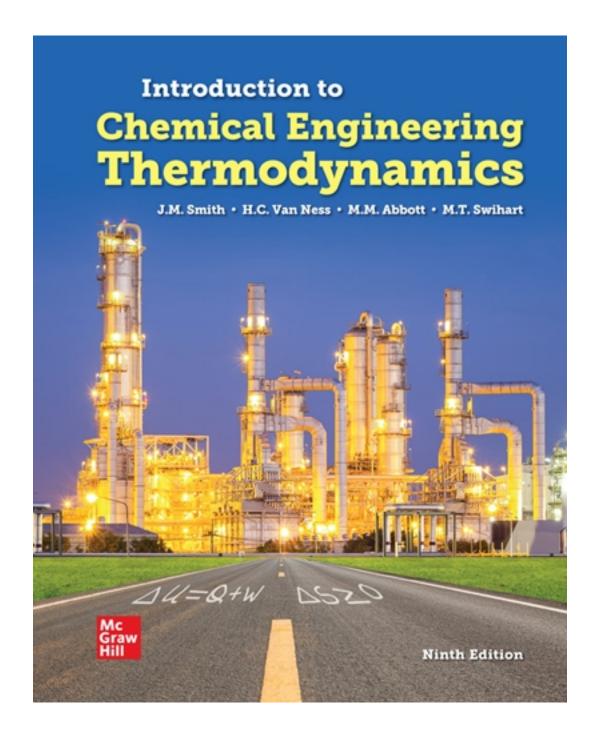
# Solutions for Introduction to Chemical Engineering Thermodynamics 9th Edition by Smith

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# Solutions

# **Solution 1.1**

# **Problem Statement**

*Electric current* is the fundamental SI electrical dimension, with the *ampere* (A) as its unit. Determine units for the following quantities as combinations of *fundamental* SI units.

- (a) Electric power
- (b) Electric charge
- (c) Electric potential difference
- (d) Electric resistance
- (e) Electric capacitance

# **Solution**

(a) Power is *power*, whether it is electrical, mechanical, or otherwise. Thus, electric power has the usual units of power:

power = 
$$\frac{\text{energy}}{\text{time}}$$
 =  $\frac{J}{s}$  =  $\frac{N \text{ m}}{s}$  =  $\frac{kg \text{ m}^2}{s^3}$ 

(b) Electric current is by definition the time rate of transfer of electrical charge. Thus

$$current = \frac{charge}{time}$$

(you probably recall that the Coulomb is the usual derived unit of charge, defined as 1 As)

(c) Because power is given by the product of current and electric potential,

$$power = \frac{energy}{time} = current*electric potential$$

or electrical potential = 
$$\frac{\text{energy}}{\text{current*time}} = \frac{\text{kg m}^2}{\text{A s}^3}$$

(you probably recall that this is defined as the volt)

(d) Because (by Ohm's Law) current is electric potential divided by resistance,

or resistance = 
$$\frac{\text{electrical potential}}{\text{current}} = \frac{\text{kg m}^2}{\text{A}^2 \text{ s}^3}$$

(this is defined as the ohm)

(e) Because electric potential is electric charge divided by electric capacitance,

$$electrical\ potential = \frac{charge}{electrical\ capacitance}$$

or electrical capacitance = 
$$\frac{\text{charge}}{\text{electrical potential}} = \frac{A \text{ s}}{\frac{\text{kg m}^2}{A \text{ s}^3}} = \frac{A^2 \text{ s}^4}{\text{kg m}^2}$$

# **Solution 1.2**

# **Problem Statement**

Liquid/vapor saturation pressure  $P_{\text{Sat}}$  is often represented as a function of temperature by the Antoine equation, which can be written in the form:

$$\log_{10} P^{\text{sat}} / (\text{torr}) = a - \frac{b}{t / {}^{\circ}C + c}$$

Here, parameters *a*, *b*, and *c* are substance-specific constants. Suppose this equation is to be rewritten in the equivalent form:

$$\ln P^{\text{sat}} / kPa = A - \frac{B}{T / K + C}$$

Show how the parameters in the two equations are related.

# **Solution**

We must convert both the units and the logarithm (between base 10 and natural logarithm). We know that t in degrees Celsius is equal to T in Kelvins minus 273.15. Also 1 kPa is equal to 7.50 torr (we might have to look up this conversion factor). So, we have

$$P^{sat} / torr = 10^{\frac{8}{6}t - \frac{b}{t/^{\circ}C + c^{\frac{0}{6}}}} = 7.5 \cdot P^{sat} / kPa = 7.5 \exp \frac{ae}{k} - \frac{B}{T/K + C^{\frac{0}{6}}}$$

Next, we might recognize that 10 can be written as  $\exp(\ln(10))$  or  $\exp(2.303)$ . That is how we convert from base 10 log to natural log in general. So,

$$\exp \overset{\mathcal{X}}{\underset{\bullet}{\text{c}}} 2.303 \overset{\mathcal{X}}{\underset{\bullet}{\text{c}}} - \frac{b}{T/K - 273.15 + c} \overset{\overset{\overset{\bullet}{\text{c}}}{\text{c}}}{\overset{\bullet}{\text{c}}} = 7.5 \exp \overset{\mathcal{X}}{\underset{\bullet}{\text{c}}} - \frac{B}{T/K + C} \overset{\overset{\overset{\bullet}{\text{c}}}{\text{c}}}{\overset{\overset{\bullet}{\text{c}}}{\text{c}}}$$

Here, I have also substituted T – 273.15 for t. Taking the natural log of both sides gives

$$2.303 \stackrel{\text{@}}{\overleftarrow{e}} - \frac{b}{T/K-273.15+c} \frac{\ddot{o}}{\ddot{o}} = \ln(7.5) + A - \frac{B}{T/K+C}$$

For the two functions to be equal for all values of *T*, each part of the functions must be the same, so we must have

$$A = 2.303a - \ln(7.5)$$
 or  $A = \ln(10)*a - \ln(7.5)$ 

$$B = 2.303b$$
 or  $B = \ln(10)*b$ 

$$C = c - 273.15$$

# **Solution 1.3**

#### **Problem Statement**

Table B.2 in Appendix B provides parameters for computing the vapor pressure of many substances by the Antoine equation (see Prob. 1.2). For one of these substances, prepare two plots of  $P^{\text{Sat}}$  versus T over the range of temperature for which the parameters are valid. One plot should present  $P^{\text{Sat}}$  on a linear scale and the other should present  $P^{\text{Sat}}$  on a log scale.

#### Problem 1.2

Liquid/vapor saturation pressure  $P_{\text{Sat}}$  is often represented as a function of temperature by the Antoine equation, which can be written in the form:

$$\log_{10} P^{\text{sat}} / (\text{torr}) = a - \frac{b}{t / {}^{\circ}C + c}$$

Here, parameters a, b, and c are substance-specific constants. Suppose this equation is to be rewritten in the equivalent form:

$$\ln P^{\text{sat}} / kPa = A - \frac{B}{T / K + C}$$

Show how the parameters in the two equations are related.

