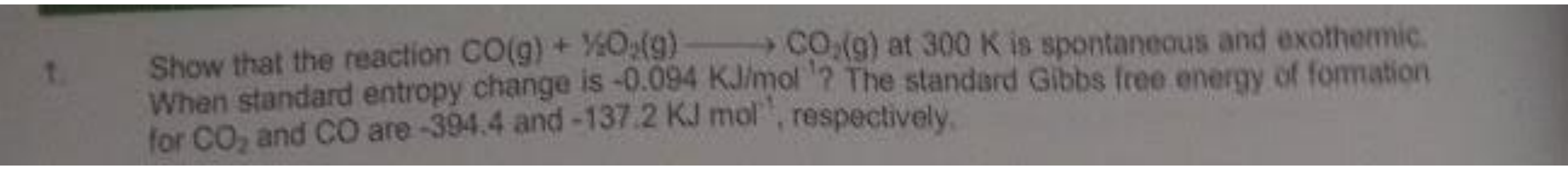
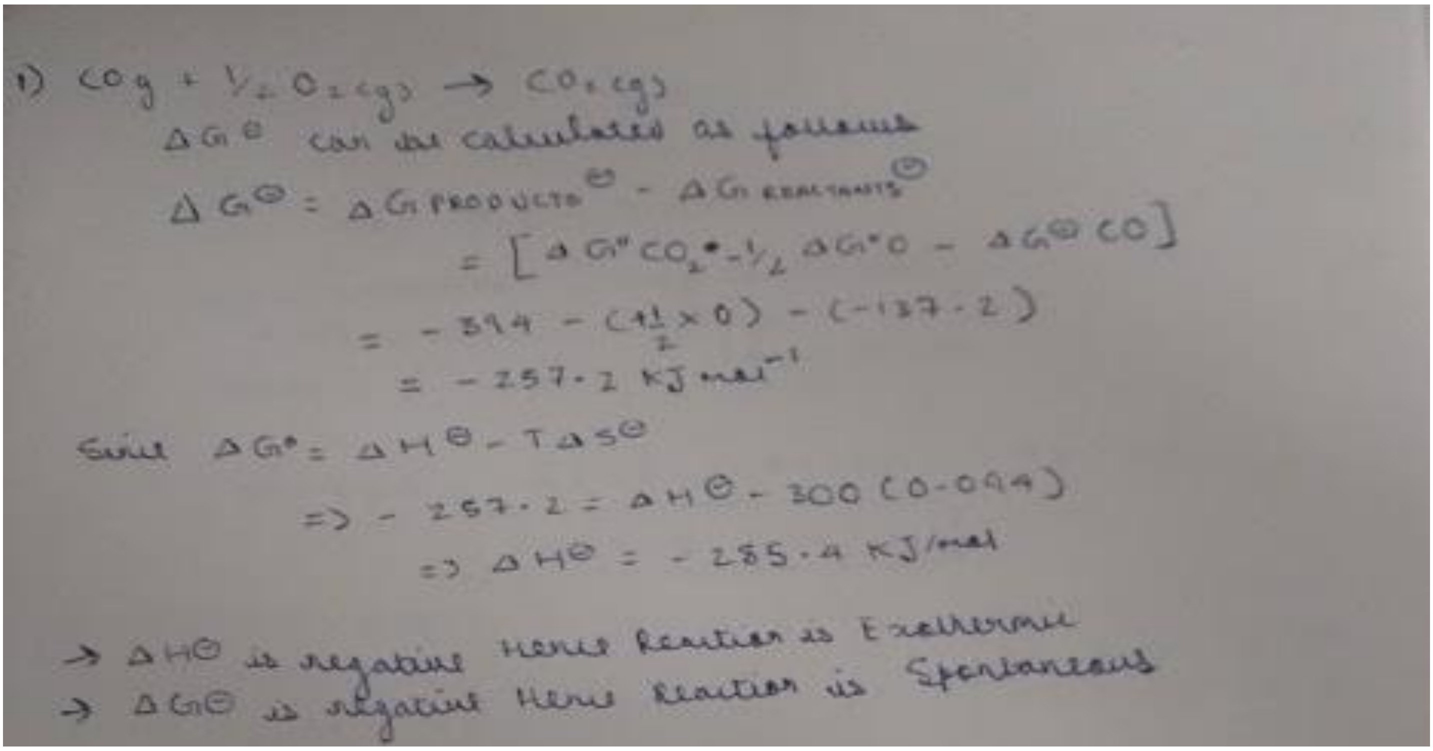
THERMODYNAMICS CHAPTER PRACTICE PROBLEMS



1. Show that the reaction $CO(g) + ½O_2(g) \longrightarrow CO_2(g)$ at 300 K is spontaneous and exothermic. When standard entropy change is -0.094 KJ/mol^{-1}? The standard Gibbs free energy of formation for CO_2 and CO are -394.4 and -137.2 KJ mol^{-1}, respectively.



