

Chapter 7 Problems: Heat, Work

1. The movie “On Golden Pond” (IPC Films, 1982, 3 Academy Awards) was based on a play that was written about a summer home on Great Pond in central Maine. The surface area of Great Pond is $3.383 \times 10^7 \text{ m}^2$ and the volume is $2.130 \times 10^8 \text{ m}^3$. Great Pond is a large lake. The solar insolation for the Boston area is given in Chapter 2, Problem 13 as $4.16 \text{ kWh m}^{-2} \text{ day}^{-1}$. Calculate the total energy received by the lake per day on average and the corresponding change in temperature.

Answer: From Chapter 2 Problem 12 the conversion factor is given as:

$$1 \text{ kWh} = 1000 \text{ J s}^{-1}(1 \text{ hr})(3600 \text{ s/1 hr}) = 3.6 \times 10^6 \text{ J}$$

The total energy received by the lake on an average day is given by:

$$\begin{aligned} q &= JA\Delta t \\ &= 4.16 \text{ kWh m}^{-2} \text{ day}^{-1}(3.6 \times 10^6 \text{ J/1 kWh})(3.383 \times 10^7 \text{ m}^2)(1 \text{ day}) = 5.066 \times 10^{14} \text{ J} \end{aligned}$$

The molar heat capacity of water is $75.291 \text{ J K}^{-1} \text{ mol}^{-1}$, Table 7.2.2. The specific heat capacity of water is:

$$C_s(\text{H}_2\text{O}) = C_{p,m}(\text{H}_2\text{O})/\mathcal{M}_{\text{H}_2\text{O}} = 75.291 \text{ J K}^{-1} \text{ mol}^{-1} (1 \text{ mol}/18.02 \text{ g}) = 4.178 \text{ J K}^{-1} \text{ g}^{-1}$$

The density of water at 20.0°C , Table 2.2.1, is 0.9982 g mL^{-1} , giving the heat capacity of the lake as:

$$C_p = (4.178 \text{ J K}^{-1} \text{ g}^{-1})(2.130 \times 10^8 \text{ m}^3)(0.9982 \text{ g mL}^{-1})(1 \times 10^6 \text{ mL}/1 \text{ m}^3) = 8.902 \times 10^{14} \text{ J K}^{-1}$$

The corresponding change in temperature is obtained from $q_p = C_p \Delta T$:

$$\Delta T = q_p/C_p = 5.066 \times 10^{14} \text{ J}/8.902 \times 10^{14} \text{ J K}^{-1} = 0.57 \text{ K}$$

As the temperature of the lake rises, there will be significant loss of energy by radiation, convection at higher winds speeds, and evaporation. These losses will moderate the temperature rise. The predominant energy loss mechanism is radiative loss.

2. The specific heat capacity of stainless steel is $0.505 \text{ J K}^{-1} \text{ g}^{-1}$. A typical spoon weighs 20.9 g. Calculate the change in temperature when you place a spoon at 21.5°C into 250. mL of hot coffee at 58.5°C . Assume the heat capacity of coffee is $4.179 \text{ J K}^{-1} \text{ g}^{-1}$ and the density is the density of water at 50°C from Table 2.2.1.

Answer: This problem is very similar to Example 7.2.1. The plan is to use the fact that:

$q_{\text{coffee}} = -q_{\text{spoon}}$. The heat capacities are constant pressure heat capacities since the system is open to the atmosphere. The density of water at 50.0°C , Table 2.2.1, is 0.9880 g mL^{-1} .

The mass of the coffee solution is $w_{\text{coffee}} = d_{\text{H}_2\text{O}} V_{\text{coffee}} = 0.9880 \text{ g mL}^{-1} (250.0 \text{ mL}) = 247.0 \text{ g}$. The energy transferred as heat to the spoon is given by:

$$q_{\text{spoon}} = w_{\text{spoon}} C_s(\text{spoon})(T_2 - T_{1,\text{spoon}})$$

The energy transferred as heat from the coffee is:

$$q_{\text{coffee}} = w_{\text{coffee}} C_s(\text{coffee})(T_2 - T_{1,\text{coffee}})$$

Using $q_{\text{coffee}} = -q_{\text{spoon}}$ gives:

$$w_{\text{coffee}} C_s(\text{coffee})(T_2 - T_{1,\text{coffee}}) = -w_{\text{spoon}} C_s(\text{spoon})(T_2 - T_{1,\text{spoon}})$$

Solving for T_2 gives:

$$247.0 \text{ g}(4.179 \text{ J K}^{-1} \text{ g}^{-1})(T_2 - 58.5^\circ\text{C}) = -20.9 \text{ g}(0.505 \text{ J K}^{-1} \text{ g}^{-1})(T_2 - 21.5^\circ\text{C})$$

$$1032.2 T_2 - 60384. = -10.555 T_2 + 227.$$

$$1042.8 T_2 = 60611.$$

$$T_2 = 58.13^\circ\text{C}$$

The change in temperature of the coffee is only $\Delta T = -0.4^\circ\text{C}$. The result has only one significant figure since $\Delta T = 58.13^\circ\text{C} - 58.5^\circ\text{C} = -0.4^\circ\text{C}$.

3. Calculate the work done as a gas expands from an initial volume of 1.00 L to a final volume of 10.00 L against a constant external pressure of 1.000 atm.

Answer: We need to convert to pascals and m^3 to find the work in joules. The conversions are:

$$1.000 \text{ atm} = 1.01325 \times 10^5 \text{ Pa} \quad \text{and} \quad 1.00 \text{ L} = 1.00 \times 10^{-3} \text{ m}^3$$

Giving the work against a constant external pressure as:

$$w = -P_{\text{ext}} \Delta V = -(1.01325 \times 10^5 \text{ Pa})(9.00 \times 10^{-3} \text{ m}^3) = -912. \text{ J}$$

The work is negative because the system loses energy pushing against the external pressure.