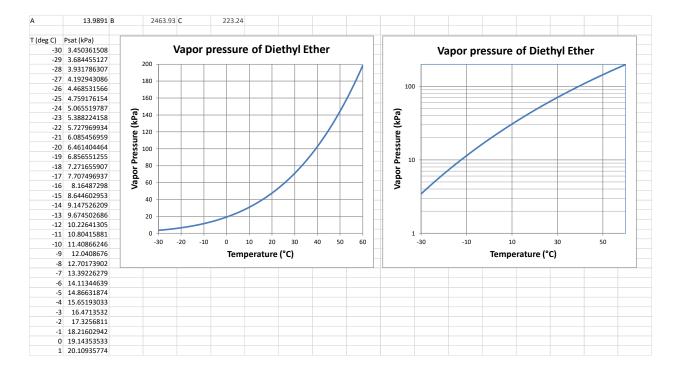
#### Solution

The point of this problem is just for you to practice evaluating and plotting a simple function. You will do many problems over the course of the semester (and many more over the course of your career) in which the results are best presented in graphical form. The only thing to be careful of in plotting the Antoine equation is to pay attention to the units of T and P<sup>sat</sup> and to whether the constants are given for use with the base 10 logarithm or the natural logarithm.

Solution continued on next page...

The parameters in Table B.2 are for use with T in °C, P in kPa, and the natural logarithm. Note that plotting  $P^{\text{sat}}$  vs. T means that we treat  $P^{\text{sat}}$  as the dependent variable and plot it on the vertical axis and treat T as the independent variable and plot it on the horizontal axis. Note also that to put the vertical axis on a log scale, we do not actually compute the logarithm of  $P^{\text{sat}}$ , but change the scaling of the axis, historically by using log-scale graphing paper, but now by changing an option in the plotting software.

I used MS Excel to prepare the plots for diethyl ether. A portion of the spreadsheet (containing the plots) is shown below:



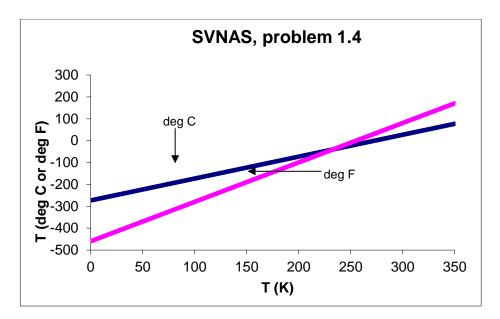
# **Solution 1.4**

# **Problem Statement**

At what absolute temperature do the Celsius and Fahrenheit temperature scales give the same numerical value? What is the value?

# **Solution**

One way to solve this problem is to write both the Celsius and Fahrenheit temperatures in terms of the absolute temperature in Kelvin, then set these equal to each other and solve for the temperature in Kelvin. The Celsius temperature is T ( $^{\circ}$ C) = T (K) – 273.15. The Fahrenheit temperature is T ( $^{\circ}$ F) = 1.8\*T (K) – 459.67. If we plot these two lines, they look like:



What we are asked to find is the point where these two lines cross. That is, where

$$T(K) - 273.15 = 1.8*T(K) - 459.67$$

Solving this for T (K) gives T (K) = (459.67 - 273.15) / 0.8 = 233.15 K. At this temperature (in K) the Fahrenheit temperature is 1.8 \* 233.15 - 459.67 = -40 °F. Likewise, the Celsius temperature is 233.15 - 273.15 = -40 °C.

# Solution 1.5

#### **Problem Statement**

The SI unit of *luminous intensity* is the candela (abbreviated cd), which is a primary unit. The derived SI unit of *luminous flux* is the lumen (abbreviated lm). These are based on the sensitivity of the human eye to light. Light sources are often evaluated based on their *luminous efficacy*, which is defined as the luminous flux divided by the power consumed and is measured in  $lm \cdot W^{-1}$ . In a physical or online store, find manufacturer's specifications for representative incandescent, halogen, high-temperature-discharge, LED, and fluorescent lamps of similar luminous flux and compare their luminous efficacy.

# Solution

I found the following on <a href="www.bulbs.com">www.bulbs.com</a> in 2016. I chose all lamps that could be screwed into a regular medium-base socket

Туре	Watts Used	Lumens Produced	Luminous Efficacy
Incandescent	150 W	1735 lm	12 lm W <sup>-1</sup>
Halogen	120 W	1850 lm	15 lm W <sup>-1</sup>
High Pressure Sodium	35 W	2300 lm	66 lm W <sup>-1</sup>
Compact Fluorescent	23 W	1650 lm	72 lm W <sup>-1</sup>
LED	19 W	1680 lm	88 lm W <sup>-1</sup>

In this light-output range, the high pressure sodium lamp, compact fluorescent, and LED are comparable. All three high-efficiency options are about a factor of 4 better than incandescent or halogen bulbs. Eventually, LED's have the potential to be much more efficient than fluorescents, but what is on the market now is not there yet. They are improving rapidly – 2016 was the first year in which the LED lamp was the most efficient when I did this exercise. Previously, the high-pressure sodium lamp was most efficient.

#### Solution 1.6

#### **Problem Statement**

Pressures up to 3000 bar are measured with a dead-weight gauge. The piston diameter is 4 mm. What is the approximate mass in kg of the weights required?

# **Solution**

Pressure is force divided by area. So, the maximum force required (to be applied by the weights) is the maximum pressure to be measured times the area of the piston. The area of the piston is

$$A = \pi d^2/4 = 4\pi \text{ mm}^2 = 12.57 \text{ mm}^2 = 1.257 \times 10^{-5} \text{ m}^2$$

The maximum pressure to be measured is 3000 bar =  $3 \times 10^8$  Pa =  $3 \times 10^8$  N m<sup>-2</sup>. Thus, the maximum force to be applied by the weights is  $F = 1.257 \times 10^{-5}$  m<sup>2</sup> \*  $3 \times 10^8$  N m<sup>-2</sup> = 3770 N. If this force is to be applied by weights, and the acceleration of gravity is 9.8 m s<sup>-2</sup>, then we have

$$F = mq = 9.8 \text{ m s}^{-2} * m = 3770 \text{ N} = 3770 \text{ kg m s}^{-2}$$

So, the mass of weights needed is approximately 3770/9.8 = 385 kg

# Solution 1.7

#### **Problem Statement**

Pressures up to 3000(atm) are measured with a dead-weight gauge. The piston diameter is 0.17(in). What is the approximate mass in  $(lb_m)$  of the weights required?

#### **Solution**

Pressure is force divided by area. So, the maximum force required (to be applied by the weights) is the maximum pressure to be measured times the area of the piston. The piston area is

$$A = \pi d^2/4 = \pi * 0.17^2/4 \text{ in}^2 = 0.0227 \text{ in}^2$$

The maximum pressure to be applied is 3000 atm = 3000 \* 14.7 psi/atm = 44090 psi = 44090 lb<sub>f</sub> in<sup>-2</sup>. For the standard acceleration of gravity (g numerically equal to  $g_c$ ) one lb<sub>m</sub> imparts one lb<sub>f</sub> to the piston. Thus, the mass of weights required is 0.0227 in<sup>2</sup> \* 44090 lb<sub>f</sub> in<sup>-2</sup> \* ( $g/g_c = 1$  lb<sub>f</sub>/lb<sub>m</sub>)<sup>-1</sup> = 1001 lb<sub>m</sub>.

