

Q1. Answer in brief

(a) What is meant by a thermodynamic equilibrium?

When a system is in thermodynamic equilibrium, it should satisfy the following three conditions. (a) Mechanical Equilibrium :- Pressure remains constant (b) Thermal equilibrium :- Temperature remains constant (c) Chemical equilibrium : There is no chemical reaction.

(b) Show that $\frac{RT}{P} dP + R dT$ is not an exact differential.

For the expression $f(P,T)dP + g(P,T)dT$ to be an exact differential, the condition $(\partial f(P,T)/\partial T)_P = (\partial g(P,T)/\partial P)_T$ must be satisfied as discussed in Section 3.1. Because

$$\left(\frac{\partial \left(\frac{RT}{P} \right)}{\partial T} \right)_P = \frac{R}{P} \quad \text{and} \quad \frac{\partial R}{\partial P} = 0$$

(c) Of the four different kinds of processes: isobaric, isothermal, isochoric and adiabatic – for which of them were heat capacities defined? If it was not possible to define a heat capacity for any of the processes listed, identify which ones and explain why.

[3 x 2 = 6]

Heat capacities defined for isobaric and isochoric processes C_p and C_v

In most cases adding heat to the system increases its temperature. One can define the heat capacity as $C = \delta Q / dT$. C is large if large amounts of heat cause only insignificant temperature increase. The heat capacity, as defined above, is proportional to the system size and thus is extensive.

Heat capacity depends on the type of the process. If the heat is added to the system while the volume is kept constant, $dV = 0$, one obtains the isochoric heat capacity $C_v = (\delta Q / dT)_v$. Also one can keep a constant pressure, $dP = 0$, to obtain the isobaric heat capacity $C_p = (\delta Q / dT)_p$. In the isochoric case no work is done, so the heat fully converts into the internal energy U and the temperature increases. In the isobaric case, the system usually expands upon heating and a negative work is done on it. This leads to a smaller increase of U and thus smaller increase of the temperature. Consequently, for most materials $C_p > C_v$ should be satisfied. Rigorous consideration at the end of this section shows, however, that $C_p > C_v$ is satisfied for all materials, including rubber that shrinks upon heating. In the isothermal process, the system receives or loses heat but $dT = 0$, thus $C_T = \pm \infty$. Finally, in the adiabatic process $\delta Q = 0$ but the temperature changes. Thus in this process $C_s = 0$. The subscript S refers to the entropy that is a state function conserved in the reversible adiabatic processes.

Q2.(a) A cloud mass moving across the ocean at an altitude of 2000 m encounters a coastal mountain range. As it rises to a height of 3500 m to pass over the mountains, it undergoes an adiabatic expansion. The pressure at 2000 m and 3500 m is 0.802 atm and 0.602 atm respectively. If the initial temperature of the cloud mass is 288 K, what is the cloud temperature as it passes over the mountains? Assume that $C_{P,m}$ for air is $28.86 \text{ J K}^{-1} \text{ mol}^{-1}$ and that the air obeys the ideal gas law. If you are on the mountain will you experience rain or snow?

$$\begin{aligned}
 \ln\left(\frac{T_f}{T_i}\right) &= -(\gamma - 1) \ln\left(\frac{V_f}{V_i}\right) \\
 &= -(\gamma - 1) \ln\left(\frac{T_f P_i}{T_i P_f}\right) = -(\gamma - 1) \ln\left(\frac{T_f}{T_i}\right) - (\gamma - 1) \ln\left(\frac{P_i}{P_f}\right) \\
 &= -\frac{(\gamma - 1)}{\gamma} \ln\left(\frac{P_i}{P_f}\right) = -\frac{\left(\frac{C_{P,m}}{C_{P,m} - R} - 1\right)}{\frac{C_{P,m}}{C_{P,m} - R}} \ln\left(\frac{P_i}{P_f}\right) \\
 &= -\frac{\left(\frac{28.86 \text{ J K}^{-1} \text{ mol}^{-1}}{28.86 \text{ J K}^{-1} \text{ mol}^{-1} - 8.314 \text{ J K}^{-1} \text{ mol}^{-1}} - 1\right)}{\frac{28.86 \text{ J K}^{-1} \text{ mol}^{-1}}{28.86 \text{ J K}^{-1} \text{ mol}^{-1} - 8.314 \text{ J K}^{-1} \text{ mol}^{-1}}} \times \ln\left(\frac{0.802 \text{ atm}}{0.602 \text{ atm}}\right) \\
 &= -0.0826 \\
 T_f &= 0.9207 T_i = 265 \text{ K}
 \end{aligned}$$

You can expect snow.

