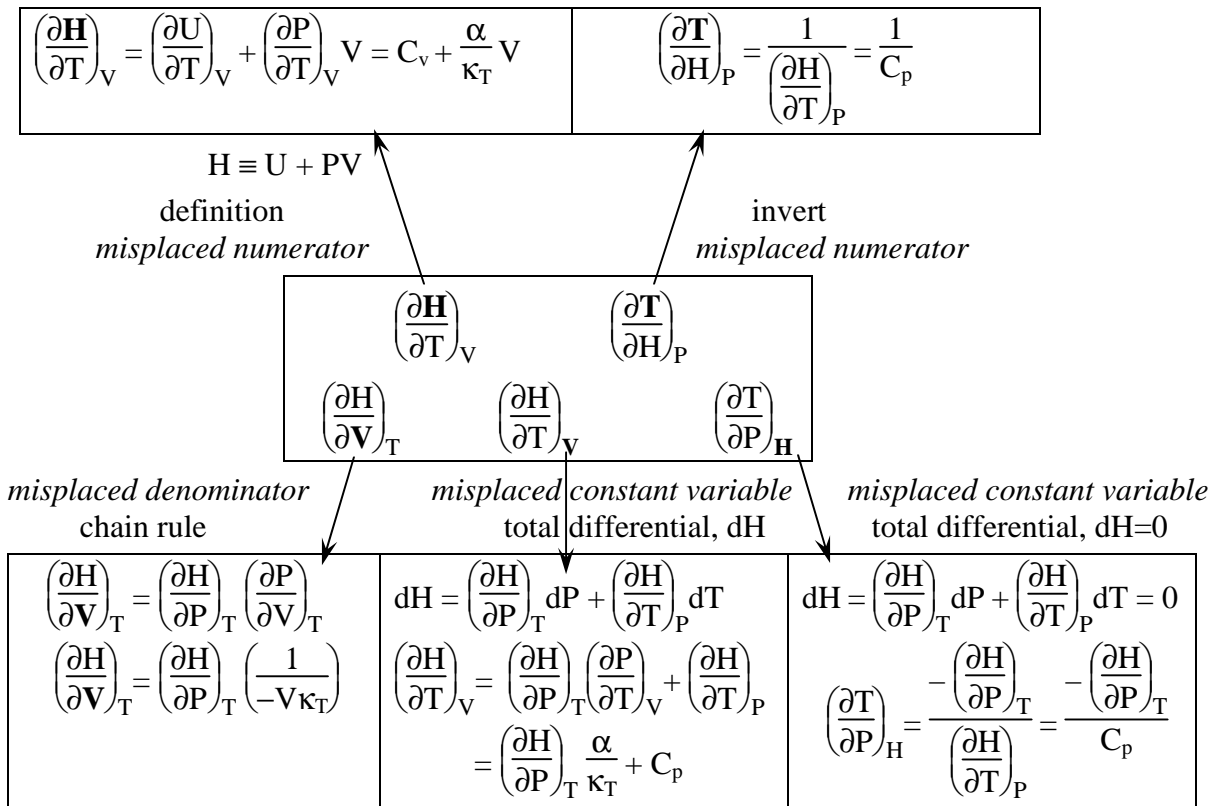
$$\left(\frac{\partial H}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial P}{\partial T}\right)_V V = C_v + \frac{\alpha}{\kappa_T} V \qquad\qquad \left(\frac{\partial T}{\partial H}\right)_P = \frac{1}{\left(\frac{\partial H}{\partial T}\right)_P} = \frac{1}{C_p}$$

$$H \equiv U + PV$$

definition   invert
misplaced numerator   *misplaced numerator*

$$\left(\frac{\partial H}{\partial T}\right)_V \qquad\qquad \left(\frac{\partial T}{\partial H}\right)_P$$

$$\left(\frac{\partial H}{\partial V}\right)_T \qquad\qquad \left(\frac{\partial H}{\partial T}\right)_V \qquad\qquad \left(\frac{\partial T}{\partial P}\right)_H$$

misplaced denominator   *misplaced constant variable*   *misplaced constant variable*
chain rule   total differential, dH   total differential, dH=0

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

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

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

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

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

$$dH = \left(\frac{\partial H}{\partial P}\right)_T dP + \left(\frac{\partial H}{\partial T}\right)_P dT = 0$$

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

Figure 9.7.2: 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 $(\partial H/\partial P)_T$.

(4). *Misplaced Constant Variable*: For $(\partial H/\partial T)_V$, the misplaced variable can also be considered to be the constant volume restriction, since the independent variables for H are usually considered to be P and T, H(P,T). Eq. 7.11.23 is one of two transformations that change the variable being held constant. The derivation begins with the total differential of the thermodynamic potential in terms of the customary independent variables, H(P,T):

$$dH = \left(\frac{\partial H}{\partial P}\right)_T dP + \left(\frac{\partial H}{\partial T}\right)_P dT \qquad 9.7.3$$

"Division" by dT at constant V gives:

$$\left(\frac{\partial H}{\partial T}\right)_V = \left(\frac{\partial H}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V + \left(\frac{\partial H}{\partial T}\right)_P \qquad 9.7.4$$

$$\left(\frac{\partial H}{\partial T}\right)_V = \left(\frac{\partial H}{\partial P}\right)_T \frac{\alpha}{\kappa_T} + C_p \qquad 9.7.5$$

where the last substitutions use Eqs. 7.8.16 and 7.6.24 to recast the results into parameters that are commonly tabulated or available from the equation of state. This example and example 1 are both for $(\partial H/\partial T)_V$; the choice of transformation depends on the information that is available.

