

Chapter 1 Problems

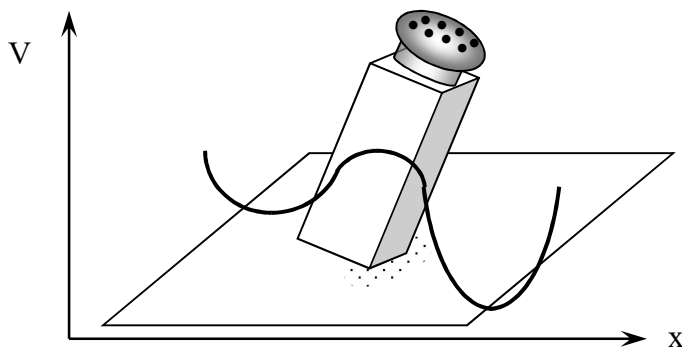
1. Consider a bowl of sugar. Sugars are our primary source of energy, so the oxidation of sucrose in our body must be thermodynamically favorable. How can a bowl of sugar exist in the open atmosphere for very long times?

Answer: A bowl of sugar is an example of meta-stable system. The oxidation of sucrose at room temperature is kinetically hindered. The addition of a catalyst or an ignition spark greatly accelerates this process. The oxidation of sucrose is thermodynamically favorable but kinetically unfavorable.

2. Consider a salt shaker balanced on one edge, Figure P.1. This state is often possible if a few salt grains are sprinkled on the table. Characterize the state of the system with respect to change in position. If the system is not at equilibrium, state the equilibrium position. Describe any spontaneous processes that might occur if the salt grains were gently blown away.

Answer: This system is meta-stable. With a small perturbation, in other words a small push, the shaker would flop over. The normal vertical position of the shaker is also meta-stable; the vertical position is a local minimum. The overall global equilibrium is with the salt shaker on its side, flat against the table. After the salt grains are gently blown away, the system is unstable and falls to equilibrium.

A plot of the potential energy of the system as a function of the x position of the center of mass is shown below.



3. Our bodies, at rest, can be considered as being in a steady state. Describe the incoming flows that keep us away from equilibrium. What are the outgoing flows? What is the equilibrium state for our bodies?

Answer: Living systems in general need an energy source, a source of electrons, and a source of carbon. The electrons are available from redox reactions involving good reducing agents, which

as you might remember from your Organic course include compounds rich in hydrogen. In other words, we need food as a source of carbon and electrons, and O_2 in combination with food as a source of energy. Of course, humans also need sources of N, P, S, Na^+ , K^+ , Ca^{2+} , Fe^{3+} , and other trace elements, which we obtain from food. The outgoing flows are heat, water vapor from perspiration, water loss through breathing, CO_2 , feces, and urine as waste products.

4. Are spontaneous processes always irreversible? Explain.

Answer: Yes: Returning a spontaneous process to its initial state requires energy input from the surroundings in the form of heat and work that is different from the heat and work for the forward process. The reverse of a spontaneous process is not the exact reverse of the change for the original forward process. The forward spontaneous process is irreversible. Equilibrium processes are reversible (always). The only way for a process to be reversible is for the system to be at equilibrium.

5. (a). In what way is a steady state and an equilibrium system similar? (b). In what ways are a steady state and an equilibrium system different?

Answer: (a). Steady state and equilibrium systems are time invariant. In other words, the concentrations of the various chemical species are constant. (b). They are different in that a steady state process requires the continual input of energy or matter to remain at steady state. For a system at equilibrium, all heat and work transfers are zero. For steady state systems, heat and work transfers per unit time are constant and may be non-zero. Heat is evolved at a constant rate for a steady-state process. For a steady state system, the forward processes are not the exact reverse of all the reverse processes. For an equilibrium system, the forward rates are equal and opposite to all the reverse rates.

6. Determine if the following processes are spontaneous, non-spontaneous, or reversible.

- 1 J of heat is transferred from a hot cup of coffee to the table top.
- Sugar is added to a cup of coffee and the sugar dissolves.
- Water decomposes into H_2 and O_2 from a cup of coffee.
- A small amount of ice melts in a cup of iced coffee at $0^\circ C$.
- A small amount of ice melts in a cup of coffee at $5^\circ C$.
- A small amount of water freezes in a cup of iced coffee at $0^\circ C$.
- A small amount of water freezes in a cup of coffee that is placed outdoors at $-10^\circ C$.
- Too much sugar is added to a cup of coffee producing a super-saturated solution. After bumping the cup on the table, some of the sugar crystallizes out of solution.

Answers: (a). 1 J of heat is transferred from a hot cup of coffee to the table top: spontaneous.

(b). Sugar is added to a cup of coffee and the sugar dissolves: spontaneous.

(c). Water decomposes into H_2 and O_2 from a cup of coffee: non-spontaneous.
Rather, $H_2 + \frac{1}{2} O_2 \rightarrow H_2O (l)$ is the spontaneous direction; the reverse of a spontaneous process is non-spontaneous.

(d). A small amount of ice melts in a cup of iced coffee at $0^\circ C$: reversible.
Any amount of ice and water can coexist, without any further changes at $0^\circ C$. Starting with an initial amount of ice at $0^\circ C$, the system begins at equilibrium. Then, if a small amount of ice melts, the final system is also at equilibrium. A reversible process occurs through a sequence of equilibrium states.

