

**CYL 110: 2012-2013**  
**Thermodynamics Tutorial 1**

- Dieterici's equation of state for a gas is  $P(\bar{V} - b)\exp(a/R\bar{V}T) = RT$ , where  $a$ ,  $b$ , and  $R$  are constants. (a) Determine  $(\partial V / \partial T)$ ,  $(\partial T / \partial P)$ , and  $(\partial P / \partial V)$  and verify that  $(\frac{\partial V}{\partial T})(\frac{\partial T}{\partial P})(\frac{\partial P}{\partial V}) = 1$ . (b) Show that the Dieterici critical constants are
 
$$p_c = \frac{a}{4b^2} e^{-2}, \quad V_c = 2b, \quad T_c = \frac{a}{4Rb}$$
- Deviation coefficients for real gases are defined as  $\frac{T}{P}(\frac{\partial P}{\partial T})_V$ ,  $\frac{P}{R}(\frac{\partial V}{\partial T})_P$ ,  $\frac{P^2}{R}(\frac{\partial V}{\partial P})_T$ . Calculate these values for an ideal gas, a van der Waals gas, and a Dieterici gas.
- (a) Express the van der Waals equation of state in virial form  $P\bar{V} = RT + B(\frac{1}{\bar{V}}) + C(\frac{1}{\bar{V}})^2 + \dots$  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.
- 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  $[P + \frac{a}{T^{1/2}V(V+b)}](\bar{V} - b) = RT$ .
- Assume that oxygen ( $T_c = 154.6\text{K}$ ,  $P_c = 5.046 \times 10^6 \text{ Pa}$ ,  $V_c = 7.32 \times 10^{-5} \text{ m}^3/\text{mol}$ ) and water ( $T_c = 647.3\text{K}$ ,  $P_c = 2.205 \times 10^7 \text{ Pa}$ ,  $V_c = 5.6 \times 10^{-5} \text{ m}^3/\text{mol}$ ) 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  $200^\circ\text{C}$  and  $2.5 \times 10^6 \text{ Pa}$ , find their specific volumes.
- 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.
- Show that for an ideal gas  $dq = C_V dT + RT d \ln V$  is not an exact differential, but  $dz = C_V d \ln T + R d \ln V$  is an exact differential.
- A kettle containing 1 kg of boiling water is heated until evaporation is complete. Calculate  $w$ ,  $q$ ,  $\Delta U$  for this process. Assume water vapour behaves ideally.
- (a) Write the expression for  $dV$  given that  $V$  is a function of  $p$  and  $T$ . deduce an expression for  $d(\ln V)$  in terms of the expansion coefficient  $\alpha$  and the isothermal compressibility  $\kappa_T$ .  
(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  $\kappa_T R = \alpha(\bar{V} - b)$ .
- When a fluorocarbon gas was allowed to expand reversibly and adiabatically to twice its 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.
- 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 integrated to obtain  $V = K e^{-\alpha T} e^{-\kappa T}$ . Show that  $V$  is a state function.
- One mole of chlorine undergoes adiabatic expansion from  $1 \text{ dm}^3$  to  $10 \text{ dm}^3$  against an external pressure of 0.1013 Mpa. What is the final temperature of gas?  $a = 665 \text{ dm}^6 \text{ Kpa mol}^{-2}$ ,  $b = 0.055 \text{ dm}^3 \text{ mol}^{-1}$  and  $C_{V,m} = 33.91 \text{ JK}^{-1} \text{ mol}^{-2}$
- 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  $100.00^\circ\text{C}$ ? (c) What change of pressure indicates a change of 1.00 K at the latter temperature?

14. Derive a general relation between  $C_p$  and  $C_v$  to get the general result

$$C_p - C_v = \left[ P + \left( \frac{\partial U}{\partial V} \right)_T \right] \left( \frac{\partial V}{\partial T} \right)_p$$

15. Show for a van der Waals gas  $C_p - C_v = \alpha^2 TV / \kappa_T$ . You will need to use an identity (to be derived later in this course)
- $$\pi_T = T \left( \frac{\partial P}{\partial T} \right)_V - P$$

16. A mole of ideal gas is compressed adiabatically to one-half of its original volume when the temperature of the gas is increased from 273 K to 433 K. Assuming  $\overline{C}_V$  is independent of the temperature, calculate the value of  $\overline{C}_V$  for this gas.