(5). *Misplaced Constant Variable*: For $(\partial T/\partial P)_H$, the misplaced variable is the constant enthalpy restriction. In this case the set of variables is conventional, H(P,T), but the order of appearance is scrambled from the normal case of a potential energy function in the numerator. The <u>Euler Chain</u> relationship, Eq. 7.11.20, is useful in these cases. The relationship was derived earlier, Eq. 9.6.9.

Notice that these transformations are completely general; no approximations are necessary. After the transformation, integration using parameters specific to the specified system gives the result.

Example 9.7.1:
Calculate the change in internal energy for one mole of an ideal diatomic gas that is heated from 298.2 K to 310.2 K at a constant pressure of 1.00 bar. Assume a constant heat capacity.

Answer: Figure 9.7.1 shows the implied partial derivative to be $(\partial U/\partial T)_P$. The "misplaced" variable is the restriction to constant P, since internal energy is conventionally considered to have independent variables V and T. Reference to Figure 9.7.2 suggests working through the total differential dH and dividing by dT at constant P. The result is given by Eqs. 9.5.3-9.5.5. Using the definition of the constant volume heat capacity, Eq. 7.8.7, $(\partial U/\partial T)_V = C_v$ and the fact that for an ideal gas $(\partial U/\partial V)_T = 0$ gives:

$$\left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial U}{\partial T}\right)_V = C_v \qquad \text{(ideal gas)} \qquad 9.7.6°$$

In the absence of any specific information concerning the value of the heat capacity, assume the equipartition result; $C_v = {}^5\!/_2\, nR$ for a diatomic gas, neglecting vibration:

$$\Delta U = C_v \Delta T = {}^5\!/_2\, R\,(310.2 - 298.2\ K) = 249.\ J\ mol^{-1}$$

The internal energy and enthalpy change for an ideal gas depends only on the temperature and is independent of the change in pressure or volume.

Example 9.7.2:
Given $(\partial U/\partial V)_T$ find $(\partial H/\partial P)_T$.

Answer: There are two choices for the "misplaced" variable, H and P. Whenever you need to relate a function of H to a function of U, the definition $H \equiv U + PV$ is useful, which suggest trying H in the numerator of $(\partial H/\partial P)_T$ as the misplaced variable, Figure 9.7.2 top-left. Substituting $H \equiv U + PV$ into $(\partial H/\partial P)_T$:

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

using the product rule. The derivative $(\partial U/\partial P)_T$ is not in standard form, since internal energy is usually considered a function of independent variables V and T. The "misplaced" variable in $(\partial U/\partial P)_T$ is the P in the denominator, Figure 9.7.2 bottom-left. $(\partial U/\partial P)_T$ can be related to the internal pressure using the chain rule, Eq. 7.11.18:

$$\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T + P\left(\frac{\partial V}{\partial P}\right)_T + V\left(\frac{\partial P}{\partial P}\right)_T = \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\left(\frac{\partial V}{\partial P}\right)_T + V \qquad 9.7.7$$

The derivation is complete because only "fundamental" partial derivatives remain. We will show that each term on the right can be evaluated using the equation of state of the substance in Chapt. 16. In this example, we started by choosing H in the numerator as the "misplaced" variable, but choosing P in the denominator works as well. There are usually multiple ways of deriving thermodynamic relationships (which enhances student grades on tests).

Now that we have more thoroughly discussed the theoretical background of thermodynamics, we should put these new tools to use for some example problems. To avoid complications that might obscure the important points we focus on an ideal gas.

9.8 The First Law and Ideal Gases

The First Law of thermodynamics is the primary tool for "balancing the books" on the interconversions of heat and work, $dU = đq + đw$. What are the heat and work transfers, the change in internal energy, and the change in enthalpy for ideal gas expansions? In the following examples we determine q, w, ΔU, and ΔH for isothermal and adiabatic, reversible and irreversible expansions in a closed system for an ideal gas. One immediate general simplification for an ideal gas is the internal energy and enthalpy only depend on temperature, Eqs. 9.5.1° and 9.5.4°, because $(\partial U/\partial V)_T = 0$ and $(\partial H/\partial P)_T = 0$. Assuming constant heat capacities over the given temperature range, then the total differentials simplify to:

$$dU = C_v \, dT \quad \Delta U = C_v \, \Delta T \quad dH = C_p \, dT \quad \Delta H = C_p \, \Delta T \quad \text{(ideal gas, cst. } C_v \& C_p) \quad 9.8.1°$$

For Isothermal Expansions of an Ideal Gas, đq = – đw: Consider an isothermal expansion of an ideal gas from V_1, P_1 to V_2, P_2. From Eqs. 9.8.1°, for an isothermal process in a closed system $\Delta U = 0$ and $\Delta H = 0$. We can then directly relate the heat and work transfer using the First Law, $dU = đq + đw = 0$, giving:

$$đq = – đw \qquad \text{and } q = – w \qquad\qquad \text{(closed, isothermal, ideal gas)} \qquad 9.8.2°$$