4. Calculate the work done by one mole of an ideal gas in a reversible isothermal expansion from an initial volume of 1.00 L to a final volume of 10.00 L at 298.2 K. Compare the work done to the constant pressure expansion given in Problem 3.

Answer: For a reversible isothermal expansion the work is given by Eq. 7.3.6°:

$$\begin{aligned} w &= -nRT \ln\left(\frac{V_2}{V_1}\right) = -1.00 \text{ mol}(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K}) \ln\left(\frac{10.00}{1.00}\right) = -5708. \text{ J} \\ &= -5.71 \text{ kJ} \end{aligned}$$

Reversible expansions do the maximum amount of work, in magnitude, for the given initial and final states of the system. The magnitude of the work for a reversible expansion is maximal because the system pressure is equal to the external opposing pressure, $P = P_{\text{ext}}$, so the system always pushes against the maximum external pressure.

5. Calculate the work done by one mole of an ideal gas in a reversible isothermal expansion from an initial pressure of 10.00 bar to a final pressure of 1.00 bar at 298.2 K. Compare the work done to the isothermal reversible expansion in Problem 4.

Answer: For an isothermal process in an ideal gas $P_1V_1 = P_2V_2$ or:

$$\frac{V_2}{V_1} = \frac{P_1}{P_2}$$

Substitution into Eq. 7.3.6° gives:

$$\begin{aligned} w &= -nRT \ln\left(\frac{V_2}{V_1}\right) = -nRT \ln\left(\frac{P_1}{P_2}\right) \\ &= -1.00 \text{ mol}(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K}) \ln\left(\frac{10.00}{1.00}\right) = -5708. \text{ J} \\ &= -5.71 \text{ kJ} \end{aligned}$$

Comparing to Problem 4, if the volume increases by a factor of 10 for an isothermal expansion, the pressure will drop by a factor of 10. So this problem and Problem 4 are the same problem. This expansion is reversible, so the system does maximum work for the given initial and final states.

6. How ideal is water vapor? To answer this question, try the following problem: Assume a volume for a closed flask of 10.000 L, a temperature of 298.15K, and 0.01280 moles of water vapor. Calculate the pressure of water vapor in the flask using the ideal gas law and the Van der Waals equation of state and compare. (For comparison with the results of this problem, note that the vapor pressure of water at 298K is $P_{\text{vap}} = 23.8 \text{ torr}$.)

Answer: From the Van der Waals equation, Eq. 7.5.1:

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2} \quad \text{as compared to the ideal gas } P = nRT/V$$

with $a = 5.536 \text{ bar L}^2 \text{ mol}^{-2}$ and $b = 0.03049 \text{ L mol}^{-1}$, Table 7.5.1. The Van der Waals result is:

$$\begin{aligned} P &= \frac{0.01280 \text{ mol}(0.0831447 \text{ bar L K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}{10.0 \text{ L} - 0.01280 \text{ mol}(0.03049 \text{ L mol}^{-1})} - \frac{5.536 \text{ bar L}^2 \text{ mol}^{-2}(0.01280 \text{ mol})^2}{10.0^2} \\ P &= 0.031732 - 9.07 \times 10^{-6} \text{ bar} = 0.031723 \text{ bar} \\ \text{or } P &= 0.031308 \text{ atm} = 23.794 \text{ torr} \end{aligned}$$

The ideal gas result is:

$$\begin{aligned} P &= \frac{0.01280 \text{ mol}(0.0831447 \text{ bar L K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}{10.000 \times 10^{-3} \text{ m}^3} = 0.031731 \text{ bar} \\ P &= 0.031316 \text{ atm} = 23.800 \text{ torr} \end{aligned}$$

Water vapor at its equilibrium vapor pressure at room temperature is well described by the ideal gas law.

7. Find the formula for the work done in the reversible isothermal expansion of a Van der Waals gas. (i.e. derive the equation corresponding to the ideal gas result: $w = -nRT \ln(V_2/V_1)$)

Answer: For a reversible process $P = P_{\text{ext}}$ and then $w = - \int P \, dV$. From the Van der Waals equation, Eq. 7.5.1:

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

which upon substitution into the formula for the work gives:

$$\begin{aligned} w &= - \int_{V_1}^{V_2} \left(\frac{nRT}{V - nb} - \frac{an^2}{V^2} \right) dV \\ w &= - \int_{V_1}^{V_2} \left(\frac{nRT}{V - nb} \right) dV + \int_{V_1}^{V_2} \frac{an^2}{V^2} dV \\ w &= -nRT (\ln(V - nb)) \Big|_{V_1}^{V_2} - \frac{an^2}{V} \Big|_{V_1}^{V_2} \\ w &= -nRT \ln \left(\frac{V_2 - nb}{V_1 - nb} \right) - an^2 \left(\frac{1}{V_2} - \frac{1}{V_1} \right) \end{aligned}$$

Notice the effect of the second term. The Van der Waals a-coefficient is proportional to the average intermolecular forces that exist between gas molecules. For an expansion, V_2 is bigger than V_1 making $(1/V_2 - 1/V_1) < 0$. The overall sign of the second term is then positive. The resulting work done will be less than an ideal gas expansion, since the intermolecular force term is opposite in sign to the main work term. One way of thinking about this effect is that some energy goes into separating the gas molecules against their intermolecular forces, thus decreasing the work that can be done by the gas.

8. Derive the relationships between the second and third virial coefficients and the Van der Waals coefficients, as listed in Eqs. 7.5.9. Assume that the virial equation is truncated after the cubic term. [Hint: use the Taylor series approximation that for small x : $1/(1 - x) \approx 1 + x + x^2$]

Answer: The plan is to rearrange the Van der Waals equation to find z and then arrange this expression into a power series in (n/V) .

