

CML 100: 2015-2016
Thermodynamics Tutorial 2

(Submit answers to Q. 11, 15, 21, 25, 28, 32 on 19th August 2014 during the lecture: Remember to write your group # along with the name and entry #)

- 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 and a van der Waals gas.
- (a) Express the van der Waals equation of state in virial form $P\bar{V} = RT + B \left(\frac{1}{\bar{V}} \right) + C \left(\frac{1}{\bar{V}} \right)^2 + \dots$ 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.
- 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, ΔU 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 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 $\kappa_T R = \alpha(\bar{V} - b)$.
- 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 $V = K e^{\alpha T} e^{-\kappa p}$. Show that V is a state function.
- One mole of chlorine undergoes adiabatic expansion from 1 dm³ to a 10 dm³ 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°C? (c) What change of pressure indicates a change of 1.00 K at the latter temperature?
- Derive a general relation between C_p and C_V to get the general result

$$C_p - C_V = \left[P + \left(\frac{\partial U}{\partial V} \right)_T \right] \left(\frac{\partial V}{\partial T} \right)_P$$
- Show for a van der Waals gas $C_p - C_V = \alpha^2 TV / \kappa_T$. You will need to use an identity $\pi_T = T \left(\frac{\partial P}{\partial T} \right)_V - P$
- 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 \bar{C}_V is independent of the temperature, calculate the value of \bar{C}_V for this gas.

14. 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.

15. 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 temperature, (b) Reversible, adiabatic expansion back to its initial temperature, (c) reversible isothermal compression back to 1.00 atm. Calculate q , w , ΔU , and ΔH for each step and overall.
16. 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 ΔH_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 $C_{p,m} = 7/2R$.
17. (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.
18. Calculate the work done during the isothermal reversible expansion of a gas that satisfies the virial equation of state, $P\bar{V} = RT + B\left(\frac{1}{\bar{V}}\right) + C\left(\frac{1}{\bar{V}}\right)^2 + \dots$. 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 cm^3 to 1000 cm^3 in each case.
19. 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.
20. Calculate the heat needed to raise the temperature of air in a house from 20 to 25 °C. Assume that the house contains 600 m^3 of air, which should be taken to be a perfect diatomic gas. The density of air is 1.21 kg m^{-3} at 20 °C Calculate ΔU and ΔH for the heating of the air.
21. 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.
22. 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.
23. 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 $PV = nRT + nP(b - a/RT)$].
24. An important application of adiabatic cooling/heating is in atmospheric physics. Pressure varies with altitude as $dP/dh = -g\rho$, where ρ 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.
25. Which of these cyclic integrals must vanish for a closed system with P-V work only? (a) $\oint PdV$, (b) $\oint(PdV + VdP)$, (c) $\oint dq_{rev}/T$.
26. One mol of hydrogen occupies a volume of 0.1 m^3 at 300 K and one mol of argon also occupies the same volume but at 400 K. While isolated from their surroundings, each undergoes a free expansion, the hydrogen to 5 times and argon 8 times its initial volume. The two masses are then placed in contact with each other and reach thermal equilibrium. What is the total change in entropy? ($C_v^{H_2} = 10 \text{ kJ/K/kg}$, $C_v^{Ar} = 10 \text{ kJ/K/kg}$).
27. One mole of an ideal monatomic gas undergoes an irreversible adiabatic process in which the gas ends up at STP and for which ΔS is 21 JK^{-1} and w is 1.26 kJ. The entropy of the gas at STP is $270 \text{ JK}^{-1}\text{mol}^{-1}$. Calculate ΔU and ΔG for the process and also the initial state of the gas.

28. It is possible to cool liquid water below its freezing point of 273.15 K without the formation of ice if proper care is taken to prevent nucleation. A kilogram of sub-cooled liquid water at 263.15 K is contained in a well-insulated vessel. Nucleation is induced by the introduction of a speck of dust, and a spontaneous crystallization process ensues. Find the final state of the water and calculate the total entropy change for the process. (Heat of fusion is 334 Jg^{-1} , $C_p(\text{l}) = 4.185 \text{ Jg}^{-1}\text{K}^{-1}$; $C_p(\text{s}) = 2.092 \text{ Jg}^{-1}\text{K}^{-1}$)
29. 100 g of ice at 0°C is dropped into an insulated beaker containing 150 g of water at 100°C . Calculate ΔS for this process.
30. Calculate the maximum work and the maximum non-expansion work that can be obtained from the freezing of supercooled water at -5°C and 1.0 atm. The densities of water and ice are 0.999 and 0.917 g cm^{-3} , respectively at -5°C .
31. One mole of He is heated from 200°C to 400°C at a constant pressure of 1 atm. Given that the absolute entropy of He at 200°C is $810 \text{ JK}^{-1}\text{mol}^{-1}$, and assuming He is a perfect gas, comment on the spontaneity of the process.
32. Derive the relations: (i) $C_p - C_v = T \left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_p$; (ii) $C_p - C_v = \frac{\alpha^2 TV}{\beta}$; (iii) $\mu_{JT} = -\left(\frac{v}{c_p}\right)(\beta C_v \mu_J - \beta p + 1)$; (iv) $\left(\frac{\partial H}{\partial V}\right)_S = \frac{\gamma}{\beta}$; (v) $\left(\frac{\partial V}{\partial T}\right)_p = \frac{C_v \beta}{T \alpha}$
33. Calculate the temperature change when the pressure on 1 kg of water is increased from 0 to 10^8 Pa reversibly and adiabatically. The initial temperature of water is 273.15 K, the specific volume is $10^{-3} \text{ m}^3 \text{ kg}^{-1}$, the coefficient of thermal expansion, $\alpha = 10^{-6} / \text{K}$ and C_p is $4184 \text{ J}/(\text{kg K})$.