(b) A Carnot cycle uses 1.00 mole of a monatomic ideal gas as the working substance from an initial state of 10.0 atm and 600 K. It expands isothermally to a pressure of 1.00 atm (step 1), and then adiabatically to a temperature of 300 K (step 2). This expansion is followed by an isothermal compression (step 3) and then an adiabatic compression (step 4) back to the initial state. Determine the values of q , w , ΔU , ΔH , ΔS , and ΔS_{total} for step 1 and step 2 of the cycle. Express your answers in units of kJ or J K^{-1} . Show your work.

[3+5=8]

- [1] A Carnot cycle uses 1.00 mole of a monatomic ideal gas as the working substance from an initial state of 10.0 atm and 600 K. It expands isothermally to a pressure of 1.00 atm (step 1), and then adiabatically to a temperature of 300 K (step 2). This expansion is followed by an isothermal compression (step 3) and then an adiabatic compression (step 4) back to the initial state.

Determine the values of q , w , ΔU , ΔH , ΔS , and ΔS_{total} for step 1 and step 2 of the cycle. Express your answers in unit of kJ or J K⁻¹, where appropriate, and be sure to show your work.

	Step 1	Step 2	Step 3	Step 4	Cycle
q	+11.5 kJ	0	-5.74 kJ	0	5.8 kJ
w	-11.5 kJ	-3.74 kJ	+5.74 kJ	3.74 kJ	-5.8 kJ
ΔU	0	-3.74 kJ	0	+3.74 kJ	0
ΔH	0	-6.23 kJ	0	+6.23 kJ	0
ΔS	+19.1 J K ⁻¹	0	-19.1 J K ⁻¹	0	0
ΔS_{sur}	-19.1 J K ⁻¹	0	+19.1 J K ⁻¹	0	0
ΔS_{tot}	0	0	0	0	0

Step 1

$$\Delta U = \Delta H = \boxed{0} \text{ [isothermal]}$$

$$w = -nRT \ln\left(\frac{V_f}{V_i}\right) = nRT \ln\left(\frac{p_f}{p_i}\right) \text{ [2.13, and Boyle's law]}$$

$$= (1.00 \text{ mol}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (600 \text{ K}) \times \ln\left(\frac{1.00 \text{ atm}}{10.0 \text{ atm}}\right) = \boxed{-11.5 \text{ kJ}}$$

$$q = -w = \boxed{11.5 \text{ kJ}}$$

$$\Delta S = nR \ln\left(\frac{V_f}{V_i}\right) \text{ [4.17]} = -nR \ln\left(\frac{p_f}{p_i}\right) \text{ [Boyle's law]}$$

$$= -(1.00 \text{ mol}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln\left(\frac{1.00 \text{ atm}}{10.0 \text{ atm}}\right) = \boxed{+19.1 \text{ J K}^{-1}}$$

$$\Delta S(\text{sur}) = -\Delta S(\text{system}) \text{ [reversible process]} = \boxed{-19.1 \text{ J K}^{-1}}$$

$$\Delta S_{\text{tot}} = \Delta S(\text{system}) + \Delta S(\text{sur}) = \boxed{0}$$

Step 2

$$q = \boxed{0} \text{ [adiabatic]}$$

$$\Delta U = nC_{V,m} \Delta T \text{ [2.21b]}$$

$$= (1.00 \text{ mol}) \times \left(\frac{3}{2}\right) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K} - 600 \text{ K}) = \boxed{-3.74 \text{ kJ}}$$

$$w = \Delta U = \boxed{-3.74 \text{ kJ}}$$

$$\Delta H = \Delta U + \Delta(pV) = \Delta U + nR \Delta T$$

$$= (-3.74 \text{ kJ}) + (1.00 \text{ mol}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (-300 \text{ K})$$

$$= \boxed{-6.23 \text{ kJ}}$$

$$\Delta S = \Delta S(\text{sur}) = \boxed{0} \text{ [reversible adiabatic process]}$$

$$\Delta S_{\text{tot}} = \boxed{0}$$

Q3(a) A sample of carbon dioxide that initially occupies 15.0 L at 250 K and 1.00 atm is compressed isothermally. Into what volume must the gas be compressed to reduce its entropy by 10.00 J K⁻¹?

First calculate the number of moles of gas:

$$n = \frac{pV}{RT} = \frac{(1.00)(15.0)}{(0.0820578)(250)} = 0.7312 \text{ mol}$$

For the isothermal expansion/compression of a perfect gas:

$$\Delta S^o = nR \ln \frac{V_f}{V_i}$$

Solving for V_f :

$$V_f = V_i e^{\Delta S^o / nR}$$

For an entropy change of -10.0 J/K :

$$V_f = (15.0) e^{-10.0 / (0.7312)(8.3145)} = 2.90 \text{ L}$$

(b) A sketch of the phase diagram of carbon is given.