For an isothermal <u>reversible</u> process the work is given by Eq. 7.4.6° so that:

$$w = -nRT \ln \frac{V_2}{V_1} \quad \text{and} \quad q = -w = nRT \ln \frac{V_2}{V_1} \quad \text{(isothermal reversible, ideal gas)} \quad 9.8.3°$$

If the problem is given with changes in pressure instead of changes in volume, then we can use the ideal gas law to relate the volumes and pressures by:

$$\frac{P_2 V_2}{P_1 V_1} = \frac{nRT_2}{nRT_1} = \frac{T_2}{T_1} \qquad \text{(closed, ideal gas)} \quad 9.8.4°$$

which for an isothermal expansion, $T_2 = T_1$, gives:

$$P_2 V_2 = P_1 V_1 \quad \text{or} \quad \frac{P_2}{P_1} = \frac{V_1}{V_2} \qquad \text{(closed, isothermal, ideal gas)} \quad 9.8.5°$$

Next, consider an <u>irreversible</u> isothermal expansion against a constant external pressure, P_{ext}. From Eq. 7.4.4, the work is given by $w = -P_{ext} \Delta V$. These results are summarized in Table 9.8.1.

For Adiabatic Expansions dU = đw: For an adiabatic expansion, $đq = 0$, and then for <u>any</u> closed system:

$$dU = đw \qquad \text{or} \qquad \Delta U = w \qquad \qquad \text{(closed, adiabatic)} \quad 9.8.6$$

Now consider a <u>reversible</u> adiabatic expansion of an ideal gas in a closed system. Eqs. 9.8.1° relate the change in internal energy and enthalpy to the change in temperature. If the temperature change for the expansion is given, then $w = \Delta U = C_v \Delta T$ is easily calculated. However, how do we proceed if the change in volume or pressure is specified? In addition to $dU = C_v dT$, for a reversible process, $P_{ext} = P$, and the work becomes:

$$dU = đw = -P \, dV \qquad \qquad \text{(closed, adiabatic reversible)} \quad 9.8.7$$

We can solve $dU = C_v \, dT$ and $dU = -P \, dV$ simultaneously to find the change in temperature:

$$C_v \, dT = -P \, dV \qquad \qquad \text{(closed, adiabatic reversible)} \quad 9.8.8$$

Using the ideal gas law relates the pressure and temperature:

$$C_v \, dT = -\frac{nRT}{V} \, dV \qquad \qquad \text{(closed, adiabatic reversible, ideal gas)} \quad 9.8.9°$$

Dividing both sides of this last equation by T separates the variables, giving:

$$C_v \frac{dT}{T} = -nR \frac{dV}{V} \qquad \qquad \text{(closed, adiabatic reversible, ideal gas)} \quad 9.8.10°$$

Integrating both sides of the last equation, assuming a constant heat capacity:

$$C_v \int_{T_1}^{T_2} \frac{dT}{T} = -nR \int_{V_1}^{V_2} \frac{dV}{V} \qquad \text{(closed, adiabatic reversible, ideal gas, cst. } C_v) \quad 9.8.11°$$

results in:

$$C_v \ln \frac{T_2}{T_1} = -nR \ln \frac{V_2}{V_1} \qquad \text{(closed, adiabatic reversible, ideal gas, cst. } C_v) \quad 9.8.12°$$

Dividing by nR and exponentiation of both sides of this equation gives:

$$\left(\frac{T_2}{T_1}\right)^{C_v/nR} = \left(\frac{V_1}{V_2}\right) \qquad \text{(closed, adiabatic reversible, ideal gas, cst. } C_v) \quad 9.8.13°$$

and cross multiplication relates the final and initial states directly:

$$V_2 T_2^{C_v/nR} = V_1 T_1^{C_v/nR} \qquad \text{(closed, adiabatic reversible, ideal gas, cst. } C_v) \quad 9.8.14°$$

Given the change in volume for the process, Eq. 9.8.13° or 9.8.14° is solved for the change in temperature. For a monatomic gas, $C_v/nR = {}^3/_2$ and for a diatomic gas, neglecting the vibration, $C_v/nR = {}^5/_2$, Table 8.8.1.

If, instead, the pressure change for the adiabatic reversible expansion is specified we can take a similar approach. Choosing P and T as the independent variables, the enthalpy is the natural choice as the basis for our calculations, instead of the internal energy. The total differential of the enthalpy is given by Eq. 9.3.5, dH = dU + PdV + VdP. However, for an adiabatic reversible process from Eq. 9.8.7, dU = – PdV, giving (Eq. 7.8.31):

$$dH = dU + PdV + VdP = V\,dP \qquad \text{(closed, adiabatic, reversible) } 9.8.15$$

Solving dH = V dP and dH = C_p dT simultaneously and using V = nRT/P gives:

$$C_p\,dT = V\,dP = \frac{nRT}{P}\,dP \qquad \text{(closed, adiabatic, reversible, ideal gas)} \quad 9.8.16°$$