(e). A small amount of ice melts in a cup of coffee at $5^\circ C$: spontaneous.
The melting of ice is reversible only at $0^\circ C$, the normal melting point.

(f). A small amount of water freezes in a cup of iced coffee at $0^\circ C$: reversible.
As in part (d), any amount of ice and water can coexist at the normal melting point, so the system remains at equilibrium and can be reversed by melting a small amount of ice, without any change in the surroundings for the overall forward and reverse process.

(g). A small amount of water freezes in a cup of coffee that is placed outdoors at $-10^\circ C$: spontaneous.
This process is spontaneous in the same way as making ice in a freezer is spontaneous (otherwise ice would not exist; the formation of ice must be spontaneous under some circumstances).

(h). Too much sugar is added to a cup of coffee producing a super-saturated solution. After bumping the cup on the table, some of the sugar crystallizes out of solution: spontaneous.
A super-saturated solution is a meta-stable system with a kinetic bottleneck. Bumping provides a bubble or a fresh surface that acts as a nucleation center for sugar crystal formation. The sugar concentration in a super-saturated solution exceeds the amount the solution can hold at equilibrium, at the given temperature.

7. Prove that if the reverse of a spontaneous process is also spontaneous, it is possible to construct a perpetual motion machine.^{1,2}

Answer: A cyclic process is a process that begins and ends at the same state of the system. Consider a cyclic process that is made from the combined forward process and the reverse process, so that the system remains unchanged. Since the forward process is spontaneous and the reverse process is spontaneous, the cyclic process is overall spontaneous. The system is unchanged by the cyclic process, which can then reoccur, again spontaneously. The net result is that the cyclic process can reoccur an infinite number of times, which is an example of perpetual motion. Perpetual motion has never been observed, and because of our experience, we never expect perpetual motion to occur.

In proving a statement we often assume the converse and work through the ramifications until we come to an impossibility. Having reached an impossible condition we must conclude the original assumption was wrong. In this problem we show that the forward and reverse processes cannot both be spontaneous. We therefore conclude: the reverse of a spontaneous process is non-spontaneous.

8. Calculate the molar density, in mol m^{-3} , and the mass density, in kg m^{-3} and g L^{-1} , for an ideal gas at standard pressure, $P^\circ = 1.00 \text{ bar}$, and 298.15 K . Assume the gas is air with an effective molar mass given by Eq. 1.3.17.

Answer: $P^\circ = 1.00 \text{ bar} = 1.00 \times 10^5 \text{ Pa}$. The molar density is:

$$\frac{n}{V} = \frac{P}{RT} = \frac{1.000 \times 10^5 \text{ Pa}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} (298.15 \text{ K})} = 40.3 \text{ mol m}^{-3}$$

and in mol L^{-1}

$$\frac{n}{V} = 40.3 \text{ mol m}^{-3} (1 \text{ m}^3/1000 \text{ L}) = 0.0403 \text{ mol L}^{-1}$$

The mass density can be calculated from the molar density by

$$d = \frac{\mathcal{M} n}{V} = \frac{\mathcal{M} P}{RT} = 28.8 \times 10^{-3} \text{ kg mol}^{-1} (40.3 \text{ mol m}^{-3}) = 1.16 \text{ kg m}^{-3}$$

or $d = 28.8 \text{ g mol}^{-1} (0.0403 \text{ mol L}^{-1}) = 1.16 \text{ g L}^{-1}$

Alternatively, directly using $R = 0.082058 \text{ L atm K}^{-1} \text{ mol}^{-1}$ and $1 \text{ bar} = 0.9869 \text{ atm}$:

$$d = \frac{\mathcal{M} n}{V} = \frac{\mathcal{M} P}{RT} = \frac{28.8 \times 10 \text{ g mol}^{-1} (0.9869 \text{ atm})}{0.082058 \text{ L atm K}^{-1} \text{ mol}^{-1} (298.15 \text{ K})} = 1.16 \text{ g L}^{-1}$$

9. Calculate the number of moles of an ideal gas in a volume of 1.000 L for a pressure of 1.000 bar and a temperature of 298.15 K . Do this problem using three different sets of units and the corresponding value for R : (a) using L atm , (b) using Pa m^3 , and (c) using L bar .

Answer: Note that $1 \text{ bar} = 0.9869 \text{ atm}$, $1 \text{ bar} = 1.00 \times 10^5 \text{ Pa}$, $1 \text{ m}^3 = 1000 \text{ L}$.

(a) using L atm ,

$$n = \frac{PV}{RT} = \frac{0.9869 \text{ atm} (1.000 \text{ L})}{0.082058 \text{ L atm K}^{-1} \text{ mol}^{-1} (298.15 \text{ K})} = 0.04034 \text{ mol}$$

(b) using Pa m^3 :

$$n = \frac{PV}{RT} = \frac{1.000 \times 10^5 \text{ Pa} (1.000 \times 10^{-3} \text{ m}^3)}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1} (298.15 \text{ K})} = 0.04034 \text{ mol}$$

(c) using L bar :

$$n = \frac{PV}{RT} = \frac{1.000 \text{ bar} (1.000 \text{ L})}{0.083145 \text{ L bar K}^{-1} \text{ mol}^{-1} (298.15 \text{ K})} = 0.04034 \text{ mol}$$

10. The density of a mixture of H_2 and O_2 is 0.982 g L^{-1} at 298.2 K and 1.00 bar pressure. Calculate the mole fraction of H_2 in the mixture.