#### Solution 1.8

#### **Problem Statement**

The reading on a mercury manometer at 25°C (open to the atmosphere at one end) is 56.38 cm. The local acceleration of gravity is  $9.832~\mathrm{m\cdot s}^{-2}$ . Atmospheric pressure is  $101.78~\mathrm{kPa}$ . What is the absolute pressure in kPa being measured? The density of mercury at 25°C is  $13.534~\mathrm{g\cdot cm}^{-3}$ .

# **Solution**

The total pressure is equal to atmospheric pressure plus the weight per area ( $\rho gh$ ) of the mercury column. This is, in SI units,  $p = 101780 \text{ Pa} + 13534 \text{ kg/m}^3 * 9.832 \text{ m s}^{-2} * 0.5638 \text{ m} = 176800 \text{ Pa} = 176.8 \text{ kPa}$ .

#### **Solution 1.9**

#### **Problem Statement**

The reading on a mercury manometer at  $70(^{\circ}F)$  (open to the atmosphere at one end) is 25.62(in). The local acceleration of gravity is  $32.243(ft)\cdot(s)^{-2}$ . Atmospheric pressure is 29.86(in Hg). What is the absolute pressure in (psia) being measured? The density of mercury at  $70(^{\circ}F)$  is  $13.543 \text{ g}\cdot\text{cm}^{-3}$ .

#### **Solution**

The total pressure is equal to atmospheric pressure plus the weight per area ( $\rho(g/g_c)h$ ) of the mercury column. The only trick is to do this in the non-SI units given. Let us compute the pressure in psia (pounds-force per square inch, absolute). To do so, we should convert the density of mercury from g cm<sup>-3</sup> to lb<sub>m</sub> in<sup>-3</sup>.

Thus,  $\rho = 13.543$  g cm<sup>-3</sup> \* (2.54 cm/in)<sup>3</sup> / 453.59 g/lb = 0.4893 lb<sub>m</sub> in<sup>-3</sup>. We also need to convert atmospheric pressure from in Hg to psia by multiplying by 0.4912 psi/(in Hg).

So, p = 29.86 in Hg \* 0.4912 lbf in  $^{-2}$  (in Hg) $^{-1}$  + 0.4893 lbm in  $^{-3}$  \* 32.243 ft s $^{-2}$  / (32.1740 lbm ft lbf $^{-1}$  s $^{-2}$ ) \* 25.62 in = 27.2 lbf in  $^{-2}$  = 27.2 psia.

#### Solution 1.10

#### **Problem Statement**

An absolute pressure gauge is submerged 50 m (1979 inches) below the surface of the ocean and reads P = 6.064 bar. This is P = 2434 (inches of H<sub>2</sub>O), according to the unit conversions built into a particular calculator. Explain the apparent discrepancy between the pressure measurement and the actual depth of submersion.

# **Solution**

The pressure unit "inches of water" is defined as the pressure exerted by one inch of water under standard gravitational conditions (density of water =  $1 \text{ g/cm}^3$ , g =  $9.8 \text{ m/s}^2$ ). The pressure exerted on the gauge is given by

 $P = P_{atm} + \rho g h$ s the absolute pressure at the position of the gauge.  $\rho$  is the density of the

Here P is the absolute pressure at the position of the gauge,  $\rho$  is the density of the water, g is the acceleration of gravity ( $\sim$ 9.8 m/s²), and h is the depth of the water (50 m). We can take  $P_{atm}$  = 1.013 bar = 1.013×10<sup>5</sup> Pa. The pressure difference caused by the mass of the column of water above the pressure gauge (excluding atmospheric pressure) is then  $P - P_{atm}$  = 6.064 – 1.013 = 5.051 bar = 5.051×10<sup>5</sup> Pa. Converting that value to inches of water using my calculator gives 2028 inches of water. This is much closer to the actual depth, but still about 2.5% higher. This remaining discrepancy can be attributed to the density of seawater. If we take h = 50 m and g = 9.8 m/s², then we can use our pressure measurement to estimate the density of the seawater:  $\rho = (P - P_{atm})/(gh) = 5.051 \times 10^5$ 

$N/m^2/(9.8 m/s^2 \cdot 50 m) = 1030.8 kg^4 m/(m \cdot s^2)/(m^2/s^2) = 1030.8 kg/m^3$ . This is a typical value for the density of seawater, which is higher than the density of fresh water because of its dissolved salt content.						
	$N/m^2/(9.8 \text{ m/s}^2*50 \text{ m}) = 1030.8 \text{ kg*m/(m s}^2)/(m^2/s^2) = 1030.8 \text{ kg/m}^3$ . This is a typical value for the density of seawater, which is higher than the density of fresh water because of its dissolved salt content.					
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# **Solution 1.11**

#### **Problem Statement**

Liquids that boil at relatively low temperatures are often stored as liquids under their vapor pressures, which at ambient temperature can be quite large. Thus, *n*-butane stored as a liquid/vapor system is at a pressure of 2.581 bar for a temperature of 300 K. Large-scale storage (>50 m<sup>3</sup>) of this kind is sometimes done in *spherical* tanks. Suggest two reasons why.

#### Solution

The advantages of spherical tanks stem from the fact that a spherical container has the minimum surface area for a given interior volume. Because of this:

- (a) A minimum quantity of metal is required for tank construction (for a given metal thickness).
- (b) The tensile stress within the tank wall is everywhere uniform, with no sites of stress concentration, and the stress is purely tensile (everywhere tangential to the tank surface). Moreover, the maximum stress within the tank wall is kept to a minimum.
- (c) The surface area for heat transfer is minimized, optimizing the efficiency of insulating the tank.

#### Solution 1.12

#### **Problem Statement**

The first accurate measurements of the properties of high-pressure gases were made by E. H. Amagat in France between 1869 and 1893. Before developing the dead-weight gauge, he worked in a mineshaft and used a mercury manometer for measurements of pressure to more than 400 bar. Estimate the height of manometer required.

#### **Solution**

We know that 1 bar is equal to 750 torr or 750 mm of Hg or 0.75 meters of mercury. So, to measure a pressure of 400 bar, he needed a column of mercury 400 bar \* 0.75 mHg/bar = 300 m of mercury.

#### Solution 1.13

# **Problem Statement**

An instrument to measure the acceleration of gravity on Mars is constructed of a spring from which is suspended a mass of 0.40 kg. At a place on earth where the local acceleration of gravity is  $9.81~\text{m}\cdot\text{s}^{-2}$ , the spring extends 1.08~cm. When the instrument package is landed on Mars, it radios the information that the spring is extended 0.40 cm. What is the Martian acceleration of gravity?