(i) How many triple points are there and what are the phases that coexist at each triple point?

Two triple points

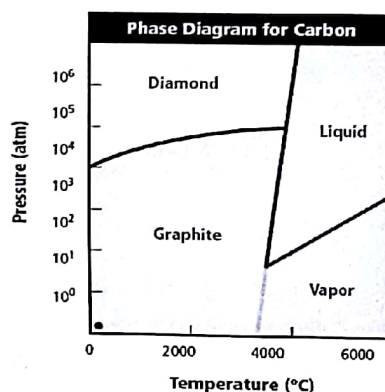
1: Graphite - Liquid - Vapour

2: Diamond - Graphite - Liquid

(ii) What is the main condition at which diamond is the favourable structure?

Pressure > 10⁴ atm

Temperature < 4000°C



(iii) Write an expression for the Gibbs energy dependence on pressure.

[3+5=8]

$$dG = VdP - SdT$$

$$dG = \left(\frac{\partial G}{\partial P} \right)_T dP - \left(\frac{\partial G}{\partial T} \right)_P dT$$

$$\therefore \left(\frac{\partial G}{\partial P} \right)_T = V$$

for isothermal change in pressure $\Delta G = \int_{P_1}^{P_2} \left(\frac{\partial G}{\partial P} \right)_T dP$

$$\Delta G = \int_{P_1}^{P_2} V dP$$

for ideal gases $V = \frac{nRT}{P}$

for condensed phases $V \sim \text{constant}$

Q4(a) Calculate the slope of the solid-liquid curve at 273.15K in atm K⁻¹ given that $\Delta \bar{H}_{fus} = 6.01$ kJ mol⁻¹, $\bar{V}_L = 0.0180$ L mol⁻¹ and $\bar{V}_S = 0.0196$ L mol⁻¹

Clapeyron equation $\frac{dP}{dT} = \frac{\Delta H_{fus}}{T_f \Delta V_{fus}}$ 1

$\frac{dP}{dT} = \frac{(6010 \text{ J mol}^{-1})(9.87 \times 10^{-3} \text{ L atm J}^{-1})}{273.15 \text{ K} (0.0180 - 0.0196) \text{ L}}$ 1

$= -136 \text{ atm K}^{-1}$ 1

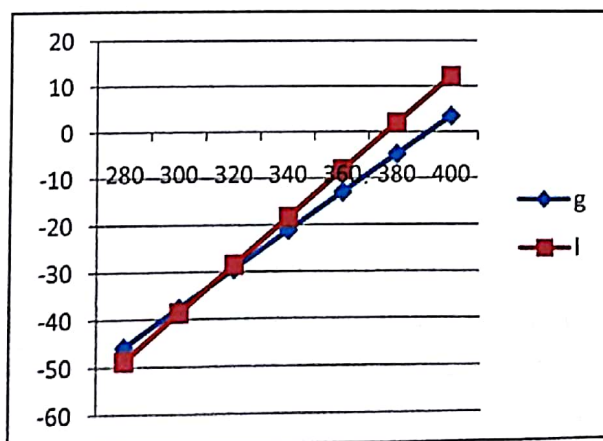
(b) The impact of a comet many years ago brought a deeply buried deposit of NiS to the surface of the earth. To obtain pure Ni, the ore is reduced to an impure metallic Ni and purified by reacting with carbon monoxide, CO, to form Ni(CO)₄, which is isolated and converted back to pure Ni. Depending on the temperature, the reaction is one or the other of these two reactions:

Reaction	ΔH (kJ/mol _{rxn})	ΔS (J/K·mol _{rxn})
Ni(s) + 4CO(g) → Ni(CO) ₄ (g)	-160.8	-410.5
Ni(s) + 4CO(g) → Ni(CO) ₄ (l)	-190.9	-507.6

The desired product is Ni(CO)₄(g) because it is easier to separate a gas from solid impurities than it is to remove a liquid from these same impurities. Using the thermodynamic values provided, plot a graph of ΔG vs T (use a range from 280 K – 400 K in increments of 20) and identify the range of possible temperatures for which the formation of Ni(CO)₄(g) is favourable.

[3+5=8]

T	ΔG_g	ΔG_l
280	-45.86	-48.772
300	-37.65	-38.62
320	-29.44	-28.468
340	-21.23	-18.316
360	-13.02	-8.164
380	-4.81	1.988
400	3.4	12.14



$\Delta G = \Delta H - T\Delta S$ 1

$\Delta G_{T} < 0$ spontaneous 1

for Ni(CO)₄(g) formation favourable compared to Ni(CO)₄(l) from 320 K to 380 K. 1

From graph Ni(CO)₄(g) line below Ni(CO)₄(l) line and also value of ΔG is negative.