Answer: The plan is to calculate the effective molar mass of the sample, using Eq. 1.3.9°, and then use the weighted average to calculate the original composition, as was done in Eq. 1.3.17.

Convenient units for this problem are L and bar , with $R = 0.083145 \text{ L bar K}^{-1} \text{ mol}^{-1}$. The effective molar mass is given from the mass density as:

$$d = \frac{\mathcal{M}P}{RT}$$

$$0.982 \text{ g L}^{-1} = \frac{\mathcal{M}(1.00 \text{ bar})}{0.083145 \text{ L bar K}^{-1} \text{ mol}^{-1}(298.15 \text{ K})} \quad \text{or} \quad \mathcal{M} = 24.34 \text{ g mol}^{-1}$$

The effective molar mass is the weighted average of the pure molar masses, as in Eq. 1.3.17:

$$\mathcal{M} = x(2.02 \text{ g mol}^{-1}) + (1 - x)32.00 \text{ g mol}^{-1} = 24.34 \text{ g mol}^{-1}$$

Solving for x gives $x = 0.2555$ or 25.5%. We will show in the next chapter that volume and mole fractions are equivalent.

11. Two containers, which are separated by a stopcock, are held in a constant temperature bath at 298.2 K, Figure P10.1. The first container has a volume of 24.80 L and the second 12.39 L. The two containers are filled with 2.00 mol and 1.00 mol of ideal gas, respectively. Calculate the initial pressures. After the stopcock is opened, calculate the final volume and pressure. Of P , V , and n , in this experiment, which are intensive and which are extensive?

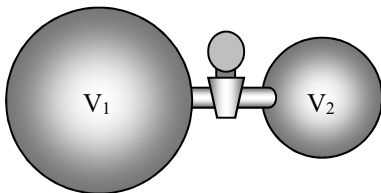


Figure P10.1: Two closed containers are opened to form a combined system.

Answer: The initial pressures are calculated using the ideal gas law in each separate volume:

$$P_1 = n_1RT/V_1 = 2.00 \text{ mol}(0.083145 \text{ bar L K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})/24.80 \text{ L} = 2.00 \text{ bar}$$

$$P_2 = n_2RT/V_2 = 1.00 \text{ mol}(0.083145 \text{ bar L K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})/12.39 \text{ L} = 2.00 \text{ bar}$$

After the stopcock is opened, the total volume is $V_{\text{tot}} = V_1 + V_2 = 37.19 \text{ L}$ and total moles of gas is $n_{\text{tot}} = n_1 + n_2 = 3.00 \text{ mol}$. The final pressure is:

$$P_{\text{tot}} = n_{\text{tot}}RT/V_{\text{tot}} = 3.00 \text{ mol}(0.083145 \text{ bar L K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})/37.19 \text{ L} = 2.00 \text{ bar}$$

The mole amount and volume add, so they are extensive. The pressure remains the same and is intensive. Repeating a similar problem with constant pressures shows that the temperature is the same before and after, so the temperature is also intensive.

12. Classify the following variables as intensive or extensive:

- molar concentration of a solution.
- molar density.
- density (mass density).
- surface area of an interface between two dissimilar phases. The air-water, olive oil-water, and olive oil-glass interfaces are three examples. The interface can be the planar interface between two bulk samples or the surface of a spherical droplet.

- (e). surface tension, which is defined as the change in surface energy of an interface divided by the change in surface area: $\gamma = dU/d\sigma$.
- (f). temperature.
- (g). coefficient of thermal expansion at constant pressure, which is defined as:

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

where $(\partial V/\partial T)_P$ is the rate of change of the volume of a sample with temperature, while holding the pressure constant.

Answers: The ratio of any two extensive properties of a system is intensive.

- (a). molar concentration = n/V , which is the ratio of two extensive quantities: intensive. The concentration of a drop or a bucket full of solution is the same.
- (b). molar density = n/V , which is the ratio of two extensive quantities of the system: intensive
- (c). density = $d = w/V$, where w is the mass of the system. The density is the ratio of two extensive quantities of the system: intensive
- (d). surface area depends on the size of an interface or a droplet: extensive
- (e). surface tension = $\gamma = dU/d\sigma$, where dU is the change in surface energy and $d\sigma$ is the change in surface area. Surface tension is the ratio of two extensive quantities: intensive
- (f). temperature is independent of the size of the system: intensive. Combining 50 mL of water at 25°C with another 50 mL of water at 25°C gives 100 mL of water at 25°C
- (g) coefficient of thermal expansion, $\alpha = (1/V)(\partial V/\partial T)_P$. $(\partial V/\partial T)_P$ is the ratio of the change in volume, which is extensive, to the change in temperature which is intensive, giving the derivative as extensive. The coefficient of thermal expansion is the ratio of $(\partial V/\partial T)_P$, which is extensive, to the total volume, which is also extensive, giving an overall intensive property. The coefficient of thermal expansion is a primary property of a substance. The coefficient of thermal expansion for a drop and a gallon of water is the same.