# Solution

The spring constant can be determined from a force balance on the mass on earth. The gravitational force is  $F = mg = 0.40 \text{ kg} * 9.81 \text{ m s}^{-1} = 3.924 \text{ kg m s}^{-1} = 3.924 \text{ N}.$ 

The spring force is F = kx, where k is the spring constant and x is the distance it is extended from its equilibrium length. These forces must be equal, so we have

$$kx = 3.924 \text{ N} = k * 1.08 \text{ cm} = k * 0.0108 \text{ m}.$$

So, 
$$k = 3.924/0.0108 = 363.3 \text{ N/m}.$$

Now, we do the same force balance on Mars, with g (for Mars) as the unknown.

$$F = kx = 363.3 \text{ N/m} * 0.40 \text{ cm} = 363.3 \text{ N/m} * 0.004 \text{ m} = 1.453 \text{ N}.$$

and 
$$F = 1.453 \text{ N} = mg = 0.40 \text{ kg} * g$$

So, 
$$g = 3.63 \text{ N/kg} = 3.63 \text{ m s}^{-2}$$
.

#### Solution 1.14

# **Problem Statement**

The variation of fluid pressure with height is described by the differential equation:

$$\frac{dP}{dz} = -rg$$

Here,  $\rho$  is specific density and g is the local acceleration of gravity. For an *ideal gas*,  $\rho = \mathbb{Z}P/RT$ , where  $\mathbb{Z}$  is molar mass and R is the universal gas constant. Modeling the atmosphere as an isothermal column of ideal gas at  $10^{\circ}$ C, estimate the ambient pressure in Denver, where z = 1 (mile) relative to sea level. For air, take  $\mathbb{Z} = 29 \text{ g·mol}^{-1}$ ; values of R are given in App. A.

#### **Solution**

Substituting the ideal gas expression for density into the equation for variation of fluid pressure with height gives

$$\frac{dP}{dz} = -\frac{MP}{RT}g$$

If *T* is constant (along with molar mass, M, and *g*) then this is a separable equation that can be rearranged to give:

$$\frac{dP}{P} = -\frac{M g}{RT} dz$$

Solution continued on next page...

This can be directly integrated to give

$$\ln \frac{\stackrel{\mathcal{E}}{R}P \frac{\ddot{o}}{\dot{e}}}{P_o \frac{\dot{c}}{\dot{e}}} = -\frac{M g}{RT} (z - z_o)$$

Or

$$P = P_o \exp \frac{\partial}{\partial z} \frac{M g}{RT} (z - z_o) \frac{\ddot{o}}{\ddot{b}}$$

The standard pressure at sea level is  $P_0 = 101325$  Pa. If Denver is 1 mile = 1609 m above sea level, g = 9.8 m s<sup>-2</sup>,

M = 0.029 kg/mol,  $T = 10 \, ^{\circ}\text{C} = 283 \text{ K}$ , and  $R = 8.314 \text{ kg m}^2 \text{ mol}^{-1} \text{ K}^{-1}$ , then

$$P = 101325 \exp \frac{e}{\xi} \frac{0.029*9.8}{8.314*283} (1609) = 83430 \text{ Pa}$$

The estimated pressure is 83430 Pa = 0.834 bar = 0.823 atm.

#### Solution 1.15

#### **Problem Statement**

A group of engineers has landed on the moon, and they wish to determine the mass of some rocks. They have a spring scale calibrated to read pounds mass at a location where the acceleration of gravity is  $32.186(ft)(s)^{-2}$ . One of the moon rocks gives a reading of 18.76 on this scale. What is its mass? What is its weight on the moon?

Take  $g(moon) = 5.32(ft)(s)^{-2}$ .

# **Solution**

The force on the scale, whether on earth or on the moon, can be written at  $F = mg/g_c$ , and it is the force that is actually measured by the scale. The reading (displayed in lb<sub>m</sub>) is therefore proportional to the actual mass and proportional to the gravitational constant. It can be written as  $m_{read} = A m_{true}$ , where A, the calibration constant for the scale, is numerically equal to  $g/g_c$ . On earth, where  $g = 32.186 \text{ ft/s}^2$ , A = 1. On the moon, where  $g = 5.32 \text{ ft/s}^2$ , A needs to be corrected by the ratio of g on the moon to g on earth. A = 5.32/32.186 = 0.1653. So, on the moon,  $m_{read} = 0.1653*m_{true}$ . The true mass of the rock is  $m_{true} = m_{read}/0.1653 = 18.76/0.1653 = 113.5 \text{ lb}_m$ . Its weight on the moon is numerically equal to the reading. It is  $18.76 \text{ lb}_f$ .

#### **Solution 1.16**

#### **Problem Statement**

In medical contexts, *blood pressure* is often given simply as numbers without units.

- (a) In taking blood pressure, what physical quantity is actually being measured?
- (b) What are the units in which blood pressure is typically reported?
- (c) Is the reported blood pressure an absolute pressure or a gauge pressure?
- (d) Suppose an ambitious zookeeper measures the blood pressure of a standing adult male giraffe (18 feet tall) in its front leg, just above the hoof, and in its neck, just below the jaw. By about how much are the two readings expected to differ?
- (e) What happens to the blood pressure in a giraffe's neck when it stoops to drink?
- (f) What adaptations do giraffes have that allow them to accommodate pressure differences related to their height?

# **Solution**

(a) "Blood pressure" refers to the pressure exerted by the blood on the interior walls of the major arteries. The higher number (systolic pressure) represents the maximum pressure during the cardiac cycle, and the lower number (diastolic pressure) represents the minimum pressure during the cardiac cycle. In certain situations where patients require continuous, accurate, and rapid blood pressure monitoring, it is measured directly. This can be done

by simply inserting a cannula (big needle) into a large artery and connecting it to a pressure transducer. This is much the same way that one measures pressure in a piece of chemical process equipment. Ordinarily, the blood pressure is measured indirectly using a sphygmomanometer. This is the familiar device with the inflatable cuff. What is measured is the pressure inside the cuff that is needed to stop the flow of blood through the artery it is squeezing (usually the brachial artery in the upper arm). The systolic pressure is the lowest pressure at which flow is completely stopped throughout the cardiac cycle, and the diastolic pressure is the pressure at which the flow is not stopped at any point in the cardiac cycle. Blood flow is detected by a health care practitioner listening for it using a stethoscope, or by a small transducer built into the inflatable cuff.

- (b) Although they are often omitted, the units for blood pressure are mm of mercury. In SI units, a blood pressure of 120 over 80 would be a systolic pressure of 16000 Pa over 10700 Pa.
- (c) It is a gauge pressure, measured and reported as the difference in pressure between the pressure in the blood vessels and the ambient pressure. For example, when a scuba diver descends 30 feet below the surface, her blood pressure remains the same, even though the ambient pressure has roughly doubled from its value at the surface.
- (d) To a first approximation, we expect the pressure difference to just be the hydrostatic pressure difference due the difference in elevation between the hoof and the head. Taking this to be 17 feet (5.2 m) and taking the density of giraffe blood to be  $1000 \text{ kg/m}^3$ , the pressure difference should be roughly

 $P = \rho g h = 1000 \text{ kg/m}^3 * 9.8 \text{ m/s}^2 * 5.2 \text{ m} = 51,000 \text{ Pa} = 0.5 \text{ bar}$ . The pressure in the giraffe's hooves is about half an atmosphere higher than that in its head (when it is standing).