Starting with Eqs. 7.5.1 and solving for P gives:

$$P = \frac{nRT}{V - nb} - \left(a \frac{n^2}{V^2} \right)$$

Next solving for z by multiplying by (V/nRT) gives:

$$z = \frac{PV}{nRT} = \frac{V}{V - nb} - \frac{a}{RT} \left(\frac{n}{V} \right)$$

$$z = \frac{1}{\left(1 - b\left(\frac{n}{V}\right)\right)} - \frac{a}{RT}\left(\frac{n}{V}\right)$$

The last term is already in the form expected for a term in a power series expansion. However, the first term is not. Using the Taylor series approximation, $1/(1-x) \approx 1 + x + x^2$, for the first term gives:

$$z = 1 + b\left(\frac{n}{V}\right) + b^2\left(\frac{n}{V}\right)^2 - \frac{a}{RT}\left(\frac{n}{V}\right)$$

Gathering the terms in (n/V) and comparing this result to the virial expansion, Eq. 7.5.7, gives:

$$\begin{aligned} z &= 1 + \left(b - \frac{a}{RT}\right)\left(\frac{n}{V}\right) + b^2\left(\frac{n}{V}\right)^2 \\ z &= 1 + B\left(\frac{n}{V}\right) + C\left(\frac{n}{V}\right)^2 \end{aligned} \quad (7.5.7)$$

$$B = b - \frac{a}{RT} \quad \text{and} \quad C = b^2$$

At this level of approximation, we see clearly why B is a function of temperature.

9. Show that the Van der Waals equation is a cubic equation in the volume. In other words, rearrange the Van der Waals equation to give a cubic polynomial in V .

Answer: Starting with Eq. 7.5.1, multiply both sides of the equation by V^2 and then take the product of the pressure and volume terms:

$$\begin{aligned} \left(P + a\frac{n^2}{V^2}\right)(V - nb) &= nRT & 7.5.1 \\ (PV^2 + an^2)(V - nb) &= nRT V^2 \\ PV^3 + an^2V - nbPV^2 - abn^3 &= nRT V^2 \\ PV^3 - (nbP + nRT)V^2 + an^2V - abn^3 &= 0 \end{aligned}$$

Luckily, we can usually avoid having to solve this equation for V . The cubic form explains the shape of the isotherms at temperatures below the critical point in Figure 7.5.3.

10. Use the virial equation to find the compressibility factor and the pressure for 10.00 mol of O_2 contained in a 1.000 L vessel at 298.15 K. Do attractive or repulsive forces dominate?

Answer: Using the virial expansion, Eq. 7.5.7 and the coefficients from Table 7.5.4 gives:

$$z = 1 + B(T)\left(\frac{n}{V}\right) + C(T)\left(\frac{n}{V}\right)^2$$

$$\begin{aligned}
 &= 1 + (-0.0161 \text{ L mol}^{-1}) \left(\frac{10.00 \text{ mol}}{1.000 \text{ L}} \right) + (0.001200 \text{ L}^2 \text{ mol}^{-2}) \left(\frac{10.00 \text{ mol}}{1.000 \text{ L}} \right)^2 \\
 &= 1 - 0.161 + 0.1200 = 0.959
 \end{aligned}$$

Since $z < 1$, attractive forces dominate. Using $PV = z nRT$ gives:

$$P = z nRT/V = 0.959(10.00 \text{ mol})(0.08314 \text{ bar L K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})/1.000 \text{ L} = 238. \text{ bar}$$

which is a factor of $(1 - 0.959)$ or 4.1% less than the ideal value.

11. Integrate Eq. 7.6.9 for a small change in pressure during an isothermal process; that is, integrate $dV = -V \kappa_T dP$.

Answer: Integrating from V_o, P_o to V, P gives:

$$\int_{V_o}^V dV = - \int_{P_o}^P V \kappa_T dP$$

For small changes in pressure we can approximate the volume in the integrand as $V \approx V_o$. Then the factor of $(V_o \kappa_T)$ is a constant, which factor out of the integral to give:

$$V - V_o = - \int_{P_o}^P V_o \kappa_T dP = - V_o \kappa_T (P - P_o)$$

or succinctly as $\Delta V = - V_o \kappa_T \Delta P$. We can also solve for the final volume as:

$$V = V_o - V_o \kappa_T (P - P_o)$$

12. If the isothermal compressibility of acetone is $111. \times 10^{-6} \text{ atm}^{-1}$ at 14.2°C , what is the change in volume if the pressure is increased from 10.0 atm to 35.0 atm? Assume an initial volume of 1.00 L, the ΔP is small so that $V \approx V_o$, and the isothermal compressibility is constant.

Answer: From Eq. 7.6.9, for a constant temperature:

$$dV = - V \kappa_T dP$$

Assuming a small enough temperature change to give $V \approx V_o$ and a constant isothermal compressibility gives:

$$\begin{aligned}
 \Delta V &= V_o \kappa_T \Delta P \\
 &= -(1.00 \text{ L})(111. \times 10^{-6} \text{ atm}^{-1})(35.0 - 10.0 \text{ atm}) = -2.78 \times 10^{-3} \text{ L} \\
 &= -2.78 \text{ mL}
 \end{aligned}$$

