CYL 110: 2009-2010 Thermodynamics Tutorial 1
11th – 15th January 2010

1. Dieterici's equation of state for a gas is $\mathrm{P}(\overline{\mathrm{V}} - \mathrm{b})\exp(\mathrm{a}/\mathrm{R}\overline{\mathrm{V}}\,\mathrm{T}) = \mathrm{RT}$, where a, b, and R are constants. (a) Determine $(\partial \mathrm{V}/\partial \mathrm{T})$, $(\partial \mathrm{T}/\partial \mathrm{P})$, and $(\partial \mathrm{P}/\partial \mathrm{V})$ and verify that $\left(\frac{\partial \mathrm{V}}{\partial \mathrm{T}}\right)\left(\frac{\partial \mathrm{T}}{\partial \mathrm{P}}\right)\left(\frac{\partial \mathrm{P}}{\partial \mathrm{V}}\right) = 1$.(b) Show that the Dieterici critical constants are
$$p_c = \frac{a}{4b^2}\, e^{-2}, \quad V_c = 2b, \quad T_c = \frac{a}{4Rb}$$

2. Deviation coefficients for real gases are defined as $\frac{T}{P}\left(\frac{\partial P}{\partial T}\right)_V, \frac{P}{R}\left(\frac{\partial V}{\partial T}\right)_P, \frac{P^2}{R}\left(\frac{\partial V}{\partial P}\right)_T$. Calculate these values for an ideal gas, a van der Waals gas, and a Dieterici gas.

3. (a) Express the van der Waals equation of state in virial form $\mathrm{P}\overline{\mathrm{V}} = \mathrm{RT} + \mathrm{B}\left(\frac{1}{\overline{\mathrm{V}}}\right) + \mathrm{C}\left(\frac{1}{\overline{\mathrm{V}}}\right)^2 + \cdots$ and determine B and C in terms of a and b. (b) Use the virial form of the van der Waals equation to determine the Boyle temperature.

4. The critical pressure and temperature for hydrogen are 1.30 MPa and 33.2 K. Calculate the a and b parameters of the Redlich-Kwong equation $\left[P + \frac{a}{T^{1/2}\bar{V}(\bar{V}+b)}\right](\bar{V} - b) = RT$.

5. Assume that oxygen (Tc = 154.6K, Pc = 5.046 x 10^6 Pa, Vc = 7.32 x 10^{-5} m^3/mol) and water (T_c = 647.3K, P_c = 2.205 x 10^7 P_a, V_c = 5.6 x 10^{-5} m^3/mol) can be considered as van der Waals fluids. a) Find the value of the reduced volume both fluids would have at T_r = 3/2 and P_r = 3. b) Find the T, P, and V of each gas at T_r = 3/2 and P_r = 3. c) If oxygen and water are both at 200 °C and 2.5 x 10^6 Pa, find their specific volumes.

6. A quantity of 0.850 mol of an ideal gas initially at a pressure of 15 atm and 300 K is allowed to expand isothermally until its final pressure is 1 atm. Calculate the work done if the expansion is carried out (a) against a vacuum, (b) against a constant external pressure of 1 atm, and (c) reversibly. (d) Calculate also the work done if the same process is carried out adiabatically and reversibly and comment on the difference.

7. Show that for an ideal gas $dq = C_V dT + RTd\ln V$ is not an exact differential, but $dz = C_V d\ln T + Rd\ln V$ is an exact differential.

8. A kettle containing 1 kg of boiling water is heated until evaporation is complete. Calculate w, q, ΔU for this process. Assume water vapour behaves ideally.

9. (a) Write the expression for *dV* given that *V* is a function of *p* and *T*. deduce an expression for *d*(*lnV*) in terms of the expansion coefficient α and the isothermal compressibility κ_T.
   (b) Show that $(\partial p/\partial T)_V = \alpha/\kappa_T$.
   (c) Evaluate the ratio for a perfect gas.
   (d) For a van der Waals gas, show that $\kappa_T R = \alpha(\bar{V} - b)$.

10. When a fluorocarbon gas was allowed to expand reversibly and adiabatically to twice it volume the temperature fell from 298.15 to 248.44 K and its pressure fell from 1522.2 Torr to 613.85 Torr. Evaluate C_v and C_p. You may assume that the gas behaves perfectly.

11. Over narrow range of temperature and pressure, the differential expression for the volume of a fluid as a function of temperature and pressure can be integrate to obtain $V = K\, e^{-\alpha T} e^{-\kappa T}$. Show that V is a state function.

12. One mole of chlorine undergoes adiabatic expansion from 1 dm^3 to a 10 dm^3 against an external pressure of 0.1013 Mpa. What is the final temperature of gas? a = 665 dm^6 Kpa mol^{-2}, b = 0.055 $dm^3 mol^{-1}$and $C_{V,m}$ = 33.91 JK^{-1} mol^{-2}

13. A constant-volume perfect gas thermometer indicates a pressure of 6.69 kPa at the triple point temperature of water (273.16 K). (a) What change of pressure indicates a change of 1.00 K at this temperature? (b) What pressure indicates a temperature of 100.00°C? (c) What change of pressure indicates a change of 1.00 K at the latter temperature?