13. Calculate the pressure inside your mouth that would be necessary to drink a soft drink through a straw of length 20.0 cm. Assume the drink has the density of water at 20.0°C, 0.9982 g mL⁻¹ and the atmospheric pressure is 1.000 bar.

Answer: This problem is just like a closed end manometer, with your mouth acting as the volume in the closed end. Then $P_{\text{ext}} = P_{\text{in}} + P_{\text{liq}}$ and $P_{\text{liq}} = dgh$. The density of water at 20.0°C is needed in kg m⁻³ to match the units of g :

$$d = 0.9982 \text{ g mL}^{-1} (1 \text{ kg}/1000 \text{ g})(1 \times 10^3 \text{ mL}/1 \text{ L})(1000 \text{ L}/1 \text{ m}^3) = 998.2 \text{ kg m}^{-3}$$

Then $P_{\text{liq}} = dgh = 998.2 \text{ kg m}^{-3} (9.807 \text{ m s}^{-2})(0.200 \text{ m}) = 1958 \text{ Pa}$

Solving $P_{\text{ext}} = P_{\text{in}} + P_{\text{liq}}$ for P_{in} gives:

$$P_{\text{in}} = P_{\text{ext}} - P_{\text{liq}} = 1.00 \times 10^5 \text{ Pa} - 1958 \text{ Pa} = 98042 \text{ Pa} = 0.980 \text{ bar}$$

If you would like to see the pressure in torr:

$$P_{\text{in}} = 0.980 \text{ bar} (1 \text{ atm}/1.01325 \text{ bar})(760 \text{ torr}/1 \text{ atm}) = 735. \text{ torr}$$

So, by decreasing the pressure in your mouth, the atmosphere pushes the water up the straw.

14. Calculate the height of a column of water at 20.0°C in a closed end manometer for an atmospheric pressure of 1.000 bar. Assume the liquid has a constant density. The density of water at 20°C is 0.9982 g mL⁻¹. The vapor pressure of water at 20.0°C is 2.338 kPa.

Answer: For a closed end manometer, $P_{\text{ext}} = P_{\text{in}} + P_{\text{liq}}$ with $P_{\text{liq}} = dgh$ and P_{in} given by the vapor pressure of the liquid in the manometer, 2.338 kPa. Solving for P_{liq} :

$$P_{\text{liq}} = P_{\text{ext}} - P_{\text{in}} = 1.000 \times 10^5 \text{ Pa} - 2338 \text{ Pa} = 97662 \text{ Pa}$$

The density of water at 20.0°C is needed in kg m⁻³ to match the units of g:

$$d = 0.9982 \text{ g mL}^{-1} (1 \text{ kg}/1000 \text{ g})(1 \times 10^3 \text{ mL}/1 \text{ L})(1000 \text{ L}/1 \text{ m}^3) = 998.2 \text{ kg m}^{-3}$$

Then $P_{\text{liq}} = 97662 \text{ Pa} = dgh = 998.2 \text{ kg m}^{-3} (9.807 \text{ m s}^{-2}) h$

Solving for $h = 9.976 \text{ m}$

In English units for comparison:

$$h = 9.976 \text{ m} (100 \text{ cm}/1 \text{ m})(1 \text{ in}/2.540 \text{ cm})(1 \text{ ft}/12 \text{ in}) = 32.7 \text{ ft}$$

15. Long's Peak in the Colorado Rocky Mountains is 3962. m high. What is the predicted pressure on the top of Long's Peak? Assume a constant temperature of 20.0°C. Compare the molar density on top of Long's Peak with the molar density of air at sea level.

Answer: Assuming the atmospheric pressure at sea level is 1 atm and the mole fraction averaged molar mass of air is 28.8 g mol⁻¹ gives the barometric formula as:

$$\left(\frac{-\mathcal{M}_{\text{gas}} g h}{RT} \right) = \frac{-28.8 \times 10^{-3} \text{ kg}(9.807 \text{ m s}^{-2})(3962. \text{ m})}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1}(293.15 \text{ K})} = -0.4591$$

$$P = P_o e^{\left(\frac{-\mathcal{M}_{\text{gas}} g h}{RT} \right)} = 1.00 \text{ atm } e^{-0.4591} = 0.632 \text{ atm}$$

The molar density at sea level assuming 1 atm = 1.01325x10⁵ Pa and at 293.15 K, is:

$$\frac{n}{V} = \frac{P}{RT} = \frac{1.01325 \times 10^5 \text{ Pa}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}(293.15 \text{ K})} = 41.6 \text{ mol m}^{-3}$$

The molar density at the top of the mountain is based on $P = 0.632 \text{ atm}(1.01325 \times 10^5 \text{ Pa}/1 \text{ atm}) = 6.404 \times 10^4 \text{ Pa}$:

$$\frac{n}{V} = \frac{P}{RT} = \frac{6.404 \times 10^4 \text{ Pa}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}(293.15 \text{ K})} = 26.3 \text{ mol m}^{-3}$$

which is why hiking at high altitude is so difficult.