13. From the definition of κ_T prove that for moderate changes in pressure:

$$V = V_o - V_o \kappa_T (P - P_o) + \frac{V_o \kappa_T^2}{2} (P - P_o)^2.$$

Answer: Integrating from V_o, P_o to V, P gives:

$$\int_{V_o}^V dV = - \int_{P_o}^P V \kappa_T dP$$

For moderate changes in pressure we can approximate the volume in the integrand using the result of Problem 11 as $V = V_o - V_o \kappa_T (P - P_o)$. The integral is then:

$$\begin{aligned} V - V_o &= - \int_{P_o}^P [V_o - V_o \kappa_T (P - P_o)] \kappa_T dP \\ &= - \int_{P_o}^P V_o \kappa_T dP + \int_{P_o}^P V_o \kappa_T^2 (P - P_o) dP \end{aligned}$$

Then the factors of $(V_o \kappa_T)$ and $(V_o \kappa_T^2)$ are constants, which factor out of the integrals to give:

$$\begin{aligned} V - V_o &= - V_o \kappa_T (P - P_o) + \frac{V_o \kappa_T^2}{2} (P - P_o)^2 \Big|_{P_o}^P \\ V - V_o &= - V_o \kappa_T (P - P_o) + \frac{V_o \kappa_T^2}{2} (P - P_o)^2 \end{aligned}$$

14. Find the relationship between $\left(\frac{\partial T}{\partial P}\right)_V$ and α and κ_T . Use the Euler chain relationship in your proof.

Answer: Noting that $\alpha \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P$ and $\kappa_T \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T$, neither derivative is taken at constant volume. The key to finding the relationship is to focus on the constant volume constraint. For a constant volume process the total differential of the volume is zero; from Eq. 7.6.7:

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP = 0 \quad 1$$

Subtracting the pressure dependent term from both sides of the equation gives:

$$\left(\frac{\partial V}{\partial T}\right)_P dT = - \left(\frac{\partial V}{\partial P}\right)_T dP \quad 2$$

We can then solve for the differential of the temperature:

$$dT = \frac{-\left(\frac{\partial V}{\partial P}\right)_T}{\left(\frac{\partial V}{\partial T}\right)_P} dP \quad 3$$

To find the partial derivative $(\partial T/\partial P)_V$ “divide” by dP and specify constant volume conditions:

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

We can relate these partial derivatives to α and κ_T by dividing the numerator and denominator of this expression by the volume:

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T}{\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P} = \frac{\kappa_T}{\alpha} \quad 5$$

The result is that the behavior of the system can be expressed as a function of only α and κ_T .

15. Calculate the expansion work done by 1.00 L of water when the temperature is raised by 100.0°C. Assume the pressure is constant at 1.00 bar. This problem is an important issue when considering upwelling in the ocean.¹ The effect is small on the laboratory scale, but important on an oceanic scale.

Answer: The plan is to use Eq. 7.6.29 and the value of the thermal expansion coefficient from Table 7.6.1. We need to be careful about units, to get joules we need to work with volume in m³ and pressures in Pa, 1 bar = 1x10⁵ Pa:

$$\begin{aligned} w &= -PV_o \alpha \Delta T = -(1.00 \times 10^5 \text{ Pa})(1.00 \text{ L})(1 \text{ m}^3/1000 \text{ L})(2.57 \times 10^{-4} \text{ K}^{-1})(100.0 \text{ K}) \\ &= -2.57 \text{ J} \end{aligned}$$

In the laboratory, we can neglect the work of expansion of liquids and solids under most circumstances.

16. The upwelling of deep-sea water is caused by large scale ocean currents such as the Atlantic current, which brings warm water north in the Atlantic. This current keeps western Europe warmer than other areas at similar latitude. As a packet of water rises, the pressure drops, the volume of the packet expands and the system does work.¹ The work is given by: $\delta w = PV\kappa_T dP$ at constant temperature. Derive this relationship.

Answer: The work is given by $\delta w = -P_{\text{ext}} dV$. A packet of water is surrounded by and is in contact with its surroundings so that $P = -P_{\text{ext}}$, where P_{ext} is the pressure at the given depth for the packet of water. The process is reversible. The change in volume with pressure at constant temperature is given by the definition of the isothermal compressibility, Eq. 7.6.9 and Eq. 7.6.10:

$$\kappa_T \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \quad \text{with } dV = V \alpha dT - V \kappa_T dP$$

For constant temperature this last equation reduces to:

$$dV = -V \kappa_T dP \quad (\text{cst. } T)$$

Substituting this last equation into the general equation for the work of the system gives:

$$\delta w = -P dV = PV\kappa_T dP \quad (\text{reversible, cst. } T)$$

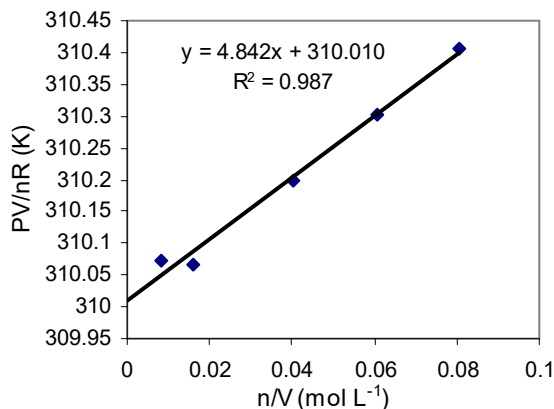
17. The empirical temperature scale is based on the ideal gas thermometer. However, how can you build an ideal gas thermometer when there is no such thing as an ideal gas? The answer is that the effective temperature based on the ideal gas law is measured for differing amounts of gas and the results are extrapolated to zero gas density. The ideal gas thermometer can then be used to calibrate more convenient thermometers. An ideal gas thermometer using helium is constructed with an internal volume for the gas of 0.500 L. The following table gives the number of moles of gas and the corresponding pressure at the fixed external temperature to be measured. Use the ideal gas law to calculate the effective temperature and then extrapolate the results to zero density.

n mol	0.040342	0.030256	0.020171	0.008068	0.004034
P (bar)	2.08225	1.56116	1.04042	0.41602	0.20797

Answer: A spreadsheet was set up to calculate the molar density of the gas and PV/nR from the measured parameters.

n	n/V	PV/nR
0.040342	0.080684	310.4108
0.030256	0.060513	310.3071
0.020171	0.040342	310.2017
0.008068	0.016137	310.0884
0.004034	0.008068	310.0306

slope	4.842429	310.0098	intercept
±	0.32278	0.015895	±
r ²	0.986846	0.019524	s(y)
F	225.0679		3 df
SS _{reg}	0.085789	0.001144	SS _{resid}



The extrapolated temperature in the ideal gas limit is 310.01 ± 0.02 K.

