EVERYDAY EXAMPLES OF ENGINEERING CONCEPTS

T9: Non-reacting mixtures

This is an extract from 'Real Life Examples in Thermodynamics: Lesson plans and solutions' edited by Eann A. Patterson, first published in 2010 (ISBN: 978-0-9842142-1-1*) and contains suggested exemplars within lesson plans for Sophomore Thermodynamics Courses. They were prepared as part of the NSF-supported project (#0431756) entitled: "Enhancing Diversity in the Undergraduate Mechanical Engineering Population through Curriculum Change".*

INTRODUCTION

(from *'Real Life Examples in Thermodynamics: Lesson plans and solutions'*)

These notes are designed to enhance the teaching of a sophomore level course in thermodynamics, increase the accessibility of the principles, and raise the appeal of the subject to students from diverse backgrounds. The notes have been prepared as skeletal lesson plans using the principle of the 5Es: Engage, Explore, Explain, Elaborate and Evaluate. The 5E outline is not original and was developed by the Biological Sciences Curriculum Study[1] in the 1980s from work by Atkin & Karplus[2] in 1962. Today this approach is considered to form part of the constructivist learning theory[3].

These notes are intended to be used by instructors and are written in a style that addresses the instructor, however this is not intended to exclude students who should find the notes and examples interesting, stimulating and hopefully illuminating, particularly when their instructor is not utilizing them. In the interest of brevity and clarity of presentation, standard derivations, common tables/charts, and definitions are not included since these are readily available in textbooks which these notes are not intended to replace but rather to supplement and enhance. Similarly, it is anticipated that these lesson plans can be used to generate lectures/lessons that supplement those covering the fundamentals of each topic.

This is the third in a series of such notes. The others are entitled 'Real Life Examples in Mechanics of Solids' (ISBN: 978-0-615-20394-2), 'Real Life Examples in Dynamics'(ISBN: 978-0-9842142-0-4).

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[1] Engleman, Laura (ed.), *The BSCS Story: A History of the Biological Sciences Curriculum Study*. Colorado Springs: BSCS, 2001.
[2] Atkin, J. M. and Karplus, R. (1962). Discovery or invention? *Science Teacher* 29(5): 45.
[3] e.g. Trowbridge, L.W., and Bybee, R.W., *Becoming a secondary school science teacher*. Merrill Pub. Co. Inc., 1990.

THERMODYNAMIC APPLICATIONS

9. Topic**: Non-reacting mixtures**

Engage:

Take a CO_2 fire extinguisher into class and discharge it for a short period to produce a cloud of white gas. This is spectacularly noisy and so will attract the attention of the students. The unit responsible for maintaining fire extinguishers in your institution will almost certainly have one that they will lend you, or may come to class and do the demonstration for you.

Explore:

Discuss with the students that air is a mixture of gases including oxygen (typically about 21%), nitrogen (about 79%), and other gases such as argon and carbon dioxide in very small concentrations. For instance, carbon dioxide is present in the atmosphere at approaching 385 parts per million or 0.000385%; so by discharging a relatively large amount of CO_2 from the fire extinguisher a local step-change in the concentration is produced. Of course carbon dioxide is heavier than oxygen so it initially settles on the floor which would shut off the supply of oxygen from a fire and hence halt the combustion process.

The carbon dioxide and the other gases in the atmosphere do not react with one another but are mixed together as a result of the second law of thermodynamics which ensures a gradual process of dispersion to achieve maximum entropy as in the case of the balloons in lesson 4. So the carbon dioxide from the fire extinguisher will not stay on the floor but will gradually disperse and mix with the oxygen and nitrogen in the air.

Explain:

Define the apparent molecular weight, *M* of such a mixture as simply the sum of the products of the molar fraction and molecular weight of each component.

$$M = \sum_{i=1}^{j} y_i M_i$$

where y_i is the molar fraction and M_i the molar weight of the *i*th component. Also, by definition, the apparent molecular weight is ratio of the mass of a substance, *m* to the number of moles, *N* i.e. $M = m/N$.

Discuss that in an ideal gas, molecules are sufficiently sparsely populated that the behavior of one molecule does not influence another. Explain that real gases can closely approximate this behavior when they are at low pressure or high temperatures relative to their critical point, such that

$$PV = ZRT$$

where Z is the compressibility factor. To obtain the compressibility factor, most charts are based on the reduced pressure and reduced temperature which are the actual absolute pressure and temperature values divided by the critical pressure and temperature of fluid species being studied. A typical compressibility chart can be found at: http://www.ent.ohiou.edu/~thermo/property_tables/gas/Zfactor.html

For mixtures, Dalton's law assumes that each component of a gas behaves as an ideal gas as if it were alone at the temperature and volume of the mixture, i.e.,

$$P_{mixture} = \sum_{i=1}^{k} P_i\left(T_{mixture}, V_{mixture}\right)$$

And there is a corresponding relationship for volume known as Amagat's law

$$V_{mixture} = \sum_{i=1}^{k} P_i\left(T_{mixture}, P_{mixture}\right)$$

Elaborate:

