

### CYL110 2012-2013 Classical Thermodynamics Sample Problems

1. Dieterici's equation of state for a gas is  $P(V - b) \exp(a/RVT) = RT$ , where  $a$ ,  $b$ , and  $R$  are constants. Determine  $(\partial V/\partial T)$ ,  $(\partial T/\partial P)$ , and  $(\partial P/\partial V)$  and verify that  $(\partial V/\partial T) (\partial T/\partial P) (\partial P/\partial V) = -1$ .
2. 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.
3. At high densities the molecules themselves make up an appreciable fraction of the available volume, and an equation of state of 1 mol of gas can be written in the form  $P(V - b) = RT$ , where 'b' is a constant which is related to the size of the molecules. (i) Calculate the work done when 1 mole of this nonideal gas at 298 K is compressed reversibly and isothermally from 22.4 L to 0.224 L if 'b' is 0.04L. (ii) What is the work done if the gas behaves ideally in (i) and explain why the answers differ in (i) and (ii).
4. 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.
5. For each of the following processes deduce whether each of the quantities  $q$ ,  $w$ ,  $\Delta U$ ,  $\Delta H$  is positive, zero, or negative. (a) Reversible melting of solid benzene at 1 atm and the normal melting point. (b) Reversible melting of ice at 1 atm and 0°C. (c) Reversible adiabatic expansion of a perfect gas. (d) Reversible isothermal expansion of a perfect gas. (e) Adiabatic expansion of a perfect gas into a vacuum. (f) Joule-Thomson adiabatic throttling of a perfect gas. (g) Reversible heating of a perfect gas at constant  $P$ . (h) Reversible cooling of a perfect gas at constant  $V$ .
6. 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.
7. The isothermal compressibility of lead is  $2.3 \times 10^{-6} \text{ atm}^{-1}$ . A cube of lead of 10 cm length at 298K is inserted under 1000m of water where the temperature is 268K. Calculate the change in the volume of the cube given that the mean density of water is  $1.03 \text{ g cm}^{-3}$  and  $\alpha_{Pb}$  is  $8.61 \times 10^{-5}$ .
8. A piece of zinc of mass 5.0 g is dropped into a beaker of dilute hydrochloric acid. Calculate the work done by the system as a result of the reaction. The atmospheric pressure is 1.1 atm and the temperature is 23 °C.
9. 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<sup>3</sup> of air, which should be taken to be a perfect diatomic gas. The density of air is  $1.21 \text{ g m}^{-3}$  at 20 °C. Calculate  $\Delta U$  and  $\Delta H$  for the heating of the air.
10. Below 100K the specific heat of diamond varies as  $C = aT^3$ , where  $T$  is the absolute temperature. A 100 mg piece of diamond at 77K is dropped into a bath of liquid helium at 4.2K, which is the boiling point of helium at atmospheric pressure. In cooling the diamond to 4.2 K, some of the helium is boiled off. The gas is collected and found to occupy a volume of  $2.48 \times 10^{-5} \text{ m}^3$  when measured at 0°C and 1 atm pressure. (a) Does this experiment measure  $C_P$  or  $C_V$ ? (b) What is the value of  $a$  in the specific heat of diamond? (c) Discuss whether there would be much difference between  $C_P$  and  $C_V$  for diamond under the conditions of the experiment. The heat of vaporization of helium is  $84 \text{ J mol}^{-1}$ . Helium gas behaves ideally.
11. An average human body produces about 10 MJ of heat each day through metabolic activity. If a human body were an isolated system of mass 65 kg with the heat capacity of water, what temperature rise would the body experience? Human bodies are open systems, and the main mechanism of heat loss is through the evaporation of water. What mass of water should be evaporated each day to maintain constant temperature?  $\Delta H_{vap}$  of water is 2.41 kJ/g.
12. 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.

