

CHEM 3410: Physical Chemistry I — Fall 2009

September 2, 2009

Lecture 1: Introduction and Thermodynamic Variables

References

1. Levine, *Physical Chemistry*, Sections 1.1–1.10

Key Concepts

- Thermodynamics will help us describe how systems and when systems approach equilibrium. Kinetics will give us insight into the at which this happens. The two are connected and are complementary.
- To describe a system consisting of an ideal gas we need to determine values for the thermodynamic parameters or variables: P, V, T, n .
- All of these variables are linked through the equation of state known as the ideal gas law:

$$PV = nRT$$

- Assuming that we fix the number of moles at $n = 1$, then we can write volume as a function of temperature and pressure:

$$V(T, P) = \frac{RT}{P}$$

- If we want to consider how the volume changes when the pressure and temperature change, we can take advantage of the fact that the order in which we change the T and P doesn't matter (i.e. it is an exact differential):

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

where dV is the infinitesimal change in volume resulting from an infinitesimal change in pressure (dP) and temperature (dT).

- $\left(\frac{\partial V}{\partial P}\right)_T dP$ is how the volume changes when the pressure is changed. We use this to define the isothermal compressibility as:

$$\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T$$

- Similarly, $\left(\frac{\partial V}{\partial T}\right)_P$ is how the volume changes when the temperature is changed. We use this to define volumetric thermal expansion as:

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

- We can actually evaluate these derivatives since we have a functional form for $V(T, P)$

$$\left(\frac{\partial V}{\partial P}\right)_T = -\frac{RT}{P^2}$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$$

Related Exercises in Levine

Exercises 1.37, 1.49, 1.52