- (e) It will fairly quickly increase by half an atmosphere, at least relative to the pressure in the giraffe's hooves. The actual increase is not quite so big, because the giraffe's heart moves to a slightly lower level when it stoops, and there accompanying changes in the giraffe's pulse rate, etc. that have some effect.
- (f) The biggest problem would occur when the giraffe raises its head. Without special adaptations, the rapid change in pressure would drain all of the blood out of its head and it would faint (compare to the head rush you may sometimes get when changing the elevation of your head by just 3 feet or so). However, giraffes have a collapsible jugular vein and unusually strong ability to constrict the veins in their neck. This allows them to dramatically increase the flow resistance in their veins as they raise their heads, which prevents all of the blood from draining out. It seems that through differential contraction of different arterial paths, they can divert blood flow around the brain, or force a larger fraction through the brain. Overall, they have a much more sophisticated arrangement for controlling cranial blood pressure than most other animals.

#### Solution 1.17

#### **Problem Statement**

A 70 W outdoor security light burns, on average, 10 hours a day. A new bulb costs \$5.00, and the lifetime is about 1000 hours. If electricity costs \$0.10 per kW·h, what is the yearly price of "security," per light?

# Solution

70 Watts times 10 hours per day is 700 Watt-hours per day or 0.7 kW-hour/day. Multiplying this by 365 days per year gives 255.5 kW-hours/year of electricity use at \$0.10 per kW-hour, for a total annual electricity cost of \$25.55. If the light is on 3650 hours per year, one will use an average of 3.65 bulbs (each lasting 1000 hours, or 100 days at 10 hours per day) each year, at an average annual cost of \$5\*3.65 = \$18.25/year. So the total annual cost to operate the light is about \$18.25 + \$25.55 = \$44.

# Solution 1.18

#### **Problem Statement**

A gas is confined in a 1.25(ft) diameter cylinder by a piston, on which rests a weight. The mass of the piston and weight together is  $250(lb_m)$ . The local acceleration of gravity is  $32.169(ft)(s)^{-2}$ , and atmospheric pressure is 30.12 (in Hg).

- (a) What is the force in (lbf) exerted on the gas by the atmosphere, the piston, and the weight, assuming no friction between the piston and cylinder?
- (b) What is the pressure of the gas in (psia)?
- (c) If the gas in the cylinder is heated, it expands, pushing the piston and weight upward. If the piston and weight are raised 1.7(ft), what is the work done by the gas in (ft)(lbf)? What is the change in potential energy of the piston and weight?

# **Solution**

(a) The force exerted on the gas has two parts, the weight of the piston and the pressure of the atmosphere on the top of the piston. The force due to the weight of the piston is  $mg/g_c$  where m is the piston mass and g is the acceleration of gravity. We have to use  $g_c$  to make the units work out right. The force due to the pressure of the atmosphere is PA where P is the pressure and A is the cross-sectional area of the piston. The cross-sectional area of the piston is  $A = \pi d^2/4 = 0.7854*(1.25 \text{ ft})^2 = 1.227 \text{ ft}^2$ . So, the total force is:

$$F = 250 \text{ lb}_m * 32.169 \text{ ft s}^{-2} / (32.1740 \text{ lb}_m \text{ ft lb}_f^{-1} \text{ s}^{-2}$$

$$+ 30.12 \text{ (in Hg)} * 0.49116 \text{ lb}_f \text{in}^{-2} / \text{ (in Hg)} * 1.227 \text{ ft}^2 * 144 \text{ in}^2 \text{ ft}^{-2}$$

$$F = 249.96 \text{ lb}_f + 2613.85 \text{ lb}_f = 2863.8 \text{ lb}_f$$

(b) The pressure of the gas is the force divided by the area

$$P = F / A = 2863.8 \text{ lb}_f / (1.227 \text{ ft}^2 * 144 \text{ in}^2 \text{ ft}^{-2}) = 16.21 \text{ lb}_f \text{ in}^{-2} = 16.21 \text{ psia}$$

(c) Because the weight of the piston, its cross-sectional area, and the pressure of the atmosphere on it all remain constant, the force on the gas and the gas pressure also remain constant. So, the work done by the gas can be computed as either  $F \Delta h$  or  $P \Delta V$ , using the pressure and force that we have already computed. Because we are given  $\Delta h = 1.7$  ft, it is easiest to calculate it as

$$W = 2863.8 \text{ lb} f^* 1.7 \text{ ft} = 4868 \text{ ft lb} f$$

Most of this work is done against the pressure of the atmosphere, so only a small part of it changes the potential energy of the piston. The potential energy of the piston changes by  $mg/g_c\Delta h = 249.96 \ lbf^* 1.7 \ ft = 424.9 \ ft \ lbf$ 

#### Solution 1.19

#### **Problem Statement**

A gas is confined in a 0.47 m diameter cylinder by a piston, on which rests a weight. The mass of the piston and weight together is 150 kg. The local acceleration of gravity is 9.813 m·s $^{-2}$ , and atmospheric pressure is 101.57 kPa.

- (a) What is the force in newtons exerted on the gas by the atmosphere, the piston, and the weight, assuming no friction between the piston and cylinder?
- (b) What is the pressure of the gas in kPa?
- (c) If the gas in the cylinder is heated, it expands, pushing the piston and weight upward. If the piston and weight are raised 0.83 m, what is the work done by the gas in kJ? What is the change in potential energy of the piston and weight?

#### Solution

(a) The force applied by the atmosphere (if the piston and weight were 'massless') would be the atmospheric pressure (101.57 kPa) times the cross-sectional area of the piston ( $A = \pi d^2/4 = (0.47)^2\pi/4$  m<sup>2</sup> = 0.173 m<sup>2</sup>. So, the force due to the atmosphere is 0.173 m<sup>2</sup> \* 1.0157 × 10<sup>5</sup> N m<sup>-2</sup> = 17600 N. The additional force applied by the piston and weight is F = mg = 150 kg \* 9.813 m s<sup>-2</sup> = 1472 N. Thus, the total force applied to the gas is about

19090 N.

(b) The pressure of the gas is the total force found in (a) divided by the cross sectional area of the piston.

$$P = 19090 \text{ N} / 0.173 \text{ m}^2 = 1.101 \times 10^5 \text{ N m}^{-2} = 1.101 \times 10^5 \text{ Pa} = 110.1 \text{ kPa}.$$

(c) Because the mass of the piston and the pressure of the atmosphere don't change in this process, the pressure of the gas inside the piston is constant as it expands, and the force applied by the piston and atmosphere to the gas is constant as the gas expands. We can compute the work either as the pressure times the change in volume or the force times the distance the piston moves. Because we've already computed the force in part (a), the simplest method is to multiply this force by the distance that the piston travels:

$$W = Fl = 19090 \text{ N} * 0.83 \text{ m} = 15850 \text{ N} \text{ m} = 15850 \text{ J}.$$

The change in potential energy of the piston and weight is:

$$\Delta E_P = mg\Delta z = 150 \text{ kg} * 9.813 \text{ m s}^{-2} * 0.83 \text{ m} = 1222 \text{ kg m}^2 \text{ s}^{-2} = 1222 \text{ J}.$$

Thus, most of the work done by the gas goes toward 'pushing back' the atmosphere, not raising the piston and weight. This is a result of the fact that most of the pressure being applied to the gas is due to the atmosphere, and not to the weight and piston.

# Solution 1.20

#### **Problem Statement**

Verify that the SI unit of kinetic and potential energy is the joule.