The entropy change during the mixing of gases such as occurred after the fire extinguisher was discharged can be shown to be

$$\Delta S_{mixing} = \sum_i N_i\left(\left(s_F\right)_i - \left(s_I\right)_i\right) = -R_u \sum_i N_i \ln y_i$$

where N_i is the number of moles of the ith component of the mixture, s_I and s_F are the initial and final specific entropies, y_i is the mole fraction of the ith component and R_u is the universal gas constant. This can be used to calculate the minimum energy required to separate fluids by assuming the mixing is reversible, i.e. that the work required for separation is equal to the exergy destroyed in mixing

$$W_{\min} = X_{destroyed} = T_0 S_{generated} = -R_u T_0 \sum_i n_i \ln y$$

In order to sequestrate carbon dioxide generated during the combustion process in power stations, it is necessary to separate it from the exhaust gases. If we assume that the mole fraction of carbon dioxide is one third and the separation is to be performed at 100°C (after cooling of the gases in a heat exchanger) then

$$\frac{W_{\min}}{n} = -8.314 \times 373 \times 1 \times \ln 0.3 = 3734 \,\text{J/mol}$$

And since a mole of carbon dioxide has a molecular mass, M = 44 (=12+(16×2)) and $M = m/n$ so substituting:

$$\frac{W_{\min}}{m} = 3734 \times 44 = 164 \,\text{kJ/kg}$$

You can look up the carbon dioxide production and generating capacity for your local power plant at http://carma.org/dig/show/energy+plant. Using data for the editor's local coal-fired power-station which generates 0.83 kg of CO_2 per MJ of power so, assuming an ideal process, 13.6% (=0.83×164/1000) of the energy generated would be required to sequestrate the carbon dioxide it produces.

Evaluate:

Invite students to attempt the following examples:

<u>*Example 9.1*</u>

Determine the minimum daily power required to obtain enough fresh water for your needs from seawater.

<u>Solution</u>

The minimum energy required is obtained by assuming the mixing of fresh water and sea water is reversible, i.e. work required for separation is equal to the exergy destroyed on mixing

$$W_{\min} = X_{destroyed} = T_0 S_{generated} = -R_u T_0 \sum_i N_i \ln y$$

The average salinity of seawater is 3.5% by mass so the mass fraction of salt, $(m_f)_{salt} = 0.035$ and of water is $(m_f)_{H_2O} = 0.965$ (=1-0.035); and the molecular masses of salt and water are 58.44 and 18 respectively; so for the mixture

$$M_{mixture} = \frac{m_{mixture}}{N_{mixture}} = \frac{m_{mixture}}{\sum m_i / M_i} = \frac{1}{\sum m_i / (M_i m_{mixture})} \text{ and } (m_f)_i = {}^{m_i}\!/_{m_{mixture}}$$

So $$M_{mixture} = \frac{1}{\sum m_i / (M_i m_{mixture})} = \frac{1}{\sum ((m_f)_i / M_i)} = \frac{1}{\frac{0.035}{58.44} + \frac{0.965}{18.0}} = 18.45$$

And the mole fraction of water is given by

$$y_{H_2O} = (m_f)_{H_2O} \frac{M_{mixture}}{M_{H_2O}} = 0.965 \times \frac{18.45}{18.0} = 0.989$$

Now, when the number of moles in a mixture of A and B, $N_{mixture} = N_A + N_B$ and N_A>>1, the minimum work to separate 1 mol of substance A from a mixture of $N_{mixture}$ mols is the difference between minimum work required to separate the initial mixture and the minimum work required to separate the remaining mixture, i.e., with 1 kmol removed, which is

$$(W_{\min})_{1kmol} = -R_u T_0 (N_A \ln y_A + N_B \ln y_B) + -R_u T_0 ((N_A - 1) \ln y_A + N_B \ln y_B) = -R_u T_0 \ln y_A$$

So for 1kmol of fresh water at 21°C, the minimum work will be

$$(W_{\min})_{H_2O} = -R_u T_0 \ln y_{H_2O} = R_u T_0 \ln (1/y_{H_2O}) = 8.314 \times 294 \times \ln(1/0.989) = 27.2 \text{ kJ/kmol}$$

In 2000, the per capita average usage of water in the United States was 1,430 gallons per day[4]; this is equivalent to 5.413 m^3 or 5415kg which is 301kmols (=5415/18), so to produce each persons daily requirement by desalination would require

$$\text{Minimum energy required } = 27.0 \times 301 = 8183\,\text{kJ [per day per person]}$$

This 2.273kWh (=8183/3600) each day for every person or 0.42kWh/m^3 (=2.273/5.413) which compares to 3 to 28 kWh/m^3 for typical (non-ideal) industrial plants[5].

Example 9.2

Consider landfill gas at 30°C being pumped into a tanker truck with a volume capacity of 25m^3 and design pressure of 1.77MPa. If a molar analysis of the landfill gas has shown it to be 52% methane (M=16); 46% carbon dioxide (M=44); and 2% hydrogen (M=2) then calculate the apparent molecular weight, M.

Solution:

$$M = \sum_{i=1}^{j} y_i M_i = (0.52 \times 16) + (0.46 \times 44) + (0.02 \times 2) = 28.6\,\text{kg/kmol}$$

where y_i is the mole fraction and M_i the molar weight of the ith component. If we assume the mixture to be an ideal gas then

$$N_{mixture} = \frac{(PV)_{mixture}}{R_u T_{mixture}} = \frac{(1.77 \times 10^6) \times 25}{8.314 \times 308} = 17280\,\text{mols}$$

And by definition the apparent molecular weight is the ratio of the mass of the mixture to the number of moles, so the mass of the mixture in the tanker is

$$m = MN = 28.6 \times 17.280 = 494\,\text{kg}$$

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[4] http://ga.water.usgs.gov/edu/wateruse2000.html

[5] Encyclopedia of Desalination and Water Resources (DESWARE), UNESCO Encyclopedia of Life Support Systems (EOLSS), www.desware.net/desa4.aspx