16. Calculate the altitude in the atmosphere that corresponds to a pressure of 0.500 bar if the surface pressure is 1.000 bar. Assume the temperature is constant at 18°C.

Answer: Use Eq. 1.3.15°:

$$\ln \frac{P}{P_o} = - \frac{\mathcal{M}_{\text{gas}} g h}{RT}$$

$$\ln(0.500/1.00) = -\frac{28.8 \times 10^{-3} \text{ kg} (9.807 \text{ m s}^{-2}) h}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} (291.2 \text{ K})} = -1.1667 \times 10^{-4} h$$

$$h = -0.6931 / -1.1667 \times 10^{-4} = 5941 \text{ m} = 5.94 \times 10^3 \text{ m}$$

17. For liquids with moderate changes in pressure, the density is given by:

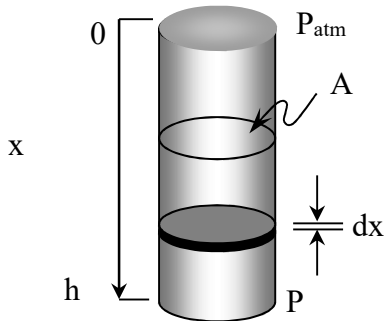
$$d = d_o [1 + \kappa_T (P - P_o)]$$

where κ_T is the isothermal compressibility, d_o is the density of the liquid at the surface pressure P_o and d is the density at final pressure P . (a). Show that the formula for the pressure as a function of depth is given by:

$$\frac{1}{\kappa} \ln(1 + \kappa_T (P - P_o)) = d_o g h$$

(b). Calculate the pressure in the Mariana Trench at a depth of 10911 m (35798 ft) given $\kappa_T = 4.587 \times 10^{-10} \text{ Pa}^{-1}$ at 20°C . Use the density of pure water, 0.9982 g mL^{-1} at 1 bar, for this problem, instead of the density of sea water. Assume the surface pressure is 1.000 bar.

Answer: The depth below the surface is x . The surface corresponds to the depth $x = 0$. The change in pressure for a thin disk of water is given by $dP = df/A = d g dx$. The differential has a positive sign since as x increases the column of water above your head increases and the pressure increases.



Substituting the density as a function of pressure gives:

$$dP = [1 + \kappa_T (P - P_o)] d_o g dx$$

Separating variables gives:

$$\frac{dP}{[1 + \kappa_T (P - P_o)]} = d_o g dx$$

Integrating gives:

$$\int_{P_o}^P \frac{dP}{[1 + \kappa_T (P - P_o)]} = \int_0^h d_o g dx$$

The general form of the left-hand integral is $\int \frac{1}{1+ax} dx = \frac{1}{a} \ln(1+ax)$. Which gives:

$$\int_{P_0}^P \frac{dP}{[1 + \kappa_T (P - P_0)]} = \frac{1}{\kappa} \left(\ln(1 + \kappa_T (P - P_0)) \right) \Big|_{P_0}^P = \frac{1}{\kappa_T} \ln(1 + \kappa_T (P - P_0))$$

The final result is then:

$$\frac{1}{\kappa_T} \ln(1 + \kappa_T (P - P_0)) = d_0 g h$$

We can solve for P by rearranging in the following steps:

$$\ln(1 + \kappa_T (P - P_0)) = \kappa_T d_0 g h$$

$$1 + \kappa_T (P - P_0) = e^{\kappa_T d_0 g h}$$

$$(P - P_0) = \frac{1}{\kappa} \left(e^{\kappa_T d_0 g h} - 1 \right)$$

With $h = 10911. \text{ m}$, $d_0 = 998.2 \text{ kg m}^{-3}$, and $\kappa_T = 4.587 \times 10^{-10} \text{ Pa}^{-1}$:

$$\kappa_T d_0 g h = (4.587 \times 10^{-10} \text{ Pa}^{-1})(998.2 \text{ kg m}^{-3})(9.8067 \text{ m s}^{-2})(10911. \text{ m}) = 4.8993 \times 10^{-2}$$

Notice that the units are $1 \text{ Pa} = 1 \text{ N m}^{-2} = 1 \text{ kg m}^{-1} \text{ s}^{-2}$

and then $\left(e^{\kappa_T d_0 g h} - 1 \right) = 5.0213 \times 10^{-2}$ giving:

$$(P - P_0) = \frac{1}{\kappa} \left(e^{\kappa_T d_0 g h} - 1 \right) = \frac{5.0213 \times 10^{-2}}{4.587 \times 10^{-10} \text{ Pa}^{-1}} = 1094.7 \times 10^5 \text{ Pa}$$

and the total pressure at depth is $1095.7 \times 10^5 \text{ Pa}$ or $1.096 \times 10^3 \text{ bar}$.

What would we have gotten if we had assumed an incompressible fluid with $P_{\text{liq}} = dgh$:

$$P_{\text{liq}} = 1068.1 \times 10^5 \quad \text{or a total pressure of } 1069.1 \times 10^5 \text{ Pa}$$

or 2.4% less. So the density of water can be considered as a constant for all but extreme conditions.

18. (a). Find the derivative of the atmospheric pressure with respect to altitude from the barometric formula, Eq. 1.3.16°. (b). Show that this derivative satisfies the original differential equation, Eq. 1.3.10°.