# Solution

Kinetic energy is given by  $E_K = \frac{1}{2} mv^2$ . Its fundamental units are therefore the fundamental unit of mass (kg) times those of velocity (length/time, m/s) squared:

$$E_K[=] \text{ kg} \cdot (\text{m/s})^2 [=] \text{ kg} \cdot \text{m}^2/\text{s}^2 [=] \text{ N} \cdot \text{m} [=] \text{ J}$$

Gravitational potential energy (EP = mgz) has units of mass·length·acceleration. Its fundamental units are therefore:

$$E_P = | kg \cdot m \cdot (m/s^2) | | kg \cdot m^2/s^2 | | N \cdot m | | J$$

# **Solution 1.21**

#### **Problem Statement**

An automobile having a mass of 1250 kg is traveling at 40 m·s<sup>-1</sup>. What is its kinetic energy in kJ? How much work must be done to bring it to a stop?

# **Solution**

The kinetic energy is KE =  $\frac{1}{2}$   $mv^2$  =  $\frac{1}{2}$  \* 1250 kg \*  $(40 \text{ m/s})^2$  = 10000000 kg m<sup>2</sup> s<sup>-2</sup> = 10000000 J. To bring this car to a stop, a minimum of 1000000 J of work must be done on the car.

#### Solution 1.22

#### **Problem Statement**

The turbines in a hydroelectric plant are fed by water falling from a 50 m height. Assuming 91% efficiency for conversion of potential to electrical energy, and 8% loss of the resulting power in transmission, what is the mass flow rate of water required to power a 200 W light bulb?

# Solution

We can either work forward, computing the energy output per mass of water, or work backward, starting from the energy requirement of the lightbulb. If we choose to work forward, then we compute that the potential energy change, per kilogram of water that falls is  $\Delta EP/m = g\Delta z = 9.8 \text{ m s}^{-2} *50 \text{ m} = 490 \text{ m}^2 \text{ s}^{-2} = 490 \text{ J kg}^{-1}$ . We are told that 91% of this energy is converted to electrical energy, and 92% of that electrical energy is transmitted to the lightbulb (8% is lost). So, the energy transmitted to the lightbulb is 490 J/kg \* 0.91 \* 0.92 = 410 J/kg. The 200-Watt light bulb requires 200 J per second. Dividing this by the energy production per kilogram gives:

Required water flow rate =  $200 \text{ J s}^{-1} / 410 \text{ J/kg} = 0.488 \text{ kg s}^{-1} = 29.3 \text{ kg per minute} = 64.5 \text{ lb}_{m}$  per minute.

To get more familiar volumetric units for water, we can divide by the density of water (about  $8.3 \text{ lb}_m$  per gallon) to get 7.7 gallons per minute.

# Solution 1.23

# **Problem Statement**

A wind turbine with a rotor diameter of 77 m produces 1.5 MW of electrical power at a wind speed of 12 m·s<sup>-1</sup>. What fraction of the kinetic energy of the air passing through the turbine is converted to electrical power? You may assume a density of  $1.25 \text{ kg} \cdot \text{m}^{-3}$  for air at the operating conditions.

# **Solution**

The kinetic energy per unit mass of the wind approaching the turbine is  $\frac{1}{2}u^2 = \frac{1}{2}(12)^2 = 72 \text{ m}^2 \text{ s}^{-2} = 72 \text{ J/kg}$ . The volumetric flow rate of air approaching the turbine is given by the velocity times the cross-sectional area:  $q = uA = 12 \text{ m/s} * \pi (77 \text{ m})^2 / 4 = 55880 \text{ m}^3/\text{s}$ . If the density of the air is 1.25 kg m<sup>-3</sup>, then the mass flow rate is:

$$\dot{m} = \rho q = 1.25 \text{ kg m}^{-3} *55880 \text{ m}^{3} \text{ s}^{-1} = 69850 \text{ kg s}^{-1}$$

If this has a kinetic energy of 72 J kg $^{-1}$ , then the total power available is  $72*69850 = 5.03 \times 10^6$  J/s = 5.03 MW. The efficiency of the turbine (electrical energy output divided by kinetic energy of the approaching air) is 1.5/5.03 = 0.30.

# **Solution 1.24**

# **Problem Statement**

The annual average insolation (energy of sunlight per unit area) striking a fixed solar panel in Buffalo, New York, is  $200 \text{ W} \cdot \text{m}^{-2}$ , while in Phoenix, Arizona, it is  $270 \text{ W} \cdot \text{m}^{-2}$ . In each location, the solar panel converts 15% of the incident energy into electricity. Average annual electricity use in Buffalo is  $6000 \text{ kW} \cdot \text{h}$  at an average cost of \$0.15 kW·h, while in Phoenix it is  $11,000 \text{ kW} \cdot \text{h}$  at a cost of  $$0.09 \text{ kW} \cdot \text{h}$ .

- (a) In each city, what area of solar panel is needed to meet the average electrical needs of a residence?
- (b) In each city, what is the current average annual cost of electricity?
- (c) If the solar panel has a lifetime of 20 years, what price per square meter of solar panel can be justified in each location? Assume that future increases in electricity prices offset the cost of borrowing funds for the initial purchase, so that you need not consider the time value of money in this analysis.

# **Solution**

- (a) One way to figure this out is to find the annual average usage by taking the total annual usage (in kW-h) and dividing by the number of hours in a year to get an average usage in kW. For Buffalo, we have (6000 kW-h/yr)/(8766 h/yr) = 0.684 kW. In Pheonix, it is 11000/8766 = 1.255 kW. In Buffalo, we get 0.15\*200 = 30 W m<sup>2</sup> of solar panel, while in Phoenix we get 0.15\*270 = 40.5 W m<sup>-2</sup>. The total area needed in Buffalo is therefore 684/30 = 22.8 m<sup>2</sup>, while the total area needed in Pheonix is 1255/40.5 = 31.0 m<sup>2</sup>.
- (b) In Buffalo, it is 6000 kW h \* 0.15 / (kW h) = \$900In Pheonix, it is 11000 kW h \* 0.09 / (kW h) = \$990

(c) Neglecting the time value of money, we need the solar panels in each case to cost less than 20 years worth of electricity. Thus, in Buffalo, we require the total cost to be less than 20\*\$900 = \$18000 and in Phoenix we require it be less than 20\*\$990 = \$19800. Dividing these by the total area needed in each location gives:

Buffalo:  $18000/22.8 \text{ m}^2 = 790 \text{ m}^{-2}$ 

Phoenix:  $$19800/31.0 \text{ m}^2 = $639 \text{ m}^{-2}$ 

This must include the total installed cost in each case, not just the panels themselves. Support structures, power inverters, etc. will be required. Sizing the panels based on average insolation assumes that electricity can be stored and retrieved for indefinite periods of time at no additional cost. This might be the case if the local electricity supplier allows the homeowner to feed power into the grid and be fully credited against any power drawn from the grid at other times (net metering).

#### Solution 1.25

# **Problem Statement**

Following is a list of approximate conversion factors, useful for "back-of-the-envelope" estimates. None of them is exact, but most are accurate to within about  $\pm 10\%$ . Use Table A.1 (App. A) to establish the exact conversions.