13. Calculate the ratio of the maximum inversion temperature to the critical temperature for a van der Waals gas.
14. 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  $PV = nRT + nPb - (a/RT)$ ]
15. An important application of adiabatic cooling/heating is in atmospheric physics. Pressure varies with altitude as  $dP/dh = -g\rho$ , 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.
16. The velocity of sound in a fluid is given as  $c = 1/\sqrt{\rho\kappa_S}$ , where  $\kappa_S$ , the adiabatic compressibility is given as  $-1/V \left( \frac{\partial V}{\partial p} \right)_S$ . What is the velocity of sound in an ideal gas?
17. Derive the thermodynamic equation of the state,  $\left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{\partial p}{\partial T} \right)_V - p$ . Apply this equation to an ideal gas and a van der Waals gas. Comment on your results.
18. Compare the difference between  $\Delta H$  and  $\Delta U$  for the following processes: (i) 1 mol  $\text{H}_2\text{O}(\text{s}) \rightarrow 1$  mol  $\text{H}_2\text{O}(\text{l})$  at 273 K [ $V_m(\text{ice})=0.0196 \text{ L}\cdot\text{mol}^{-1}$ ,  $V_m(\text{liq. water})=0.018 \text{ L}\cdot\text{mol}^{-1}$ ] (ii) 1 mol  $\text{H}_2\text{O}(\text{l}) \rightarrow 1$  mol  $\text{H}_2\text{O}(\text{g})$  at 373 K [ $V_m(\text{ice})=0.0188 \text{ L}\cdot\text{mol}^{-1}$ ,  $V_m(\text{gaseous water})=30.61 \text{ L}\cdot\text{mol}^{-1}$ ] (iii) Combustion of  $\alpha$  D-glucose (iv) 1 mol C(graphite)  $\rightarrow$  1 mol C (diamond) at a pressure of 20,000 atm
19. Which of these cyclic integrals must vanish for a closed system with  $P$ - $V$  work only? (a)  $\oint PdV$ ; (b)  $\oint(PdV + VdP)$ ; (c)  $\oint VdV$ ; (d)  $\oint HdT$ ; (e)  $\oint dq_{rev}$ ; (f)  $\oint dw_{rev}/P$ .
20. One mol of hydrogen occupies a volume of  $0.1 \text{ m}^3$  at 300K and one mol of argon also occupies the same volume but at 400K. 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? ( $C_v^{H_2} = 10 \text{ kJ/K/kg}$ ,  $C_v^{Ar} = 0.31 \text{ kJ/K/kg}$ )
21. One mole of an ideal monoatomic gas undergoes an irreversible adiabatic process in which the gas ends up at STP and for which  $\Delta S$  is  $21 \text{ JK}^{-1}$  and  $w$  is  $1.26 \text{ kJ}$ . The entropy of the gas at STP is  $270 \text{ JK}^{-1} \text{ mol}^{-1}$ . Calculate  $\Delta U$  and  $\Delta G$  for the process and also the initial state of the gas.
22. The molar heat capacity of oxygen at constant pressure for temperatures in the range 300 to 400 K and for low or moderate pressures can be approximated as  $C_P(\text{J mol}^{-1} \text{ K}^{-1}) = 25.73 + 0.013 T$ . (a) Calculate  $q$ ,  $w$ ,  $\Delta U$ ,  $\Delta H$  when 2 mol of  $\text{O}_2$  is reversibly heated from 27 to 127 °C with  $P$  held fixed at 1 atm. (b) Repeat the calculation if the same change is effected at constant  $V$ .
23. By a thermodynamic analysis show that the following familiar processes are spontaneous: (a) A book is pushed off a table and falls to the floor. (b) One mole of an ideal gas in a vessel that is connected to another identical evacuated vessel through a valve. The valve is opened and the gas occupies both vessels. (c) Melting of ice when brought in contact with an object at a temperature above 0 °C.
24. 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 subcooled 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  $334 \text{ J g}^{-1}$ ,  $C_P(\text{l}) = 4.185 \text{ J g}^{-1} \text{ K}^{-1}$ ,  $C_P(\text{s}) = 2.092 \text{ J g}^{-1} \text{ K}^{-1}$ ).
25. 100 g of ice at 0 °C is dropped into an insulated beaker containing 150 g of water at 100 °C. Calculate  $\Delta S$  for this process.
26. Calculate the maximum work and the maximum non-expansion work that can be obtained from the freezing of supercooled water at  $-5 \text{ °C}$  and 1.0 atm. The densities of water and ice are 0.999 and  $0.917 \text{ g cm}^{-3}$ , respectively at  $-5 \text{ °C}$ .

27. 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 JK<sup>-1</sup> mol<sup>-1</sup>, and assuming He is a perfect gas, comment on the spontaneity of the process.
28. 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)  $\mu_{JT} = -(V/C_p)(\beta C_v \mu_J - \beta P + 1)$  (iv)  $\left(\frac{\partial H}{\partial V}\right)_S = \gamma/\beta$  (v)  $\left(\frac{\partial V}{\partial T}\right)_P = \frac{C_v \beta}{T \alpha}$ .
29. At what pressure can graphite be converted to diamond. Use the data given below.