[Note: Vacuum lines can be easily set up to include calibrated gas burets. Then Avagadro's Law can be used to meter out the required amounts of helium for each run. Using Avagadro's law avoids using the full, accurate equation of state, which was unknown when gas thermometry was first developed. The mole amounts need not be accurate since the intercept is the desired quantity, as long as the amounts are precise and proportional.]

18. The heat transfer at constant volume is the internal energy change and the heat transfer at constant pressure is the enthalpy change. Consider a constant volume process for an ideal gas. Even though the pressure isn't constant, you can still calculate ΔH . Calculate the change in enthalpy for a constant volume process given the temperature change, ΔT or dT . Assume a constant heat capacity over the temperature range. Give your answer in differential, derivative, and integrated (ΔH) form.

Answer: From the definition of the enthalpy, $H \equiv U + PV$, the change in enthalpy can be determined from the differential: $dH = dU + d(PV)$. For an ideal gas, $PV = nRT$ and for a closed system $d(PV) = nR dT$, giving dH as:

$$dH = dU + nR dT \quad (\text{ideal gas})$$

Then at constant volume for any system $dU = C_v dT$:

$$dH = C_v dT + nR dT \quad (\text{ideal gas})$$

Integrating this expression for a constant heat capacity gives:

$$\int_{H_1}^{H_2} dH = \int_{T_1}^{T_2} C_v dT + \int_{T_1}^{T_2} nR dT \quad (\text{ideal gas})$$

$$\text{or} \quad \Delta H = C_v \Delta T + nR \Delta T \quad (\text{ideal gas})$$

Notice that since $C_p = C_v + nR$ for an ideal gas this last equation is equivalent to $\Delta H = C_p \Delta T$. Now we need to get the derivative form $(\partial H / \partial T)_v$. Once again using the definition of the enthalpy, $H \equiv U + PV$:

$$\left(\frac{\partial H}{\partial T}\right)_v = \left(\frac{\partial U}{\partial T}\right)_v + v \left(\frac{\partial P}{\partial T}\right)_v$$

The first derivative on the right is the constant volume heat capacity. For an ideal gas, $P = nRT/v$ giving:

$$\left(\frac{\partial P}{\partial T}\right)_v = \frac{nR}{v} \quad (\text{ideal gas})$$

Substitution then gives:

$$\left(\frac{\partial H}{\partial T}\right)_v = C_v + nR \quad (\text{ideal gas})$$

which is consistent with our previous results.

19. Enthalpy is a state function. The heat transfer at constant pressure is the enthalpy change, $q_p = \Delta H$. Does this equality argue that q is a state function?

Answer: No, ΔH is a state function, but q is not. The heat transferred depends on the path. In the given expression, the path is specified as a constant pressure path. Only for the specific case of a constant pressure path is $q_p = \Delta H$.

20. Determine if the following statements are true or false. If the statement is false, describe the changes that are necessary to make the statement true, if possible. If the statement is true but too restrictive, give the more general statement.²

- (a). The work done by the system on the surroundings during a change in state is never greater than the decrease in the internal energy of the system.
- (b). The enthalpy of a system cannot change during an adiabatic process.
- (c). When a system undergoes a given isothermal change in state, the enthalpy change for the system does not depend upon the path of the process involved.
- (d). When a change in state occurs, the increase in the enthalpy of the system must equal the decrease in the enthalpy of the surroundings.
- (e). The equation $\Delta U = q + w$ is applicable to any macroscopic process, provided no electrical work is performed by the system on the surroundings.
- (f). No change in state occurring in an isolated system can cause a change in the system's internal energy or enthalpy.
- (g). For any constant pressure process, the increase in enthalpy equals the heat transferred whether or not electrical or chemical work is done during the process.
- (h). A reversible process is one in which the internal energy lost by the system is just sufficient to restore the system to its original state.
- (i). When a real gas expands into a vacuum, it does work because the molecules of the gas have been separated from one another against an attractive force.

Answers: (a). The work done by the system on the surroundings during a change in state is never greater than the decrease in the internal energy of the system.

False: Solving $\Delta U = q + w$ for the work gives $w = \Delta U - q$. The work done on the surroundings is $-w = -\Delta U + q$. The work done on the surroundings can be greater than $-\Delta U$ if heat is transferred into the system ($q > 0$). In fact, the internal energy need not change at all for work to be done. The corrected statement is: "The work done by the system on the surroundings during a change in state is equal to the decrease in the internal energy of the system added to any heat transferred into the system."

- (b). The enthalpy of a system cannot change during an adiabatic process.

False: For an adiabatic process $\delta q = 0$ giving $dU = \delta w = -P_{\text{ext}} dV$ and in general P , V , and T can all change. The definition of enthalpy then gives:

$$dH = dU + d(PV) = dU + PdV + VdP = -P_{\text{ext}} dV + PdV + VdP \quad (\text{adiabatic})$$

which can be non-zero. For example, consider a system in contact with the surroundings so that $P = P_{\text{ext}}$ in a reversible adiabatic expansion. During the expansion the pressure of the system decreases and the change in enthalpy is given by Eq. 7.8.31:

$$dH = -P dV + PdV + VdP = V dP \quad (\text{reversible adiabatic})$$

Then $dH = 0$ only for a reversible, constant pressure, adiabatic process, but not in general. The correct statement is: “The enthalpy of a system cannot change during a reversible adiabatic process at constant pressure.” An example of such a process is the Joule-Thomson expansion.