- $\cdot$  1(atm) ≈ 1 bar
- $\cdot 1(Btu) \approx 1 \text{ kJ}$
- $\cdot$  1(hp)  $\approx 0.75 \text{ kW}$
- $\cdot$  1(inch) ≈ 2.5 cm
- $\cdot 1(lbm) \approx 0.5 \text{ kg}$
- $\cdot$  1(mile) ≈ 1.6 km
- $\cdot$  1(quart) ≈ 1 liter
- $\cdot$  1(yard) ≈ 1 m

Add your own items to the list. The idea is to keep the conversion factors simple and easy to remember.

**Table A.1: Conversion Factors** 

Quantity	Conversion
Length	1  m = 100  cm = 3.28084 (ft) = 39.3701 (in)
Mass	$1 \text{ kg} = 10^3 \text{ g}$ = 2.20462 (1b <sub>m</sub> )
Force	$1 \text{ N} = 1 \text{ kg} \cdot \text{m} \cdot \text{s}^{-2}$ = $10^5 \text{ (dyne)}$ = $0.224809 \text{ (1b_f)}$
Pressure	1 bar = $10^5 \text{ kg} \cdot \text{m}^{-1} \cdot \text{s}^{-2} = 10^5 \text{ N} \cdot \text{m}^{-2}$ = $10^5 \text{ Pa} = 10^2 \text{ kPa}$ = $10^6 \text{ (dyne)} \cdot \text{cm}^{-2}$ = $0.986923 \text{ (atm)}$ = $14.5038 \text{ (psia)}$ = $750.061 \text{ (torr)}$
Volume	$1 \text{ m}^3 = 10^6 \text{ cm}^3 = 10^3 \text{ liters}$ = 35.3147 (ft) <sup>3</sup> = 264.172 (gal)
Density	1 g·cm <sup>-3</sup> = $10^3$ kg·m <sup>-3</sup> = $62.4278$ (lb <sub>m</sub> )(ft) <sup>-3</sup>
Energy	$\begin{split} 1J &= 1kg\cdot m^2 \cdot s^{-2} = 1N\cdot m \\ &= 1m^3 \cdot Pa = 10^{-5}m^3 \cdot bar = 10cm^3 \cdot bar \\ &= 9.86923cm^3 \cdot (atm) \\ &= 10^7(dyne)\cdot cm = 10^7(erg) \\ &= 0.239006(cal) \\ &= 5.12197 \times 10^{-3}(ft)^3(psia) = 0.737562(ft)(lb_f) \\ &= 9.47831 \times 10^{-4}(Btu) = 2.77778 \times 10^{-7}kW\cdot h \end{split}$
Power	$\begin{array}{l} 1 \text{ kW} = 10^3 \text{ W} = 10^3 \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-3} = 10^3 \text{ J} \cdot \text{s}^{-1} \\ = 239.006 \text{ (cal)} \cdot \text{s}^{-1} \\ = 737.562 \text{ (ft)} (1\text{bp}) \cdot \text{s}^{-1} \\ = 0.947831 \text{ (Btu)} \cdot \text{s}^{-1} \\ = 1.34102 \text{ (hp)} \end{array}$

# Solution

The exact conversion factors are:

1 atm = 1.01325 bar

1 Btu = 1.055 kJ

1 hp = 0.7457 kW

1 inch = 2.54 cm

 $1 \text{ lb}_m = 0.45359 \text{ kg}$ 

1 mile = 1.6093 km

1 quart = 0.9464 liter

1 yard = 0.9144 m

Some other useful ones to remember are:

1 ft =  $30.48 \text{ cm} \approx 30 \text{ cm} = 0.3 \text{ m}$ ,

1 bar = 14.50 psi  $\approx$  15 psi, and

1 mile/hour =  $0.447 \text{ m/s} \approx 0.5 \text{ m/s}$ .

# **Solution 1.26**

# **Problem Statement**

Consider the following proposal for a decimal calendar. The fundamental unit is the decimal year (Yr), equal to the number of conventional (SI) seconds required for the earth to complete a circuit of the sun. Other units are defined in the following table. Develop, where possible, factors for converting decimal calendar units to conventional calendar units. Discuss pros and cons of the proposal.

Decimal Calendar Unit	Symbol	Definition
Second	Sc	10 <sup>-6</sup> Yr
Minute	Mn	10 <sup>-5</sup> Yr
Hour	Hr	10 <sup>-4</sup> Yr
Day	Dy	10 <sup>-3</sup> Yr
Week	Wk	10 <sup>-2</sup> Yr
Month	Mo	10 <sup>-1</sup> Yr
Year	Yr	

# Solution

There is a little ambiguity in the number of seconds per year, because of leap year, occasional addition of "leap-seconds", etc.

Solution continued on next page...

A reasonable number is 365.25 days\*24 hours/day\*60 min/hour\*60 s/min = 31557600 s. Using this value, the above decimal calendar units are

1 Sc = 31.6 s = 0.53 minutes

1 Mn = 316 s = 5.26 minutes

1 Hr = 3156 s = 52.6 minutes = 0.877 hour

1 Dy = 526 minutes = 8.77 hour = 0.365 days

1 Wk = 87.7 hour = 3.65 days

1 Mo = 36.5 days

An inherent problem with this, or any other, decimal calendar is that a calendar needs to accommodate multiple "natural" time scales – at least the period of rotation of the earth, so that day/night cycles are reflected in the time units and the period of the earth's orbit around the sun, so that seasonal changes are reflected in the time units. Such "natural" scales that govern our everyday experience are less prevalent for other dimensions, such as mass, length, etc.

#### Solution 1.27

# **Problem Statement**

Energy costs vary greatly with energy source: coal @ \$35.00/ton, gasoline @ a pump price of \$2.75/gal, and electricity @ 0.100/kWh. Conventional practice is to put these on a common basis by expressing them in  $GJ^{-1}$ . For this purpose, assume gross heating values of 29  $MJkg^{-1}$  for coal and 37  $GJm^{-3}$  for gasoline.

- (a) Rank order the three energy sources with respect to energy cost in  $\$\cdot GJ^{-1}$ .
- (b) Explain the large disparity in the numerical results of part (a). Discuss the advantages and disadvantages of the three energy sources.

# Solution

(a) The cost of coal per GJ is 25/ton / (907.2 kg/ton \* 0.029 GJ/kg) = \$0.95 / GJ.

The cost of gasoline is  $2/gal * 264.2 gal/m^3 / 37 GJ/m^3 = 14.30 / GJ$ .

The cost of electricity is 0.1 / (kW hr) / 0.0036 GJ/(kW hr) = 27.80 / GJ.

Coal is least expensive, electricity is most expensive.

(b) One can explain this in a variety of ways, but the underlying factor is that energy that is more convenient and/or more efficiently usable costs more. Electricity can be converted to mechanical energy (work) with nearly 100% efficiency (at least >90% in a well-designed electric motor). In contrast, a gasoline-burning internal combustion engine might have a typical efficiency of 30 to 35%. Thus, with the costs in part (a), and all other things being equal, an electric car might be more cost effective to operate than a gasoline-powered one, because the higher efficiency of energy use would more than make up for the higher cost per unit of energy input. This is what makes electric or plug-in hybrid vehicles (potentially) economical.