Separating variables, by dividing by T, and integrating as before gives:

$$C_p \frac{dT}{T} = \frac{dP}{P} \qquad \text{and} \qquad C_p \int_{T_1}^{T_2} \frac{dT}{T} = nR \int_{P_1}^{P_2} \frac{dP}{P}$$

$$\text{(closed, adiabatic reversible, ideal gas, cst. } C_p) \quad 9.8.17°$$

with the final result:

$$C_p \ln \frac{T_2}{T_1} = nR \ln \frac{P_2}{P_1} \qquad \text{(closed, adiabatic reversible, ideal gas, cst. } C_p) \quad 9.8.18°$$

Dividing by nR and exponentiation gives the corresponding result to Eq. 9.8.13°:

$$\left(\frac{T_2}{T_1}\right)^{C_p/nR} = \left(\frac{P_2}{P_1}\right) \qquad \text{(closed, adiabatic reversible, ideal gas, cst. } C_p) \quad 9.8.19°$$

This relationship is used to solve for the change in temperature if the change in pressure is given.

The relationship $P_2 V_2 = P_1 V_1$ is particularly useful for an <u>isothermal</u> process. Can we derive a similar relationship for reversible adiabatic processes? How are P and V related for a reversible adiabatic expansion? The ratio of the constant pressure and constant volume heat capacities is defined as $\gamma \equiv C_p/C_v$, Eq. 9.5.9. The heat capacity ratio is found by dividing Eq. 9.8.18° by Eq. 9.8.12°:

$$\gamma = \frac{C_p}{C_v} = \frac{\ln\left(P_2/P_1\right)}{\ln\left(V_1/V_2\right)} \qquad \text{(closed, adiabatic reversible, ideal gas, cst. } C_p) \quad 9.8.20°$$

Cross multiplication by $\ln(V_1/V_2)$ and exponentiation gives the relationship between P and V:

$$\gamma \ln \frac{V_1}{V_2} = \ln \frac{P_2}{P_1} \quad \text{and} \quad \left(\frac{V_1}{V_2}\right)^\gamma = \left(\frac{P_2}{P_1}\right) \quad \text{giving} \quad P_2 \, V_2{}^\gamma = P_1 V_1{}^\gamma$$

$$\text{(closed, adiabatic reversible, ideal gas, cst. } C_p) \quad 9.8.21°$$

These expressions apply for gases that obey the ideal gas law equation of state, but do not necessarily follow the ideal gas heat capacity relationship $C_p - C_v = nR$. The relationship $P_2 \, V_2{}^\gamma = P_1 V_1{}^\gamma$ is particularly useful for comparing the changes for reversible isothermal and adiabatic expansions, Figure 9.8.1 and Table 9.8.1. For example, for an adiabatic expansion for a monatomic gas, $P_2 \, V_2{}^{5/3} = P_1 \, V_1{}^{5/3}$, but for the isothermal process $P_2 V_2 = P_1 V_1$. The pressure drops more during an adiabatic expansion because the volume dependence is greater, $5/3 > 1$.

Table 9.8.1: Thermodynamic balance sheet for ideal gas expansions in a closed system.

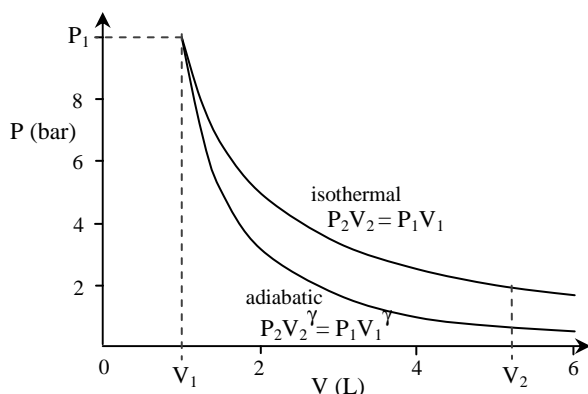| Process	PV relationship	q	w	ΔU	ΔH
isothermal reversible	$P_2 V_2 = P_1 V_1$	$q = -w$	$w = -nRT \ln \dfrac{V_2}{V_1}$	0	0
isothermal irreversible	$P_{ext} = cst$ $P_2 V_2 = P_1 V_1$	$q = -w$	$w = -P_{ext} \Delta V$	0	0
adiabatic reversible	$(T_2/T_1)^{C_v/nR} = V_1/V_2$ $(T_2/T_1)^{C_p/nR} = P_2/P_1$ $P_2 V_2{}^\gamma = P_1 V_1{}^\gamma$	0	$w = \Delta U = C_v \, \Delta T$	$\Delta U = C_v \Delta T$	$\Delta H = C_p \Delta T$
adiabatic irreversible	$P_{ext} = cst$ $C_v \Delta T = -P_{ext} \Delta V$	0	$w = \Delta U = -P_{ext} \Delta V$	$\Delta U = C_v \Delta T$	$\Delta H = C_p \Delta T$

Figure 9.8.1: An adiabatic expansion does less work than an isothermal expansion for a given change in volume, because the temperature decreases during an adiabatic expansion.