	$\Delta H_0^{298} \text{ kJ mol}^{-1}$	$S_0^{298} \text{ J K}^{-1} \text{ mol}^{-1}$	$\rho_{298} \text{ g cm}^{-3}$
graphite	0	5.69	2.22
diamond	1.9	2.44	3.51

30. Predict whether the oxidation reactions of  $\alpha$  D-glucose and CH<sub>4</sub> at 298 K are spontaneous or not. Does your prediction agree with the fact that these substances can be kept in air for very long periods without any change? The overall reaction for metabolic breakdown of glucose in our bodies is the same as the combustion of glucose in air. Is this reaction more favored at 37 °C.
31. When 1 mol of glucose is oxidized to CO<sub>2</sub> and H<sub>2</sub>O at 298K calorimetric measurements give  $\Delta U = -2808 \text{ kJ}$  and  $\Delta S = +182.4 \text{ JK}^{-1}$  at 298K and standard conditions. How much of this energy change can be extracted as (a) heat at constant pressure and (b) work? Calculate also the energy available for sustaining muscular and nervous activity from the combustion of 1 mol of glucose molecules under standard conditions at 37 °C (blood temperature)?
32. As an approximation, we can assume that proteins exist either in the native (or physiologically functioning) state and the denatured state. The standard molar enthalpy and entropy of the denaturation of a certain protein are 512 kJ/mol and 1600 J/K/mol respectively. Comment on the sign and magnitudes of these quantities and calculate the temperature at which the denaturation becomes spontaneous.
33. The molar Gibbs energy of a certain gas is given by

$$G_m = RT \ln p + A + Bp + \frac{1}{2} Cp^2 + \frac{1}{3} Dp^3$$

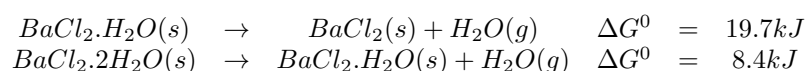
where  $A, B, C, D$  are constants. Obtain the equation of state of the gas.

34. Calculate the change in the chemical potential of a perfect gas when its pressure is increased isothermally from 1.8 atm to 29.5 atm at 40 °C.
35. (a) Calculate  $\Delta_{mix} G$  when (i) 2 mol H<sub>2</sub> at 2 atm and 4 mol N<sub>2</sub> at 3 atm are mixed at 25 °C. Calculate also the entropy change (ii) if the initial pressures of the gases are identical and (iii) if the gases are identical.
36. Use the tabulated thermodynamic data given below to calculate the equilibrium constant (in atm<sup>-1</sup>) of the reaction, N<sub>2</sub>(g) + O<sub>2</sub>(g) = 2NO(g) at 25 °C. Nitric oxide from car exhaust is a primary air pollutant. What happens to the concentration of nitric oxide at 1500 °C which is the typical temperature inside the cylinders of a car's engine after it has been running for some time.

	$\Delta H_{298}^0 \text{ kJ mol}^{-1}$	$S_{298}^0 \text{ JK}^{-1} \text{ mol}^{-1}$
N <sub>2</sub> (g)	0	191.5
O <sub>2</sub> (g)	0	205.0
NO(g)	90.4	210.6

37. Calculate the vapor pressure of water at 25 °C.  $\Delta_f H^0(\text{H}_2\text{O}, \text{l}) = -287 \text{ kJ mol}^{-1}$ ;  $\Delta_f H^0(\text{H}_2\text{O}, \text{g}) = -243 \text{ kJ mol}^{-1}$ ;  $S^0(\text{H}_2\text{O}, \text{g}) = 189.5 \text{ J K}^{-1} \text{ mol}^{-1}$ ;  $S^0(\text{H}_2\text{O}, \text{l}) = 70.2 \text{ J K}^{-1} \text{ mol}^{-1}$ .
38. Calculate the solubility product of AgCl at 25 °C. The  $\Delta_f H^0$  of aqueous Ag<sup>+</sup>, Cl<sup>-</sup>, and solid AgCl are 106.3 kJ, -168 kJ, and -127.5 kJ respectively, while their S<sup>0</sup>s are 74.2 J K<sup>-1</sup>, 55.3 J K<sup>-1</sup>, and 96.5 J K<sup>-1</sup>.

