

# 24

## **Term Projects (2): Stoichiometry**

- 24.1 A Vapor Pressure Equation
- 24.2 Chemical Plant Solid Waste

## Term Project 24.1

### A Vapor Pressure Equation

Consider the molecules of a pure liquid substance such as water standing in a container. The attractive forces acting among them tend to keep them together. The kinetic energy associated with their thermal motions tends to separate them from one another. As long as the average energy of attraction exceeds the average kinetic energy of translation, the molecules remain mainly in the condensed, liquid phase. Although the *average* velocity and *average* kinetic energy of translation per molecule is fixed for any temperature, the velocities of individual molecules differ over wide limits owing to increments of energy momentarily lost or acquired during the chaotic inter-particle collisions.

A molecule in the interior of the liquid is acted upon from all sides by the attractive forces exerted by its neighbors, but conditions are quite different at the surface. There is nothing above the liquid's surface except vapor and, perhaps, air. Based on the fact that at room temperature a gmol of water occupies roughly 18 ml in the liquid state and over 24,000 ml in the vapor state, one realizes just how sparsely populated the space above the surface or interface is. As a consequence, there is a net inward pull exerted on any molecule occupying the surface, which accounts for the phenomenon of surface tension. It follows that in order for a molecule to be at the surface at all it must acquire energy in excess of the average. This extra energy is the so called *free surface energy* and it may be visualized as the work required to move the molecule from the interior to the surface against the net inward pull.

If, in the course of the thermally induced intermolecular collisions, several molecules converge by chance of one being near the surface and hit from below simultaneously, it may impart sufficient kinetic energy to propel the other through the interface and out into the relatively empty space above. It follows that whatever molecules escape into the vapor phase are highly energized compared with those in the liquid phase. Thus, one can visualize the latent heat of vaporization from the fact that even under conditions where liquid represents the normal physical state of aggregation, some of the molecules nonetheless attain the vapor state.

If the space above the liquid is sealed off and the system is held at constant temperature, equilibrium is soon established between the liquid and its vapor, with molecules leaving and returning from each phase at the *same* rate from each unit of surface area. The space above the liquid now holds the greatest concentration of vapor molecules possible at the temperature

in question. In other words, it is saturated with vapor and there is, exerted on the walls on the container a characteristic and constant pressure called *vapor pressure* or *equilibrium vapor pressure* or *saturation pressure*. This pressure is independent of the size of the area exposed, the amount of liquid present just so long as *some* is present, or the shape of the container. Only upon changing the temperature does this characteristic equilibrium vapor pressure change; it increases with rise in temperature and decreases with fall in atmosphere pressure, the result is a temperature. When the vapor pressure of a liquid in an open vessel reaches atmospheric pressure, the result is a turbulent escape of molecules from the liquid, called *ebullition* or *boiling*. The temperature at which the liquid attains a vapor pressure of 760 mm Hg is defined as the *normal boiling point* [1].

The vapor pressure of a liquid depends on the magnitude of the forces of attraction acting among its molecules. These forces in turn depend upon molecular size, shape, and composition. At any given temperature, every liquid possesses a unique latent heat of vaporization as well as a unique vapor pressure; and although, as one would predict from molecular theory—the heat of vaporization decreases and the vapor pressure increases with rise in temperature—the function relating these variable is complex.

Vapor pressure data are available in the literature [2,3]. However, there are two equations that can be used in lieu of actual vapor pressure information—the Clapeyron equation and the Antoine equation. The two-coefficient Clapeyron equation is given by

$$\ln p' = A - (B/T) \quad (24.1)$$

where  $p'$  and  $T$  are the vapor pressure and temperature, respectively. The three-coefficient Antoine equation is given by

$$\ln p' = A - B/(T + C) \quad (24.2)$$

Note that for both equations, the units of  $p'$  and  $T$  *must* be specified for given values of  $A$  and  $B$  and/or  $C$ . Values of the Clapeyron equation coefficients— $A$  and  $B$ —are provided in Table 24.1 for some compounds [4]. Some Antoine equation coefficients— $A$ ,  $B$ , and  $C$ —are listed in Table 24.2. Additional values for these coefficients for both equations are available in the literature [2,3].