For an isothermal expansion the heat and work are equal in magnitude, $đq = -đw$, which shows the work is "paid for" by an equal transfer of heat from the surroundings. For an adiabatic process $đq = 0$, so the work is at the expense of the internal energy, $đw = dU$; the work in an adiabatic process is "paid for" by a decrease in the internal energy of the gas. The decrease in

internal energy for an adiabatic process results in a temperature decrease. An adiabatic expansion does less work than an isothermal expansion, for a given change in volume, because the temperature decreases. Therefore the pressure for the adiabatic expansion decreases more than an isothermal expansion, giving less area under the PV curve and less work.

   Now, consider an <u>irreversible</u> adiabatic expansion against a constant external pressure, P_{ext}. Once again the work is given by $w = \Delta U = C_v\Delta T$ and $w = -P_{ext}\Delta V$. We can solve both of these equations simultaneously for the change in temperature:

$$C_v\Delta T = -P_{ext}\Delta V \qquad \text{(closed, adiabatic, ideal gas, cst. } P_{ext}\&C_v\text{) } 9.8.22°$$

Explicitly in terms of the initial and final states:

$$C_v(T_2 - T_1) = -P_{ext}(V_2 - V_1) \qquad \text{(closed, adiabatic, ideal gas, cst. } P_{ext}\&C_v\text{) } 9.8.23°$$

This equation is solved for the final temperature if the initial and final volumes are specified. What if the initial and final pressures are given instead? Assume that the expansion is complete when the final pressure is equal to the external pressure, $P_2 = P_{ext}$. Substituting the ideal gas law for the final and initial states, $V_2 = nRT_2/P_2$, and $V_1 = nRT_1/P_1$:

$$C_v(T_2 - T_1) = -P_{ext}\left(\frac{nRT_2}{P_{ext}} - \frac{nRT_1}{P_1}\right) \qquad \text{(closed, adiabatic, ideal gas, cst. } P_{ext}\&C_v\text{) } 9.8.24°$$

Example 9.8.1:
Calculate q, w, ΔU, and ΔH for isothermal and adiabatic, reversible and irreversible expansions in a closed system for 1.000 mol of an ideal monatomic gas. In each case, the initial pressure is 10.00 bar, the initial temperature is 298.2 K, and the final pressure is 1.000 bar. For the irreversible expansions, the gas expands against a constant external pressure of 1.000 bar.

Answer: For the isothermal expansion, $\Delta T = 0$ so that $\Delta U = \Delta H = 0$ and $q = -w$.
(a). The work in an isothermal <u>reversible</u> expansion is given as, Eq. 7.4.6°:

$$w = -nRT \ln \frac{V_2}{V_1} \qquad \text{with } P_2V_2 = P_1V_1 \text{ or } \frac{V_2}{V_1} = \frac{P_1}{P_2} \text{ giving:}$$

$$w = -nRT \ln \frac{P_1}{P_2} = nRT \ln \frac{P_2}{P_1} \qquad \text{(isothermal reversible, ideal gas)} \qquad 9.8.25°$$

$$w = (1.000 \text{ mol})(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.2 \text{ K}) \ln \frac{1.000 \text{ bar}}{10.00 \text{ bar}} = -5710. \text{ J}$$

$$q = -w = 5710. \text{ J} \qquad\qquad \text{(isothermal reversible, ideal gas)}$$

The work is negative because the gas expands against the surroundings doing work.
(b). Now consider the <u>irreversible</u> expansion against the constant external pressure. The initial and final volumes are given by the ideal gas law at constant T:

$$V_1 = nRT_1/P_1 = (1.000 \text{ mol})(0.08314 \text{ L bar mol}^{-1}\text{K}^{-1})(289.2 \text{ K})/10.00 \text{ bar} = 2.479 \text{ L}$$
$$V_2 = nRT_1/P_2 = (1.000 \text{ mol})(0.08314 \text{ L bar mol}^{-1}\text{K}^{-1})(289.2 \text{ K})/1.00 \text{ bar} = 24.79 \text{ L}$$

When the pressure drops in an isothermal process by a factor of ten, the volume increases by a factor of ten. The work is:

$$w = - P_{ext}\Delta V = 1.000 \text{ bar}(1.00 \times 10^5 \text{ Pa/1bar})(24.79 - 2.479 \text{ L})(1 \text{ m}^3/1000 \text{ L}) = -2231. \text{ J}$$
$$q = - w = 2231. \text{ J} \qquad\qquad\qquad \text{(isothermal irreversible, ideal gas)}$$

The work for the irreversible process is smaller in magnitude because the system expands against a constant external pressure; a reversible process gives the maximum work.

For an adiabatic expansion, $q = 0$, $\Delta U = C_v\Delta T$, $\Delta H = C_p\Delta T$, $w = \Delta U$.