(c). When a system undergoes a given isothermal change in state, the enthalpy change for the system does not depend upon the path of the process involved.

True but too restrictive: The statement is too restrictive because the process does not need to be isothermal to be path independent, since enthalpy is a state function. The correct statement is “For any given change in state, the enthalpy change is independent of the path.”

(d). When a change in state occurs, the increase in the enthalpy of the system must equal the decrease in the enthalpy of the surroundings.

False: Both internal energy and enthalpy are state functions. However, while internal energy is conserved, enthalpy is not (see Section 7.8). Consider a reversible process. The change in the enthalpy is given by Eq. 7.8.30:

$$dH = \delta q + V dP \quad (\text{reversible, PV work only}) \quad 1$$

Now consider the surroundings. Assume that the surroundings are large in extent and uniform so that the pressure of the surroundings is constant. The enthalpy change for the surroundings is given by the heat transfer at the constant pressure of the surroundings:

$$dH_{\text{surr}} = dq_{p,\text{surr}} = -\delta q \quad (\text{surroundings at cst. P, PV work only}) \quad 2$$

Comparing Eq. 1 for the system and Eq. 2 for the surroundings shows that enthalpy is not in general conserved; the increase in the enthalpy of the system is not equal to the decrease in the enthalpy of the surroundings for a general reversible process.

However, the enthalpy change of the surroundings is equal in magnitude and opposite in sign to the system enthalpy change specifically for a constant pressure process. Then $dH = \delta q_p$ for the system from Eq. 1 (or Eq. 7.8.18) and $dH_{\text{surr}} = -\delta q_p$ for the surroundings. So the corrected wording is “the increase in the enthalpy of the system is equal to the decrease in the enthalpy of the surroundings for a constant pressure process.”

(e). The equation $\Delta U = q + w$ is applicable to any macroscopic process, provided no electrical work is performed by the system on the surroundings.

True but too restrictive: The First Law, $\Delta U = q + w$, holds for any form of work. The work done in expansion and electrical work is given by:

$$\delta w = -P_{\text{ext}} dV + \phi dq_i \quad \text{giving} \quad dU = \delta q + \delta w = \delta q - P_{\text{ext}} dV + \phi dq_i$$

For another example of non-PV work, for an open system with one component i gives:

$$dU = \delta q - P_{\text{ext}} dV + \mu_i dn_i$$

The correct statement is “The equation $\Delta U = q + w$ is applicable to any macroscopic process for the system.”

(f). No change in state occurring in an isolated system can cause a change in the system’s internal energy or enthalpy.

False for the enthalpy but true for the internal energy: The statement is equivalent to the First Law in the case of the internal energy, but the enthalpy is not conserved. In general, $dH = dU + d(PV) = dU + PdV + VdP$. In an isolated system $dU = 0$ and $dV = 0$ and then:

$$dH = VdP \quad \text{or since } V \text{ is constant: } \Delta H = V\Delta P \quad (\text{isolated})$$

(See also Eq. 7.8.31) So the enthalpy is not necessarily constant for an isolated system. The point here is that the “P” in the definition of the enthalpy, $H \equiv U + PV$, is the system pressure. A process in an isolated system can cause a change in pressure. The correct statement is just “No change in state occurring in an isolated system can cause a change in the system’s internal energy.”

(g). For any constant pressure process, the increase in enthalpy equals the heat transferred whether or not electrical work is done during the process.

False: Consider a process with PV and electrical work, Eq. 7.9.7:

$$dU = \delta q + \delta w = \delta q - P_{\text{ext}} dV + \phi dq_i$$

From the definition of enthalpy, $dH = dU + d(PV)$, giving:

$$dH = \delta q - P_{\text{ext}} dV + \phi dq_i + d(PV)$$

For a constant pressure process in contact with the surroundings $P = P_{\text{ext}}$ and the last equation reduces to:

$$dH = \delta q_p - P dV + \phi dq_i + PdV = \delta q_p + \phi dq_i$$

Solving for the heat transfer at constant pressure gives:

$$\delta q_p = dH - \phi dq_i$$

The correct statement is “The heat transfer at constant pressure is the change in enthalpy minus any non-PV work.”

(h). A reversible process is one in which the internal energy lost by the system is just sufficient to restore the system to its original state.

True but too restrictive: Internal energy is a state function, so the change in internal energy is independent of the path. For a given change in state, the change in internal energy for the forward and the reverse processes are always equal in magnitude and opposite in sign. This statement is true for any process, reversible and irreversible. The correct statement is something like “For any given change in state, the internal energy lost by the system is just sufficient to restore the system to its original state.” For a reversible process, specifically, the statement is “A reversible process is one in which the work transfer by the system is just sufficient to restore the system to its original state.”

(i). When a real gas expands into a vacuum, it does work because the molecules of the gas have been separated from one another against an attractive force.

False: The work is only a function of the external pressure: $\delta w = -P_{\text{ext}} dV$. For expansion into a vacuum $P_{\text{ext}} = 0$ and no work is done. The internal energy, however, does change for a real gas expansion against a vacuum. We will calculate the change of the internal energy in Chapter 9. The correct statement is “When a real or ideal gas expands into a vacuum, no work is done, because the external pressure is zero.”

21. The Gibbs free energy is usually considered a function of the temperature and the pressure, $G(T,P)$. Write the total differential of G with respect to changes in temperature and pressure.