39. From the data given below determine over what range of humidity is  $\text{BaCl}_2 \cdot \text{H}_2\text{O}(s)$  stable at 25 °C.



40. At 1 atm the  $S_{rh} \rightarrow S_{mon}$  transition takes place at 95.5 °C, and the melting point of  $S_{mon}$  is 119.3 °C. The latent heat of the rhombic to monoclinic transition is  $1.16 \times 10^4 \text{ J kg}^{-1}$  and the latent heat of fusion of  $S_{mon}$  is  $5.53 \times 10^4 \text{ J kg}^{-1}$ . The densities of rhombic, monoclinic, and liquid sulphur are  $2.07 \times 10^3$ ,  $1.96 \times 10^3$ ,  $1.90 \times 10^3 \text{ kg.m}^{-3}$ . Estimate the rhombic, monoclinic, and liquid triple point.
41. The vapor pressure of zinc varies with temperature as

$$\log p(\text{mmHg}) = -\frac{6850}{T} - 0.755 \log T + 11.24$$

and that of liquid zinc as

$$\log p(\text{mmHg}) = -\frac{6620}{T} - 1.255 \log T + 12.34.$$

Calculate (a) the boiling point of zinc, (b) the triple point, (c) the heat of evaporation at the boiling point, (d) the heat of fusion, and (e) the difference in the  $C_p$ s of solid and liquid zinc.

42. Consider the application of the van't Hoff equation to a two-phase equilibrium  $\alpha \rightleftharpoons \beta$ . Show that the van't Hoff equation leads to the Clapeyron equation in such a case.
43. The melting points of gold and silicon are 1337 and 1683 K while the heats of fusion are 12677 and 39622  $\text{J mol}^{-1}$ . Calculate the solid-liquid equilibrium lines and estimate the eutectic composition.
44. a) From the melting points of the mixtures of Al and Cu, sketch the melting point curve.
- |           |     |     |     |     |     |      |
|-----------|-----|-----|-----|-----|-----|------|
| mass % Cu | 0   | 20  | 40  | 60  | 80  | 100  |
| t/°C      | 660 | 600 | 540 | 610 | 930 | 1083 |
- b) For copper,  $T_m = 1356 \text{ K}$  and  $\Delta_{fus}H = 13.05 \text{ kJ/mol}$ ; for aluminum,  $T_m = 933 \text{ K}$  and  $\Delta_{fus}H = 10.75 \text{ kJ/mol}$ . Sketch the ideal solubility curves and compare with the experimental curve in a).
45. (a) Derive the relation:  $TdS = C_P dT - \alpha VT dP$ .  
 (b) Calculate the temperature change when the pressure on 1 kg of water is increased from 0 to  $10^8 \text{ Pa}$  reversibly and adiabatically. The initial temperature of water is 273.15 K, the specific volume is  $10^{-3} \text{ m}^3/\text{kg}$ , the coefficient of thermal expansion,  $\alpha = 10^{-6}/\text{K}$  and  $C_p$  is 4184  $\text{J}/(\text{kg K})$ .
46. For uranium hexafluoride, the vapour pressures of the liquid and solid phases are given by: [1 torr = 1 atm/760]

$$\text{solid : } \ln(p/\text{torr}) = 24.518 - 5895/(T/\text{K})$$

$$\text{liquid : } \ln(p/\text{torr}) = 17.361 - 3479/(T/\text{K})$$

- (a) Calculate the enthalpies of evaporation, sublimation and fusion.  
 (b) Calculate the pressure and temperature of the triple point.  
 (c) Can the liquid phase exist at 1 atmosphere pressure? Why or why not?
47. Your answers to this question should be supported by a brief (!) justification.
- (a) For an ideal mixture of  $N$  components, what will be the composition for which the free energy of mixing is zero?  
 (b) The molar volume of water as a function of  $T$  is minimum at 4 °C. What will happen to  $C_P - C_V$  at this point?  
 (c) If  $A$  is the free surface area of a liquid and  $\gamma$  is the surface tension will the quantity  $Ad\gamma$  represent thermodynamic work?  
 (d) Define a quasi-static process. Can such a process actually occur? If yes, give an example. If no, explain why the concept is still a useful one in thermodynamics.  
 (e) How many independent chemical species or components are present when  
 (i)  $\text{N}_2$  and  $\text{H}_2$  are present in a container at room temperature  
 (ii)  $\text{N}_2$  and  $\text{H}_2$  are present at high temperature and pressure in the presence of an iron catalyst?