(c). For the <u>reversible</u> adiabatic process, since the pressure change is specified, we can use Eq. 9.8.19 with $C_p = C_v + nR = \frac{5}{2} nR$ for a monatomic gas:

$$\left(\frac{T_2}{T_1}\right)^{5/2} = \left(\frac{P_2}{P_1}\right) \qquad \text{or} \qquad \left(\frac{T_2}{298.2 \text{ K}}\right)^{5/2} = \left(\frac{1.000 \text{ bar}}{10.000 \text{ bar}}\right)$$

$$T_2 = 298.2 \text{ K } (0.1)^{2/5} = 118.7 \text{ K}$$

The temperature drops as expected because the system does work at the expense of the internal energy. With the final temperature established:

$$w = \Delta U = C_v\Delta T = \frac{3}{2} nR (T_2 - T_1) = \frac{3}{2} (1.000 \text{ mol})(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(118.7 - 298.2\text{K})$$
$$w = \Delta U = -2238. \text{ J} \qquad\qquad \text{(adiabatic reversible, ideal gas)}$$
$$\Delta H = C_p\Delta T = \frac{5}{2} (1.000 \text{ mol})(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(118.7 - 298.2\text{K}) = -3731. \text{ J}$$

The work for the adiabatic reversible process is smaller in magnitude than the isothermal case, as expected, because the temperature decreases.

(d). Finally, for the <u>irreversible</u> adiabatic expansion against the constant external pressure, we apply Eq. 9.8.24° to find the change in temperature, with $C_v = \frac{3}{2} nR$:

$$\frac{3}{2} nR (T_2 - T_1) = - P_{ext}\left(\frac{nRT_2}{P_{ext}} - \frac{nRT_1}{P_1}\right)$$

The nR factors cancel giving:

$$\frac{3}{2} (T_2 - 298.2 \text{ K}) = - 1.000 \text{ bar}\left(\frac{T_2}{1.000 \text{ bar}} - \frac{298.2 \text{ K}}{10.00 \text{ bar}}\right) = - T_2 + 29.82 \text{ K}$$
$$\frac{5}{2} T_2 = \frac{3}{2}(298.2 \text{ K}) + 29.82 \text{ K}$$
$$T_2 = 190.8 \text{ K}$$

The temperature doesn't drop as much as the reversible case, because the gas does less work. With the final temperature established, we proceed as for the reversible case:

$$w = \Delta U = C_v\Delta T = \frac{3}{2} (1.000 \text{ mol})(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(190.8 - 298.2\text{K})$$
$$w = \Delta U = -1339. \text{ J} \qquad\qquad \text{(adiabatic irreversible, ideal gas, cst. } P_{ext})$$
$$\Delta H = C_p\Delta T = \frac{5}{2} (1.000 \text{ mol})(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(190.8 - 298.2\text{K}) = -2232. \text{ J}$$

The irreversible adiabatic expansion does the least work of the four cases, as expected. The results for the four processes are summarized in Table 9.8.2.

Isothermal and adiabatic expansions provide good examples of the use of the First Law in practical problems. Reversible isothermal and adiabatic processes will also play a central role in developing the thermodynamic definition of entropy, in Chapter 11.

Table 9.8.2: Expansion of one mole of an ideal monatomic gas at 298 K from 10 → 1 bar.

process (10 bar→1 bar)	T_2	q	w	ΔU	ΔH
isothermal reversible	298.2 K	5710. J	-5710. J	0	0
isothermal, cst. P_{ext}	298.2 K	2231. J	-2231. J	0	0
adiabatic reversible	118.7 K	0	-2238. J	-2238. J	-3731. J
adiabatic, cst. P_{ext}	131.2 K	0	-1339. J	-1339. J	-2232. J

In this chapter we have focused on the consequences of the First Law of thermodynamics. The concept of conservation of energy is a pivotal idea in many areas in science. Conservation of energy plays an important role in shaping our world on many scales (see Sec. 1.4).

9.9 Efficient Organisms Have a Competitive Advantage: Ecology

One of the central tenants in ecology is: organisms that gather and use energy efficiently are more likely to survive. Energy is typically in short supply and competition for energy shapes the relationships within an ecosystem. For example, trees and other plants compete for sunlight in dense forests. Trees in a rain forest grow tall. The ability of an organism to harvest and use energy efficiently provides a survival benefit and a competitive advantage.

The energy requirements of an organism determine the role of the organism is its biological niche. Autotrophs use sunlight or inorganic substances as energy sources to produce the molecules necessary for cell maintenance, growth, and reproduction. Heterotrophs obtain energy by feeding on other organisms. The loss of energy to metabolic activity limits the energy that is available to higher trophic levels.[30] Organisms higher up the food chain therefore have diminished available energy, and typically also have a greater impact on the environment.

The production and use of energy in ecosystems and in the human community are governed by the First Law of Thermodynamics. The conservation of energy results in competition among various organisms in an ecosystem. The energy needs of societies also are in competition. The flow of energy through an ecosystem and the flow of energy through a human society have much in common. Organisms evolve to increase efficiency; our society must also evolve to increase our efficiency in energy production and consumption.

Thermodynamics provides the fundamental structure for developing new energy technologies and energy public policy. Key ingredients in energy policy encourage increased energy efficiency and conservation. However, the First Law alone is insufficient to determine the efficiency of a process. Inefficient and efficient uses of energy obey the First Law. Efficiency, spontaneity, and the position of equilibrium are closely related concepts. We next develop the ideas central for determining the efficiency and spontaneity of physical processes.