There is debate as to which of the two equations is “better” from a statistical [4,5] and calculation perspective. These questions suggest that a better model/equation(s) can be developed to describe vapor pressure variation with temperature.

**Table 24.1** Approximate Clapeyron Equation Coefficients\*

	A	B
Acetaldehyde	18.0	$3.32 \times 10^3$
Acetic anhydride	20.0	$5.47 \times 10^3$
Ammonium Chloride	23.0	$10.0 \times 10^3$
Ammonium cyanide	22.9	$11.5 \times 10^3$
Benzyl alcohol	21.9	$7.14 \times 10^3$
Hydrogen peroxide	20.4	$5.82 \times 10^3$
Nitrobenzene	18.8	$5.87 \times 10^3$
Nitromethane	18.5	$4.43 \times 10^3$
Phenol	19.8	$5.96 \times 10^3$
Tetrachloroethane	17.5	$4.38 \times 10^3$

\*T in K, p' in mmHg.

**Table 24.2** Antoine Equation Coefficients\*

	A	B	C
Acetone	14.3916	2795.82	230.00
Benzene	13.8594	2773.78	220.07
Ethanol	16.6758	3674.49	226.45
n-Heptane	13.8587	2911.32	216.64
Methanol	16.5938	3644.30	239.76
Toluene	14.0098	3103.01	219.79
Water	16.2620	3799.89	226.35

\*T in °C, p' in kPa.

Based on the above, you are requested to develop another (and hopefully better) vapor pressure equation. Once the equation(s) has been generated, perform a comparative analysis (for numerous species) between your equation and that of Clapeyron and Antoine. Also, comment on the results.

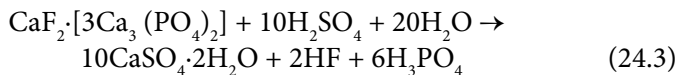
## Term Project 24.2

### Chemical Plant Solid Waste

There are four general categories of solid waste sources in chemical plants [6].

1. *Inorganic by-products or unused portions of raw materials.* These wastes are most common in plants that process inorganic materials. For instance, the production of phosphoric acid leaves behind large quantities of minerals from which the phosphates have been leached by sulfuric acid.
2. *Solid organic waste materials.* These include such things as off-spec polymers and impure or off-spec crystalline organic products.
3. *Heavy residues and sludges.* Though not strictly solids, these are heavy materials which accumulate in tank bottoms and still bottoms, or materials that are created in treating waste water.
4. *Auxiliary solid waste materials.* These are materials not directly involved in the chemical processes as products or reactants. They include such things as spent catalysts, packaging materials, old pipe and process equipment, etc.

In the wet-acid process, phosphoric acid and by-product hydrofluoric acid are made by treating phosphate rock with sulfuric acid. The overall chemical reaction is:



The rock feed contains 90% by weight  $\text{CaF}_2 \cdot [3\text{Ca}_3(\text{PO}_4)_2]$ , the remainder is insoluble rock of varying composition.

You have been hired to address the separation problem associated with the three products produced in the reaction. In addition, you are requested to develop a plan/procedure to convert and/or use the waste generated in the process.

### Reference

1. Personal communication to L. Theodore, source unknown, approximately 1965-1970.
2. L. Theodore, *Chemical Engineering: The Essential Reference*, McGraw-Hill, New York City, NY, 2014.

3. L. Theodore, F. Ricci, and T. VanVliet, *Thermodynamics for the Practicing Engineer*, John Wiley & Sons, Hoboken, NJ, 2009.
4. J. Kibuthu: Thermodynamics class assignment submitted to L. Theodore, Manhattan College, Bronx, NY, 2004.
5. S. Shaefer and L. Theodore, *Probability and Statistics Applications in Environmental Science*, CRC Press/ Taylor & Francis Group, Boca Raton, FL, 2007.
6. D. Kauffman, *Process Synthesis and Design*, A Theodore Tutorial, Theodore Tutorials, East Williston, NY, originally published by the USEPA/APTI, RTP, NC, 1992.