Answer: (a). The barometric formula at height x is: $P = P_0 e^{\left(\frac{-\mathcal{N}_{\text{gas}} g x}{RT} \right)}$

The general form of the derivative using the chain rule is: $\frac{de^{-cx}}{dx} = (-c) e^{-cx}$

The derivative is: $\frac{dP}{dx} = \left(\frac{-\mathcal{M}_{\text{gas}} g}{RT}\right) P_0 e^{\left(\frac{-\mathcal{M}_{\text{gas}} g x}{RT}\right)} = \left(\frac{-\mathcal{M}_{\text{gas}} g}{RT}\right) P$

(b). The original differential equation, Eq. Eq. 1.3.10°, rearranges to give: $\frac{dP}{dx} = \left(\frac{-\mathcal{M}_{\text{gas}} g}{RT}\right) P$ which shows that the barometric formula is the proper solution to the differential equation.

19. Chemical kinetic equations are good examples of first-order homogeneous differential equations with a constant coefficient. The rate of change of the concentration of a substance A with time in a first-order chemical reaction is given as:

$$\frac{d[A]}{dt} = -k [A]$$

where k is the rate constant. (a). Show that this expression is a first-order homogeneous differential equation with a constant coefficient. (b). Integrate the equation from an initial concentration of $[A]_0$ at time $t = 0$ to a final concentration of $[A]$ at time t .

Answer: (a). Multiplying both sides of the rate expression by dt gives:

$$d[A] = -k [A] dt$$

Comparison with Eq. 1.3.18 shows that this expression is a first-order homogeneous differential equation with a constant coefficient, where f is replaced by $[A]$ and the constant coefficient is the rate constant, k .

(b). Dividing both sides of the equation by $[A]$ to separate the variables gives:

$$\frac{d[A]}{[A]} = -k dt$$

Now the terms involving the concentration are on the left of the equal sign, and the terms involving time are on the right. The limits for the integration are at $t = 0$ the initial concentration of A is $[A]_0$ and at time t the concentration of A is given as $[A]$:

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = - \int_0^t k dt$$

$$\ln [A] \Big|_{[A]_0}^{[A]} = -k t \Big|_0^t$$

$$\ln [A] - \ln [A]_0 = -k t$$

The difference in the logs is the log of the ratio, $\ln x - \ln y = \ln(x/y)$:

$$\ln\left(\frac{[A]}{[A]_0}\right) = -k t$$

Solving for $[A]$:

$$[A] = [A]_0 e^{-kt}$$

20. Do the Taylor expansion for $\sqrt{1-x}$ for $x \approx 0$, keeping terms up to x^2 .

Answer: We need the first and second derivatives:

$$\frac{d(1-x)^{1/2}}{dx} = \frac{-(1-x)^{-1/2}}{2} = \frac{-1}{2(1-x)^{1/2}} = \frac{-1}{2(1-x)^{1/2}}$$

$$\frac{d^2(1-x)^{1/2}}{dx^2} = \frac{d\left(\frac{-1}{2(1-x)^{1/2}}\right)}{dx} = \frac{-1}{4(1-x)^{3/2}}$$

Evaluating at $x = x_0 = 0$

$$(1-x)^{1/2}\Big|_{x=0} = 1$$

$$\left(\frac{d(1-x)^{1/2}}{dx}\right)\Big|_{x=0} = \frac{-1}{2(1-0)^{1/2}} = \frac{-1}{2}$$

$$\left(\frac{d^2(1-x)^{1/2}}{dx^2}\right)\Big|_{x=0} = \frac{-1}{4(1-0)^{3/2}} = \frac{-1}{4}$$

Substituting into the Taylor series gives:

$$f \approx f(x_0) + \left(\frac{df}{dx}\right)_{x=x_0} (x - x_0) + \left(\frac{d^2f}{dx^2}\right)_{x=x_0} \frac{(x - x_0)^2}{2} = 1 - \frac{1}{2}(x) - \frac{1}{4}\left(\frac{x^2}{2}\right)$$

Giving the same result as Table 1.4.2:

$$\sqrt{1-x} \approx 1 - \frac{x}{2} - \frac{x^2}{8}$$

21. Using a Taylor series expansion, what is the linear approximation for $\ln(f_2/f_1)$ for $f_2 \approx f_1$.

Answer: From Table 1.4.2: $\ln x \approx (x - 1)$ for $x \approx 1$

Substitute $x = f_2/f_1$ giving:

$$\ln \frac{f_2}{f_1} \approx \left(\frac{f_2}{f_1} - 1\right)$$

Now we should derive $\ln x \approx (x - 1)$. The function at $x = x_0 = 1$ is:

$$(\ln x)_{x=1} = 0$$

The derivative evaluated at $x = x_0 = 1$:

$$\left(\frac{d \ln x}{dx}\right)_{x=1} = \left(\frac{1}{x}\right)_{x=1} = 1$$

Substituting into the Taylor series:

$$f \approx f(x_0) + \left(\frac{df}{dx}\right)_{x=x_0} (x - x_0) = 0 + (1)(x - 1) = (x - 1)$$

22. Determine the number of terms in the Taylor series expansion of $\ln(1 - x)$ that are necessary for 1% and 0.1% accuracy, if $x = 0.100$.