17. Show that the work involved in a reversible, adiabatic pressure change of one mole of an ideal gas is given by

$$w = c_V T_1 \left[ \left( \frac{P_2}{P_1} \right)^{R/C_p} - 1 \right]$$

where  $T_1$  is the initial temperature and  $P_1$  and  $P_2$  are the initial and final pressures, respectively.

18. A sample of 1.00 mol perfect gas molecules with  $C_{p,m} = 7/2R$  is put through the following cycle: (a) Constant volume heating to twice its initial volume, (b) Reversible, adiabatic expansion back to its initial temperature, (c) reversible isothermal compression back to 1.00 atm. Calculate  $q$ ,  $w$ ,  $\Delta U$ , and  $\Delta H$  for each step and overall.

19. Take nitrogen to be a van der Waals gas with  $a = 1.390 \text{ dm}^6 \text{ atm mol}^{-2}$  and  $b = 0.03913 \text{ dm}^3 \text{ mol}^{-1}$ , and calculate  $\Delta H_m$  when the pressure on the gas is decreased from 500 atm to 1.00 atm at 300 K. For a van der Waals gas,  $\mu_{JT} = \{(2a/RT) - b\}/C_{p,m}$ . Assume  $C_{p,m} = 7/2R$ .

20. (a) What is the total differential of  $z = x^2 + 2y^2 - 2xy + 2x - 4y - 8$ ? (b) Show that  $\partial^2 z / \partial y \partial x = \partial^2 z / \partial x \partial y$  for this function. (c) Let  $z = xy - y + \ln x + 2$ . Find  $dz$  and show that it is exact.

21. Calculate the work done during the isothermal reversible expansion of a gas that satisfies the virial equation of state,  $P\overline{V} = RT + B\left(\frac{1}{\overline{V}}\right) + C\left(\frac{1}{\overline{V}}\right)^2 + \dots$ . Evaluate (a) the work for 1.0 mol Ar at 273 K ( $B = -21.7 \text{ cm}^3 \text{ mol}^{-1}$ ) and (b) the same amount of a perfect gas. Let the expansion be from  $500 \text{ cm}^3$  to  $1000 \text{ cm}^3$  in each case.

22. A gas obeys the equation of state  $V_m = RT/p + aT^2$  and its constant-pressure heat capacity is given by  $C_{p,m} = A + BT + Cp$ , where  $a$ ,  $A$ ,  $B$ , and  $C$  are constants independent of  $T$  and  $p$ . Obtain expressions for (a) the Joule-Thomson coefficient and its constant-volume heat capacity.

23. Calculate the heat needed to raise the temperature of air in a house from 20 to 25 °C. Assume that the house contains  $600 \text{ m}^3$  of air, which should be taken to be a perfect diatomic gas. The density of air is  $1.21 \text{ kg m}^{-3}$  at 20 °C Calculate  $\Delta U$  and  $\Delta H$  for the heating of the air.

24. Find the maximum inversion temperature of the gas whose equation of state is  $\left(P + \frac{x}{TV^2}\right)(V - y) = RT$  where  $x$  and  $y$  are constants.

25. When a fluorocarbon gas was allowed to expand reversibly and adiabatically to twice its 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.

26. Verify that the enthalpy of a perfect gas is independent of its pressure while it is dependent upon pressure for a van der Waals gas. [Use the approximate form of van der Waals equation  $PV = nRT + nP(b - a/RT)$ ].

27. An important application of adiabatic cooling/heating is in atmospheric physics. Pressure varies with altitude as  $dP/dh = -\rho g$ , where  $\rho$  is the density. Calculate the change in temperature at the top of a mountain 2 km above the valley floor assuming the process is adiabatic and air behaves ideally.

28. Which of these cyclic integrals must vanish for a closed system with P-V work only? (a)  $\oint PdV$ , (b)  $\oint (PdV + VdP)$ , (c)  $\oint dq_{rev}$ , (d)  $\oint dq_{rev}/T$ .