Answer: The independent variables for G are given as T and P . So both T and P change: giving dT and dP . The form of the differential is then:

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

Then the total differential is given as:

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

22. Write the total differential of U considered as a function of T and P as independent variables.

Answer: The independent variables for U are given as T and P . So both T and P change, and these changes are dT and dP . The form of the differential is then:

$$dU = \left(\frac{\partial}{\partial T}\right) dT + \left(\frac{\partial}{\partial P}\right) dP$$

Then the total differential is given as:

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

23. (a). Integrate Eq. 7.6.10 for a constant temperature process using the total differential. Assume a narrow pressure range so that $V \approx V_0$ and κ_T is constant. (b). Integrate Eq. 7.6.9 using the “short-cut” method discussed in the Addendum, Sec. 7.11.

Answer: (a). For a constant temperature process, Eq. 7.6.10 reduces to: $dV = -V \kappa_T dP$. See problem 12 and 13 for the integration.

(b). From the definition of κ_T , Eq. 7.6.9, multiplying both sides of the equation by $-V$ gives:

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

Multiply both sides of the equation by dP and “cancel” the ∂P and dP on the left:

$$\left(\frac{\partial V}{\partial P}\right)_T dP = -V \kappa_T dP \quad \text{or} \quad dV = -V \kappa_T dP$$

which is the same as the rigorous approach starting with the total differential.

24. Find $(\partial P/\partial T)_V$ for a Van der Waals gas in a closed system.

Answer: Rearranging the Van der Waals equation, Eq. 7.5.1, to isolate P as the dependent variable on the left side of the equation gives:

$$P = \frac{nRT}{V-nb} - \frac{an^2}{V^2}$$

Only the first term on the right is temperature dependent:

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

since n and R are constants, and V is the independent variable that is held constant for the partial derivative

25. The critical point is the point of inflection on the critical isotherm. The point of inflection corresponds to:

$$\left(\frac{\partial P}{\partial V}\right)_T = 0 \quad \text{and} \quad \left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0$$

Assume the gas is described by the Van der Waals equation of state. The two equations for the inflection point, above, provide two equations in two unknowns. Show that, in terms of the Van der Waals a and b coefficients, the critical volume, temperature, and pressure are given by:

$$V_c = 3nb \quad T_c = \frac{8a}{27bR} \quad P_c = \frac{a}{27b^2}$$

Answer: Starting from Example 7.6.1: $\left(\frac{\partial P}{\partial V}\right)_T = -\frac{nRT_c}{(V_c-nb)^2} + \frac{2an^2}{V_c^3} = 0$ 1

The second derivative is: $\left(\frac{\partial^2 P}{\partial V^2}\right)_T = \frac{2nRT_c}{(V_c-nb)^3} - \frac{6an^2}{V_c^4} = 0$ 2

To solve for V_c multiply Eq. 1 by $2/(V_c - nb)$ to give:

$$-\frac{2nRT_c}{(V_c - nb)^3} + \frac{4an^2}{V_c^3(V_c - nb)} = 0 \quad 3$$

Now add Eqs. 2 and 3:

$$2 + 3: \quad -\frac{6an^2}{V_c^4} + \frac{4an^2}{V_c^3(V_c - nb)} = 0 \quad 4$$

Dividing both sides of Eq. 4 by the common factor $2an^2/V_c^3$ gives:

$$-\frac{3}{V_c} + \frac{2}{(V_c - nb)} = 0 \quad 5$$

and solving for V_c gives : $V_c = 3nb$ 6

Substituting Eq. 6 into Eq. 1 gives:

$$-\frac{nRT_c}{(3nb - nb)^2} + \frac{2an^2}{(3nb)^3} = 0 \quad \text{or} \quad T_c = \frac{8a}{27bR} \quad 7$$

Finally, substituting Eq. 6 and 7 into the original Van der Waals equation gives:

$$P_c = \frac{nRT_c}{V_c - nb} - \frac{an^2}{V_c^2} = \frac{nR\left(\frac{8a}{27bR}\right)}{3nb - nb} - \frac{an^2}{(3nb)^2} \quad 8$$

$$P_c = \frac{a}{27b^2} \quad 9$$

26. Calculate the change in internal energy for an adiabatic expansion of a gas for a change in volume from 1.00 L to 10.00 L against a constant external pressure of 1.00 bar.

Answer: Starting with Eq. 7.8.2, for the finite process $\Delta U = q + w$. However, for an adiabatic process, $q = 0$, giving $\Delta U = w$. The work done in the expansion is $w = -P_{\text{ext}} \Delta V$:

$$w = -1.00 \times 10^5 \text{ Pa} (10.00 \text{ L} - 1.00 \text{ L})(1 \text{ m}^3/1000 \text{ L}) = -900. \text{ J}$$

which gives $\Delta U = -900. \text{ J}$

27. Calculate the internal energy and enthalpy change for a constant volume process for one mole of ideal gas with a change in temperature from 298.2 K to 323.2 K. Assume the gas is diatomic with a constant volume heat capacity of $^{5/2} nR$. Explain the relative sizes of the internal energy and the enthalpy changes.

Answer: The plan is to use $\Delta U = q_v = C_v \Delta T$, since the process is at constant volume. Then Eq. 7.8.29° can be used to calculate the enthalpy, since this system is an ideal gas.