Answer: First, note that the exact value is $\ln(1 - 0.100) = -0.10536$. Using Example 1.5.6, keeping the first two terms gives a 5% error. We need to generate the next few terms in the Taylor expansion. From Example 1.5.6:

$$\ln(1 - x)|_{x=0} = 0$$

$$\frac{d \ln(1 - x)}{dx} = -\frac{1}{(1 - x)} \Big|_{x=0} = -1$$

$$\frac{d^2 \ln(1 - x)}{dx^2} = \frac{d}{dx} \frac{-1}{(1 - x)} = -\frac{1}{(1 - x)^2} \Big|_{x=0} = -1$$

$$\frac{d^3 \ln(1 - x)}{dx^3} = \frac{d}{dx} \frac{-1}{(1 - x)^2} = -\frac{2}{(1 - x)^3} \Big|_{x=0} = -2$$

$$f \cong f(x_0) + \left(\frac{df}{dx}\right)_{x=x_0} (x - x_0) + \left(\frac{d^2f}{dx^2}\right)_{x=x_0} \frac{(x - x_0)^2}{2} + \left(\frac{d^3f}{dx^3}\right)_{x=x_0} \frac{(x - x_0)^3}{3!}$$

$$\ln(1 - x) \cong (0) - 1x - \frac{x^2}{2!} - \frac{2x^3}{3!} - \frac{3x^4}{4!} = -x - \frac{x^2}{2} - \frac{2x^3}{6} - \frac{3x^4}{24} = -x - \frac{x^2}{2} - \frac{x^3}{3} - \frac{x^4}{8}$$

$$\ln(1 - 0.1) \cong -0.1$$

$$\cong -0.1 - 0.05 = -0.105$$

$$\cong -0.1 - 0.05 - 0.0033 = -0.10533$$

with 5 % error for two terms

with 0.34 % error for three terms

with 0.03 % error for four terms

Three terms, including the first zero term, are sufficient for 1% accuracy. Four terms are needed for 0.1 % accuracy. The approximation $\ln(1 - x) \cong -x$ is appropriate only for $x < 0.022$, for 1% error.

23. Calculate the derivative of $h(x) = e^{-cx}/(1 - e^{-cx})$, with respect to x for c equal to a constant.

Answer: Using the product rule with $f = e^{-cx}$ and $g = 1/(1 - e^{-cx})$:

$$\frac{d(fg)}{dx} = f \frac{dg}{dx} + g \frac{df}{dx} = e^{-cx} \frac{d(1/(1 - e^{-cx}))}{dx} + \frac{1}{(1 - e^{-cx})} \frac{d e^{-cx}}{dx}$$

Using the chain rule:

$$\frac{d e^{-cx}}{dx} = -c e^{-cx}$$

and (see Eq. 1.4.7-9):

$$\frac{d(1/(1-e^{-cx}))}{dx} = \frac{-1}{(1-e^{-cx})^2} (-(-c) e^{-cx}) = \frac{-c e^{-cx}}{(1-e^{-cx})^2}$$

Substituting back into the product rule result:

$$\begin{aligned} \frac{dh}{dx} &= e^{-cx} \left(\frac{-c e^{-cx}}{(1-e^{-cx})^2} \right) + \frac{1}{(1-e^{-cx})} (-c e^{-cx}) \\ \frac{dh}{dx} &= \left(\frac{-c e^{-2cx}}{(1-e^{-cx})^2} \right) - \frac{c e^{-cx}}{(1-e^{-cx})} \end{aligned}$$

This derivative is actually useful; it is related to the heat capacity of a normal mode of vibration.

24. Find the derivative of $P = \frac{nRT}{(V-nb)} - a \frac{n^2}{V^2}$, with respect to V . Assume that n , R , T , a , and b are all equal to a constant.

Answer: We hold n , R , T , a , and b constant and take the derivative of the two terms:

$$\frac{dP}{dV} = nRT \frac{d\left(\frac{1}{(V-nb)}\right)}{dV} - a n^2 \frac{d\left(\frac{1}{V^2}\right)}{dV} \quad (\text{cst. } n, R, T, a, \& b)$$

Consulting Table 1.5.1, we find:

$$\frac{d(1/x^n)}{dx} = \frac{-n}{x^{n+1}}$$

For the first derivative, we can use the substitution $z = (V - nb)$. The first derivative, using the chain rule, is:

$$\frac{d\left(\frac{1}{(V-nb)}\right)}{dV} = \frac{d\left(\frac{1}{z}\right)}{dz} \frac{dz}{dV} = \frac{-1}{z^2} \left(\frac{dz}{dV}\right) = \frac{-1}{(V-nb)^2} \left(\frac{d(V-nb)}{dV}\right) = \frac{-1}{(V-nb)^2} (1)$$

The next derivative is then:

$$\frac{d\left(\frac{1}{V^2}\right)}{dV} = \frac{-2}{V^3}$$

Then the partial derivative is given by:

$$\frac{dP}{dV} = -\frac{nRT}{(V-nb)^2} + \frac{2an^2}{V^3} \quad (\text{cst. } n, R, T, a, \& b)$$

This derivative is actually useful; it is related to the compressibility of a real (Van der Waals) gas. In Ch. 7 we will note that this derivative is better written as $(\partial P/\partial V)_T$.