48. The standard Gibbs energy change for the reaction  $2\text{NO}_2(\text{g}) = \text{N}_2\text{O}_4(\text{g})$  is 1255.2 J at 40°C. a) Calculate the  $K_p$  for the reaction. b) The density of an equilibrium mixture of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  gases is 5.85 g/liter at 40 °C and a certain pressure. Using the value of  $K_p$  from a), calculate the degree of dissociation of  $\text{N}_2\text{O}_4$ , the average molecular weight of the mixture, and the total pressure of the mixture.
49. (a) The removal of water in “freeze drying” involves cooling below 0 °C, reduction of pressure below the triple point (0.0098 °C, 611 Pa), and subsequent warming. How do you explain this in terms of the phase diagram of water?  
 (b) Calculate the entropy change of the universe resulting when a copper block of 0.4 kg mass and with heat capacity at constant pressure of 0.375 J/K/g at 100 °C is placed in a lake at 10 °C.  
 (c) Express  $\left(\frac{\partial p}{\partial V}\right)_S$  in terms of measurable quantities and evaluate it for an ideal gas.
50. (a) Does the chemical potential of an ideal gas increase/decrease with increasing  $p$ ? Is this change due to an enthalpy or entropy effect? Justify.  
 (b) The pressure on 0.2 kg of water is increased reversibly and isothermally from atmospheric pressure ( $1.0 \times 10^5$  Pa) to  $3 \times 10^8$  Pa at 20 °C (i) How much heat is transferred? (ii) How much work is done? (iii) Calculate the change in internal energy. ( $\rho = 998.21$  kg/m<sup>3</sup>,  $C_p = 4.1818$  kJ/kg K, volume expansivity =  $206.8 \times 10^{-6}$ /K, isothermal compressibility =  $4.5891 \times 10^{-10}$  Pa<sup>-1</sup>).  
 (c) On a  $T - S$  diagram does the isochoric curve or isobaric curve have a higher slope? Why?
51. (a) Calculate  $\Delta G$  and  $\Delta A$  for the process of vaporizing 1 mol of water at 1 atm and 100 °C. Write down any approximations that you make. ( $\Delta H_{\text{vap}}(\text{H}_2\text{O})$  is 40.66 kJ/mol,  $R = 0.082$  l atm/K/mol)  
 (b) A vessel containing 5.0 mol of an ideal gas, A, is connected to an identical vessel containing 10.0 mol of another ideal gas, B, and the two are allowed to reach equilibrium. For the process described, at 27 °C, find (i)  $\Delta G$  (gas A), (ii)  $\Delta G$  (gas B), (iii)  $\Delta G(\text{A+B})$ .  
 (c) Three equations for the oxidation of a metal are given below. One of these is for the oxidation of solid M, one is for liquid M, and one is for gaseous M.  
 $2 \text{M} + \text{O}_2(\text{g}) = 2\text{MO}(\text{s}) \quad \Delta G^\circ = -290,400 + 46.1 T$  calories  
 $2 \text{M} + \text{O}_2(\text{g}) = 2\text{MO}(\text{s}) \quad \Delta G^\circ = -358,754 + 102.6 T$  calories  
 $2 \text{M} + \text{O}_2(\text{g}) = 2\text{MO}(\text{s}) \quad \Delta G^\circ = -298,400 + 55.4 T$  calories  
 Determine which equation is for which oxidation, and calculate the melting and normal boiling temperatures of M.
52. (a) The density of solid benzene is 1.012 g/cm<sup>3</sup> and the density of the liquid at freezing point (5.5 °C) is 0.879 g/cm<sup>3</sup>. The heat of fusion is 127 J/g. (i) If the pressure is doubled from 1 atm to 2 atm, will the freezing point of benzene increase or decrease? (ii) How much will the freezing point change?  
 (b) For a two component system that forms a simple eutectic, plot the time spent at the eutectic temperature versus the composition.
53. The 59<sup>th</sup> edition of the CRC Handbook of Chemistry and Physics defines the *Latent Heat of Vaporization* as:  
 The quantity of heat necessary to change one gram of liquid to vapor without change in temperature, measured in calories per gram.  
 (i) As defined, is latent heat of vaporization an extensive, intensive, or derived intensive quantity? Why?  
 (ii) Suppose you were to measure the latent heat of vaporization of an unknown liquid. When you report your results to the rest of the world, would you need to augment the definition in any way? If so, how? Be specific.
54. (a) We can show that the criterion for a stable equilibrium is  $\left(\frac{\partial^2 U}{\partial S^2}\right)_V > 0$ . Express this in terms of measurable quantities and comment on its implication.  
 (b) The thermodynamic properties of substances are often shown on temperature ( $y$ -axis) and entropy ( $x$ -axis) diagrams. Represent on such a diagram the variation in the temperature when a liquid, say water, is heated at constant pressure (take it to be 1 atm) from room temperature past its boiling point. Identify the different regions. What is the slope of the  $T - S$  curve in the different regions?