9.10 Summary – Looking Ahead

The structure of physical phenomena is modeled by mathematical relationships that make problems easy to solve and often highlight interrelationships that are surprising and unexpected. For example, Eq. 9.4.5 gives the change in internal energy with temperature for a process at constant pressure:

$$\left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \tag{9.4.5}$$

The result is expressed in partial derivatives that relate the fundamental properties of the system under study. The values of these partial derivatives are available from tables of data or from the equation of state. This expression is not obvious. In fact you might wonder how a change in temperature for a constant pressure process can be related to partial derivatives at constant volume and constant temperature. The relationship is rigorous and completely general and a result of the path independence of state functions. The change in state for the constant pressure path may simply be accomplished using a constant volume path followed by a constant temperature path, Figure 9.10.1. The two-step path is simply a more convenient way of accomplishing the same change in state.
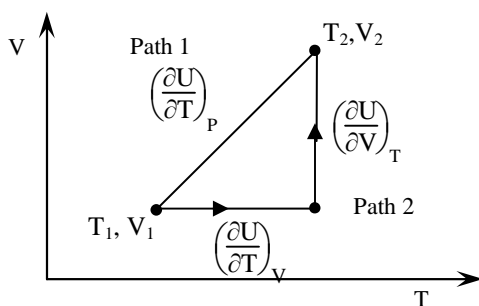

Figure 9.10.1: A constant pressure process from T_1, V_1 to T_2, V_2 can be done by two different paths. Path 1 is the direct one-step path, and Path 2 is a constant volume step followed by a constant temperature step. ΔU is a state function and is independent of the path.

The key to reconciling the various conditions in Eq. 9.4.5 is to realize that the pressure, volume, temperature, and internal energy are all related. <u>Any</u> two may be chosen as the independent variables, and then the remaining two are determined through the equation of state and the First Law. The structure of calculus keeps track of the interrelationships for us. The structure of thermodynamics often provides surprising, unexpected, and useful results.

We now have the necessary background in thermodynamics to develop the criteria for spontaneous processes and determine the position of equilibrium.

Chapter Summary

1. The total differential of a state function is exact.
2. An exact differential may be integrated knowing only the initial and final states of the system.
3. The Euler Criterion for exactness is that mixed partials are equal. Given F a state function:

$$dF = \left(\frac{\partial F}{\partial x}\right)_y dx + \left(\frac{\partial F}{\partial y}\right)_x dy \quad \text{and} \quad \left(\frac{\partial}{\partial y}\left(\frac{\partial F}{\partial x}\right)_y\right)_x = \left(\frac{\partial}{\partial x}\left(\frac{\partial F}{\partial y}\right)_x\right)_y$$

4. Differentials are formed using the normal rules of differentiation. For a function with the definition $G = F + xy$, the differential is $dG = dF + d(xy)$ and $dG = dF + xdy + ydx$

5. Differentials can be converted to partial derivatives by dividing by the infinitesimal of the independent variable and specifying all other variables constant. For $dG = dF + x\,dy + y\,dx$, the partial derivative with respect to x at constant y is:

$$\left(\frac{\partial G}{\partial x}\right)_y = \left(\frac{\partial F}{\partial x}\right)_y + x\left(\frac{\partial y}{\partial x}\right)_y + y\left(\frac{\partial x}{\partial x}\right)_y$$

6. The differentials of state functions can always be directly integrated:

$$\int_{F_1}^{F_2} dF = F_2 - F_1 = \Delta F$$

7. As a short cut, an infinitesimal can be integrated directly to a finite difference if the integrand is a constant. For $dG = dF + x\,dy$ with G and F state functions and x held constant:

$$\Delta G = \Delta F + x\,\Delta y$$

8. Enthalpy and internal energy are related by the definition $H \equiv U + PV$ giving differentials: $dH = dU + d(PV)$ or $dH = dU + P\,dV + V\,dP$. In general for a finite process:

$\Delta H = \Delta U + \Delta(PV)$

For a constant pressure process:

$\Delta H = \Delta U + P\Delta V$ (constant pressure)

For a constant volume system:

$\Delta H = \Delta U + V\Delta P$ (constant volume)

For a closed system for an ideal gas:

$\Delta(PV) = nR\Delta T$ (closed, ideal gas)

$\Delta H = \Delta U + nR\Delta T$ (closed, ideal gas)

For an isothermal process for an ideal gas:

$\Delta H = \Delta U$ (isothermal ideal gas)

9. The changes in internal energy and enthalpy with temperature are:

$$\left(\frac{\partial U}{\partial T}\right)_V = C_v \qquad \text{and} \qquad \left(\frac{\partial H}{\partial T}\right)_P = C_p$$

$$\left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial U}{\partial T}\right)_V \quad \text{and} \quad \left(\frac{\partial H}{\partial T}\right)_V = \left(\frac{\partial H}{\partial P}\right)_T\left(\frac{\partial P}{\partial T}\right)_V + \left(\frac{\partial H}{\partial T}\right)_P$$

10. The constant pressure and constant volume heat capacities are related by:

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

11. Since an ideal gas has no intermolecular forces, the internal pressure for an ideal gas is zero:

$$\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial H}{\partial P}\right)_T = 0 \qquad\qquad \text{(ideal gas)}$$

12. For an ideal gas, $C_p - C_v = nR$.

13. The heat capacity ratio $\gamma \equiv C_p/C_v$ is accessible through experiment. For an ideal monatomic gas $\gamma = {}^5/_3$.