From Eq. 7.8.10:

$$\begin{aligned}\Delta U &= C_v \Delta T = \frac{5}{2} nR \Delta T = \frac{5}{2} (1.000 \text{ mol})(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(323.2 \text{ K} - 298.2 \text{ K}) \\ &= 519.6 \text{ J}\end{aligned}$$

Using Eq. 7.8.29°:

$$\begin{aligned}\Delta H &= \Delta U + nR \Delta T = 519.6 \text{ J} + (1.00 \text{ mol})(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(25.0 \text{ K}) \\ &= 519.6 \text{ J} + 207.9 \text{ J} = 727. \text{ J}\end{aligned}$$

So even though the pressure changes in this process, the change in enthalpy can still be calculated. Now, why is the enthalpy change bigger than the internal energy change? Since the pressure of the gas increases on heating, the PV-product increases: $d(PV) > 0$. No work is done, since the volume is constant, but the PV-product does increase. Then $dH = dU + d(PV)$ for a general process and $d(PV)$ adds to dU . So the enthalpy change is bigger than the internal energy change. Notice that the difference between ΔH and ΔU is not the work done by this process, because no expansion work is done at constant volume.

28. Find the enthalpy change for a constant volume process for a change in temperature ΔT of a Van der Waals gas, starting from the internal energy change, ΔU .

Answer: The plan is to use Eq. 7.8.16 and the Van der Waals equation of state to find $\Delta(PV)$.

From the Van der Waals equation, Eq. 7.5.1:

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

The PV-product is then:

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

and for a constant volume process for a change in temperature ΔT :

$$\Delta(PV) = \left(\frac{V}{V - nb} \right) nR\Delta T \quad (\text{cst. } V)$$

Finally then from Eq. 7.8.16:

$$\Delta H = \Delta U + \left(\frac{V}{V - nb} \right) nR\Delta T \quad (\text{cst. } V)$$

You can also use Eq. 7.8.10 if the heat capacity is constant over the temperature range:

$$\Delta H = C_v \Delta T + \left(\frac{V}{V - nb} \right) nR\Delta T \quad (\text{cst. } V)$$

29. Heat capacities are often approximated by a power series: $C_{p,m} = a + b T + c T^2$. Find the change in molar enthalpy for a constant pressure process from T_1 to T_2 .

Answer: The plan is to integrate the partial derivative relationship $(\partial H/\partial T)_P = C_p$. For a constant heat capacity, $\Delta H = C_p(T_2 - T_1) = C_p\Delta T$.

The integral is:

$$\begin{aligned}\Delta H &= \int_{T_1}^{T_2} C_p \, dT = \int_{T_1}^{T_2} (a + b T + c T^2) \, dT \\ &= \int_{T_1}^{T_2} a \, dT + \int_{T_1}^{T_2} bT \, dT + \int_{T_1}^{T_2} cT^2 \, dT \\ &= a \left[T \right]_{T_1}^{T_2} + \frac{b}{2} \left[T^2 \right]_{T_1}^{T_2} + \frac{c}{3} \left[T^3 \right]_{T_1}^{T_2} \\ &= a(T_2 - T_1) + \frac{b}{2} (T_2^2 - T_1^2) + \frac{c}{3} (T_2^3 - T_1^3)\end{aligned}$$

30. Consider the surroundings as a constant temperature and pressure reservoir. Show for a reversible adiabatic expansion of a gas from P_1 to P_2 that the enthalpy change of the system is not equal in magnitude and opposite in sign to the enthalpy change of the surroundings. In other words, enthalpy is not conserved.

Answer: The plan is to note that the surroundings are at constant pressure, which gives a simple relationship for the enthalpy change of the surroundings. The enthalpy change of the system is given by Eq. 7.8.31.

Since the surroundings are at constant pressure, the enthalpy change for the surroundings is the heat transfer to the surroundings. This transfer is at constant pressure, from the perspective of the surroundings, even if the system is not at constant pressure. The heat transferred to the surroundings is then the negative of the heat transfer of the system: $\Delta H_{\text{surr}} = -\delta q$. For an adiabatic process, $\delta q = 0$ giving no change in enthalpy for the surroundings. The enthalpy change of the system for a reversible adiabatic process is given by Eq. 7.8.31: $dH = VdP$, which is non-zero. Because the enthalpy change of the system is not equal in magnitude and opposite in sign to the enthalpy change of the surroundings, enthalpy is not conserved.

31. Consider the surroundings as a constant temperature and pressure reservoir. Show for a constant pressure process that the enthalpy change of the system is equal in magnitude and opposite in sign to the enthalpy change of the surroundings.

Answer: The plan is to note that the surroundings are at constant pressure, which gives a simple relationship for the enthalpy change of the surroundings.

Since the surroundings are at constant pressure, the enthalpy change for the surroundings is the heat transfer to the surroundings. This transfer is at constant pressure, from the perspective of the

surroundings, even if the system is not at constant pressure. The heat transferred to the surroundings is then the negative of the heat transfer of the system: $\Delta H_{\text{surr}} = -\dot{q}$.

The process is at constant pressure for the system, giving $\Delta H = \dot{q} = \dot{q}_p$. As a consequence, $\Delta H = -\Delta H_{\text{surr}}$ for the special case of a constant pressure process, for the system. Note that the pressure of the system and the pressure of the surroundings do not necessarily need to be the same. For example, a gas can be confined in a cylinder with a weight on the piston, giving $P > P_{\text{surr}}$. However, if the system is held at constant pressure by contact with the surroundings, then $\Delta H = -\Delta H_{\text{surr}}$ is guaranteed since $P = P_{\text{surr}}$. This holds for example, for a solution in a beaker at ambient pressure.

For a constant pressure process, enthalpy is conserved. However, enthalpy is not conserved in general (see the previous problem for an example).

Literature Cited:

1. T. J. McDougall, R. Feistel, "What causes the adiabatic lapse rate?" *Deep-Sea Research I*, **2003**, *50*, 1523-1535.
2. J. Waser, K. N. Trueblood, C. M. Knobler, *Chem One, 2nd.Ed.*, McGraw Hill, New York, NY, 1980. pp. 414-415.