(c) Measurements of the saturated vapor pressure of liquid  $\text{NdCl}_5$  give 0.3045 atm at 478 K and 0.9310 atm at 520 K. Calculate the normal boiling point of  $\text{NdCl}_5$ .

55. Read the following statements *carefully* and decide whether (and why) they are true or false giving your thermodynamic reasoning. If the statement is false, you may either state which law or laws of thermodynamics it violates or provide a physical counter example or any other plausible physical reason. Finally, correct the false statement with a clarifying phrase that makes the statement true.
- (i) The internal energy of a system and its surroundings is not conserved during an irreversible process, but it is conserved for reversible processes.
  - (ii) No heat transfer occurs when liquid water is reversibly and isothermally compressed.
  - (iii) The entropy of a material can never decrease.
  - (iv) A body in thermal and mechanical equilibrium with a reservoir at constant temperature and pressure will have the lowest value of Gibbs energy for that body.
  - (v) The chemical potential of any species that can be exchanged between two phases will always be equal.
  - (vi) If in a reversible process the temperature of one mole of an ideal gas increases by  $1^\circ\text{C}$ , the work done on the gas must be numerically equal to the molar heat capacity at constant volume,  $C_V$ .
  - (vii) If an ideal gas increases its volume by 1 cubic meter at a constant pressure of 1 Newton per square meter, then its internal energy decreases by 1 Joule.
  - (viii) Melting of any material is an endothermic process.
56. (a) A thermally insulated cylinder, closed at both ends, is fitted with a frictionless heat conducting piston that divides the cylinder into two parts. Initially, the piston is clamped in the center with 1 liter of air at 300 K and 2 atm pressure on one side and 1 liter of air at 300 K and 1 atm pressure on the other side. The piston is released and reaches equilibrium in pressure and temperature at a new position. Compute the final pressure and temperature and increase in the entropy of air. State all the approximations you make.
- (c) The Planck function defined as

$$Y = -\frac{H}{T} + S$$

is a thermodynamic potential similar to the Gibbs energy. Obtain a “ $TdS$ ” type equation for  $dY$  and from it a Maxwell relation.

57. One mole of an ideal gas is expanded adiabatically, but irreversibly, from  $V_1$  to  $V_2$ , and no work is done,  $w = 0$ .
- (a) Does the temperature of the gas change? Explain.
  - (b) What is the  $\Delta S$  of the gas and of its surroundings?
  - (c) If the expansion is performed reversibly and isothermally, what would be the  $\Delta S$  of the gas and its surroundings?
  - (d) Explain why the values of  $\Delta S$  in parts (b) and (c) are same or different.
58. A stretched rubber band when released feels warmer, colder, or the same. Justify.
59. It is often claimed that one can skate on ice because the pressure of the skate causes the ice to melt, thus dramatically reducing the friction between skate and ice. While this makes a good story, is this quite correct? Consider a skater with a mass of 75 kg on a skate that is 3 mm wide and 20 cm long. The densities of water and ice are 0.999 and 0.917 g  $\text{cm}^3$  respectively, and the heat of fusion is 6.004 kJ  $\text{mol}^{-1}$ . Since common experience is that ice skating is possible even when the ambient temperature is well below the normal freezing point, does the pressure induced lowering of the melting point explain clearly this observation?
60. Consider a closed system containing 3.0 moles of a monoatomic ideal gas in an initial state  $(P_0, V_0)$ . After some process the gas ends up in a state  $(P_0/3, 3V_0)$ . (a) What is the change in the internal energy of the system? (b) How much work is performed by the system on the universe?
61. For a substance (one mole at atmospheric pressure) that melts at  $T_f$  and boils at  $T_b$  plot the variation of (i)  $\Delta H$  and (ii) free energy as the temperature is varied from below  $T_f$  to above  $T_b$ .