14. The internal energy and enthalpy of an ideal gas depend only on temperature: $dU = C_v dT$ and $dH = C_p\,dT$ apply to <u>all processes</u> in a closed system for an ideal gas.

15. The Joule-Thomson expansion coefficient is defined as: $\mu_{JT} \equiv \left(\frac{\partial T}{\partial P}\right)_H = -\frac{1}{C_p}\left(\frac{\partial H}{\partial P}\right)_T$

16. The internal pressure, $(\partial U/\partial V)_T$, and $(\partial H/\partial P)_T$ are related by:

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

17. C_v, C_p, α, κ_T, $(\partial U/\partial V)_T$, and $(\partial H/\partial P)_T$ are the fundamental partial derivatives that characterize the system.

18. Table 9.8.1 summarizes the First Law relationships for reversible and irreversible, isothermal and adiabatic ideal gas expansions in a closed system.

19. For an isothermal expansion the work is "paid for" by an equal transfer of heat from the surroundings: $P_2V_2 = P_1V_1$.

20. For an adiabatic process the work is at the expense of the internal energy, which results in a temperature decrease: $C_v \ln T_2/T_1 = -nR \ln V_2/V_1$, $(T_2/T_1)^{C_v/nR} = V_1/V_2$, and $P_2 V_2{}^\gamma = P_1 V_1{}^\gamma$.

21. An adiabatic expansion does less work than an isothermal expansion, for a given change in volume, because the temperature decreases.

22. One of the central tenants in ecology is: organisms that use energy efficiently are more likely to survive.

23. Autotrophs use sunlight or inorganic substances as energy sources to produce the molecules necessary for cell maintenance, growth, and reproduction. Heterotrophs obtain energy by feeding on other organisms. The loss of energy to metabolic activity limits the energy that is available to higher trophic levels.

24. A strength of thermodynamics is that non-obvious interrelationships are often uncovered.

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1. N. A. Lange, J. A. Dean, *Lange's Handbook of Chemistry, 10th Ed.*, McGraw-Hill, New York, NY, 1967. p. 1524.

2. M-H E. A. Moelwyn-Hughes, *Physical Chemistry, 2nd Ed.*, Pergammon, Oxford, England, 1965. p.695.

3. E. J. Kormondy, *Concepts of Ecology 4th Ed.*, Benjamin Cummings, Englewood Cliffs, NJ, 1995. Chapter 3.

Further Reading

Mathematical Background

I. M. Klotz, R. M. Rosenberg, *Chemical Thermodynamics: Basic Theory and Methods*, Benjamin/Cummings, Menlo Park, CA, 1986. Chapts. 2-4.

Thermodynamic Problem Solving

F. C. Andrews, *Thermodynamics: Principles and Applications*, Wiley-Interscience, New York, NY, 1971. Chapt. 17.

Ecology

E. J. Kormondy, *Concepts of Ecology 4th Ed.*, Benjamin Cummings, Englewood Cliffs, NJ, 1995.

Problems

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

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

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

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

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

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

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 $(\partial H/\partial P)_T$.

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.

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

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

9. Find ΔH in terms of ΔU for a gas that obeys the virial-type equation of state:

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

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 the expansion of 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 $B = -425$ cm^3 mol^{-1} (roughly the value for water at 373 K).[1] Compare with Example 9.3.2.

10. Show that: $\left(\dfrac{\partial H}{\partial T}\right)_V = C_v + nR + \dfrac{n^2RB}{V}$

for a gas that obeys the virial-type equation of state: $PV = nRT(1 + B\frac{n}{V})$

Assume that B is a constant (the second virial coefficient is actually temperature dependent). Compare the result to 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:

$$dH = dU + P\, dV + V\, dP \tag{9.2.5}$$

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. 9.3.18.

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

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

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

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

14. For CO_2, $\mu_{JT} = 1.11$ K bar^{-1} and $C_{p,m}$ for CO_2 is 37.11 J K^{-1}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.

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 $(\partial H/\partial P)_T$.

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:

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

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

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:

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

19. Rewrite Figure 9.7.1 for the partial derivatives:

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

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 $C_{v,m} = {}^5/_2 R$, calculate q, w, ΔU, and ΔH.

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).

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, $P_2 = P_{ext}$. The initial pressure is 5.00 bar, and the temperature is 298.2 K. Assume $C_v = {}^5/_2$ nR (equipartition neglecting vibration).

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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, $C_v = 25.3$ J K^{-1} mol^{-1}.

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 $C_v = \frac{5}{2} nR$ (equipartition neglecting vibration).

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.

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 $C_v = \frac{5}{2} nR$ (equipartition neglecting vibration).

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 $C_v = \frac{5}{2} nR$ (equipartition neglecting vibration).

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, $P_2 = P_{ext}$. 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.

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.

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.

Literature Cited:
1. P. G. Kusalik, F. Liden, and I. M. Svishchev, "Calculation of the third virial coefficient for water," *J. Chem. Phys.* **1995**, *103(23)*, 10169-75.