On the other hand, coal is inexpensive because it is very inconvenient to use. It cannot readily be used on a small scale, and is mostly consumed in large-scale industrial electricity generation and heating processes. A coal-fired power plant can convert about 1/3 of the energy of the coal into electricity. If that were the only cost of generating electricity, then with the costs in part (a), generating electricity from coal would be a very profitable business. However, the *consumer* electricity cost of \$0.10/kW\*hr reflects (along with profits) the costs of building the coal-fired power plant (although most US plants are old, and fully amortized) the cost of crushing and cleaning up the coal for combustion, the cost of pollution mitigation, and the cost of transmitting the power from the power plant to the customer. In mid-2020, the actual average coal cost for power generation was about \$2 /GJ, which leads to an electricity generation cost of something like \$0.03 per kW-hr, without including transmission costs, costs of pollution/cleanup, or capital costs of building the plant. However, coal cost varies widely by location and quality, from below \$1 /GJ for low-quality coal in a remote location, to above \$2 /GJ for higher-quality coal in a more desirable location.

#### Solution 1.28

# **Problem Statement**

Chemical-plant equipment costs rarely vary in proportion to size. In the simplest case, cost C varies with size S according to the *allometric* equation

$$C = \alpha S^{\beta}$$

The size exponent  $\beta$  is typically between 0 and 1. For a wide variety of equipment types it is approximately 0.6.

(a) For  $0 < \beta < 1$ , show that cost per *unit size* decreases with increasing size. ("Economy of scale.")

(b) Consider the case of a spherical storage tank. The size is commonly measured by internal volume  $V_i^t$  Show why one might expect that  $\beta = 2/3$ . On what parameters or properties would you expect quantity  $\alpha$  to depend?

# **Solution**

(a) The cost per unit size is  $C/S = \alpha S^{\beta}/S = \alpha S^{\beta-1}$ . If  $\beta$  is less than 1, then the exponent  $(\beta - 1)$  is negative, and the cost per size decreases with increasing size (S).

(b) To a good first approximation, the cost of the tank should be proportional to the amount (mass) of material required to construct the tank.

If the wall thickness, t, is independent of the tank volume, and is small compared to the tank diameter, then the mass of material required to make the tank will be  $m = \rho^* t^* \pi d^2$ , where d is the diameter of the spherical tank and  $\rho$  is the density of the material from which it is constructed.

The tank volume is  $V_t^t = \pi d^3/6$ .

Or, writing the diameter in terms of the volume,  $d = (6 V_t^t \pi)^{1/3}$ .

Substituting this into the expression for the mass of material gives

$$m = \rho^* t^* \pi^* (6 V_t^t / \pi)^{2/3} = \rho^* t^* (36/\pi)^{1/3} V_t^{t/2/3}$$

This shows that the exponent should be approximately  $\beta$  = 2/3. It also shows that the cost should depend on the thickness of the tank walls, which will, in turn, depend on the maximum pressure that the tank must be able to withstand. Other factors that will influence the quantity  $\alpha$  should include the material of construction and the fabrication techniques used. The material of construction will depend on the need for corrosion resistance and other such factors.

# Solution 1.29

#### **Problem Statement**

A laboratory reports the following vapor-pressure ( $P^{\text{sat}}$ ) data for a particular organic chemical:

t∕°C	<i>P</i> sat∕kPa
-18.5	3.18
-9.5	5.48
0.2	9.45
11.8	16.9
23.1	28.2
32.7	41.9
44.4	66.6
52.1	89.5
63.3	129.
75.5	187.

Correlate the data by fitting them to the Antoine equation:

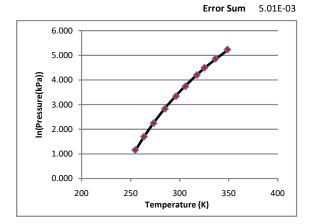
$$\ln P^{\text{sat}} / kPa = A - \frac{B}{T / K + C}$$

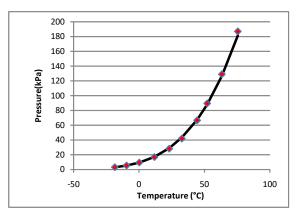
That is, find numerical values of parameters *A*, *B*, and *C* by an appropriate regression procedure. Discuss the comparison of correlated with experimental values. What is the predicted normal boiling point (i.e. temperature at which the vapor pressure is 1(atm)) of this chemical?

# Solution

This can be done using many different software packages. The Microsoft Excel spreadsheet shown below illustrates one way of doing such nonlinear regression:

Α	В	C					
12.74	2017.87	-80.87					
T (°C)	T(K)	P <sup>sat</sup> (kPa)	In (P <sup>sat</sup> )	In (P <sup>sat</sup> ) <sub>fit</sub>	Error <sup>2</sup>	P <sup>sat</sup> (kPa)	Relative Error
-18.5	254.65	3.18	1.157	1.125	1.02E-03	3.08	-3.2%
-9.5	263.65	5.48	1.701	1.697	2.03E-05	5.46	-0.4%
0.2	273.35	9.45	2.246	2.253	4.77E-05	9.52	0.7%
11.8	284.95	16.9	2.827	2.849	4.61E-04	17.27	2.2%
23.1	296.25	28.2	3.339	3.368	7.96E-04	29.01	2.9%
32.7	305.85	41.9	3.735	3.767	1.02E-03	43.26	3.3%
44.4	317.55	66.6	4.199	4.211	1.43E-04	67.40	1.2%
52.1	325.25	89.5	4.494	4.479	2.24E-04	88.17	-1.5%
63.3	336.45	129	4.860	4.841	3.50E-04	126.61	-1.9%
75.5	348.65	187	5.231	5.201	9.19E-04	181.42	-3.0%





The first and third columns have the data given in the problem statement. The second column has the temperature in K, and the  $4^{th}$  column has the natural logarithm of the vapor pressure data. The fifth column has the result of

$$\ln P^{\text{sat}} / \text{kPa} = A - \frac{B}{T / K + C}$$

With parameters A, B, and C as shown at the top of the spreadsheet. The sixth column has the square of the difference between the actual and model values of  $\ln(P^{\text{sat}})$  (column 5 – column 4)<sup>2</sup>. The cell labeled "Error Sum" has the sum of those differences. The Solver function in MS Excel was used to minimize that cell (the sum of the squares of the differences between the data and fit values) by simultaneously varying the values of A, B, and C.

The 6<sup>th</sup> column has the vapor pressure predicted by the fit, and the 7<sup>th</sup> column has the relative error in the vapor pressure at each point, which is (fit value – actual value)/actual value. The two plots show the data and fit in two formats, in each case with the data as discrete points and the fit as a smooth curve. The one on the left is what is actually used in the fitting. That is, the sum of the squares of the distances between the points and the curve was minimized to obtain the parameters. The one on the right shows the data and fit in the original format in which the data was given.

The boiling point is the temperature at which  $P^{\text{sat}} = 101.325$  kPa. If one already has the spreadsheet shown above, then the simplest way to determine this is to vary one of the temperatures until the fitted pressure is equal to 101.325 kPa. This gives a value of 56.3 °C.