25. 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 the statement is true, but too restrictive, give the more general statement.

- (a). For a spontaneous process, no work can be done by the surroundings on the system.
- (b). Fast processes are spontaneous.
- (c). On an average day at sea level, supporting a column of mercury in a closed tube higher than 760 mm requires more force per unit area than the atmosphere can provide.
- (d). Your mouth provides a partial vacuum that pulls a soft drink into your mouth through a straw.
- (e). The derivative of the potential energy with respect to a displacement in a system is zero for a system at equilibrium.

Answers: (a). False: Spontaneous processes can have heat and work transfers with the surroundings in both directions. The heat and work necessary to return the system to the initial state are different than the heat and work for the forward process. The overall result of the forward process and then returning the system back to the initial state requires a net transfer of energy from the surroundings into the system. In other words, there is a net change in the surroundings for the cyclic overall process. A true statement is “The work done in a spontaneous process is not equal to the work required to return the system to the initial state.”

(b). False: Don’t confuse kinetic and equilibrium considerations. Spontaneous processes can be fast or slow. Spontaneous processes have equilibrium constants greater than one. The equilibrium constant is the ratio of the forward and reverse overall reaction rates, $K_p = k_f/k_r$. If the forward rate constant is large, the reverse rate can be even larger, which would make the equilibrium constant small. A true statement is “spontaneous processes may be fast or slow.”

(c). True.

(d). False: A vacuum provides no force. Rather, “a partial vacuum in your mouth decreases the downward pressure on the liquid, so that the pressure of the atmosphere can provide sufficient force to raise the liquid higher in the straw.”

(e). True but too restrictive: The complete statement is “the derivative of the potential energy with respect to a displacement in the system is zero for metastable and equilibrium systems.”

26. (*Challenge Problem*) Three definitions of a reversible process are:

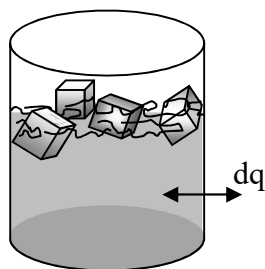
(a). A reversible process is one in which the system never deviates from equilibrium by more than an infinitesimal amount.

(b). A reversible process is not a real process, but a hypothetical succession of equilibrium states.

(c). A reversible process is one for which the system can be returned to its initial state with no net change in the surroundings.

Consider the melting of 1 mole of ice at 0°C as an example. Show how each of the three definitions is equivalent.

Answer: Consider a glass of iced tea in a refrigerator at 0°C , illustrated below, and the melting of one mole of water: $\text{H}_2\text{O}(\text{s}) \rightleftharpoons \text{H}_2\text{O}(\text{l})$. Small amounts of energy can be withdrawn or added to the glass of iced tea through heat transfers from the system, dq , to the refrigerator. To transfer heat from the system, the temperature of the refrigerator is decreased by an infinitesimal amount, until an infinitesimal amount of heat is transferred. To transfer heat to the system, the temperature of the refrigerator is increased an infinitesimal amount, until an infinitesimal amount of heat is transferred. Any amount of ice and water are in equilibrium at the normal melting point, as long as both phases are present. If the temperature of the refrigerator and the iced tea are exactly the same, no heat is transferred and the net amount of ice and liquid remain constant.



(a). An infinitesimal change in temperature gives rise to either melting or fusion, but the system remains at equilibrium as long as the temperature is returned to 0°C , after the heat transfer. One mole of ice may be melted or one mole of liquid may be frozen by a series of heat transfers using infinitesimal changes in the temperature of the refrigerator. The system remains at equilibrium during the process, or infinitesimally close to equilibrium during the heat transfers.

(b). An infinitesimal is the limit of a small change. Let the temperature of the refrigerator be $T + \delta T$. The infinitesimal change dT is the limit $\delta T \rightarrow 0$. So even though infinitesimal changes are hypothetical, such processes are realized through extrapolation of practical processes at $\delta T \rightarrow 0$. Any amount of ice and water are in equilibrium at the normal melting point, as long as both phases are present. So the process occurs through a succession of equilibrium states as one mole of ice melts or one mole of liquid freezes.

(c). If we freeze a small amount of ice by infinitesimally lowering the temperature of the refrigerator, the energy flows into the refrigerator. Because the process is an infinitesimal process, the freezing can be reversed by the transfer of exactly the same amount of heat back into the glass of iced tea: $dq_{\text{melt}} = -dq_{\text{fuse}}$. The net result is no change for the refrigerator, which acts as the surroundings in this example. Because the melting of one mole of ice or the freezing of one mole of liquid can be accomplished through a sequence of such transfers, the net change in the refrigerator (surroundings) is always zero for the overall combined forward and reverse process, no matter how big the overall transfer.

Literature Cited:

1. A. M. Lesk, *Introduction to Physical Chemistry*, Prentice-Hall, Englewood Cliffs, NJ, 1982, Ch. 5.
2. P. T. Landsberg, *Thermodynamics with Quantum Statistical Illustrations*, Wiley-Interscience, New York, NY, 1961, p. 95.