1) $CO_g + ½ O_2(g) \rightarrow CO_2(g)$

$\Delta G^\ominus$ can be calculated as follows

$\Delta G^\ominus = \Delta G_{PRODUCTS}^\ominus - \Delta G_{REACTANTS}^\ominus$

$= [\Delta G^\circ CO_2^\bullet - ½ \Delta G^\circ O - \Delta G^\ominus CO]$

$= -394 - (+\frac{1}{2} \times 0) - (-137.2)$

$= -257.2$ KJ mol^{-1}

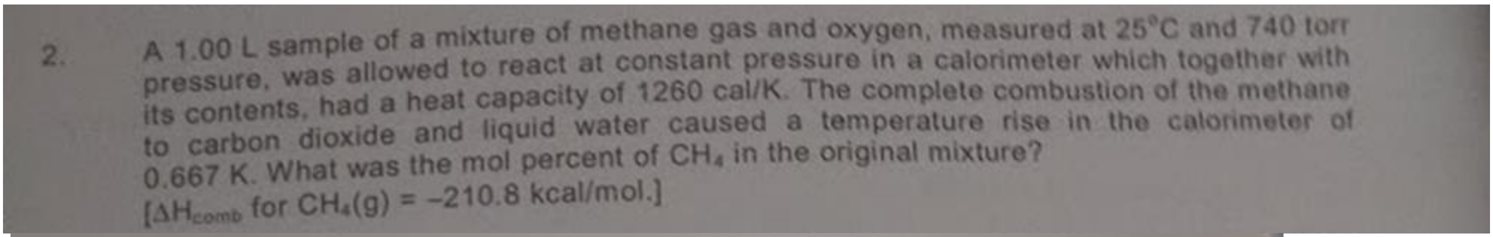
Since $\Delta G^\circ = \Delta H^\ominus - T\Delta S^\ominus$

$\Rightarrow -257.2 = \Delta H^\ominus - 300(0.094)$

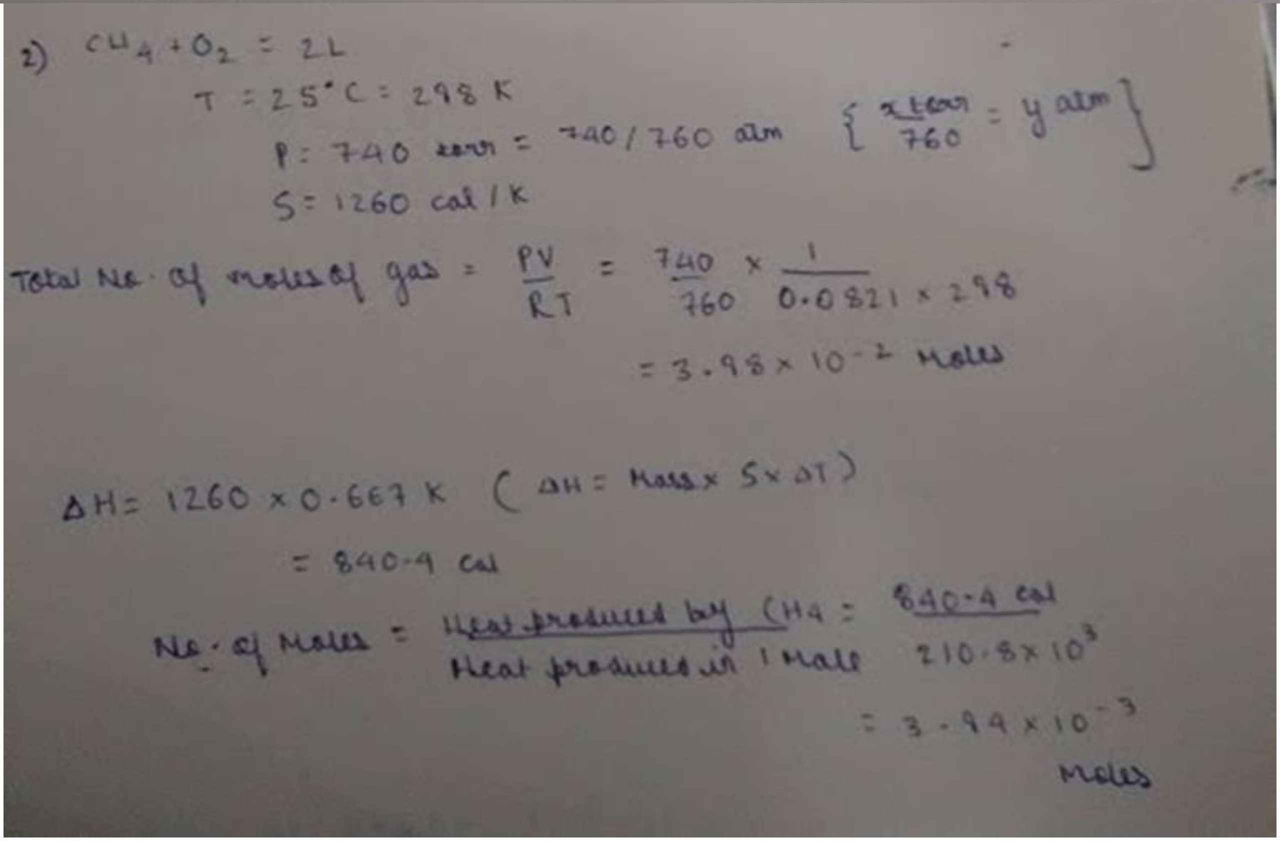
$\Rightarrow \Delta H^\ominus = -285.4$ KJ/mol

→ $\Delta H^\ominus$ is negative Hence Reaction is Exothermic

→ $\Delta G^\ominus$ is negative Hence Reaction is Spontaneous



2. A 1.00 L sample of a mixture of methane gas and oxygen, measured at 25°C and 740 torr pressure, was allowed to react at constant pressure in a calorimeter which together with its contents, had a heat capacity of 1260 cal/K. The complete combustion of the methane to carbon dioxide and liquid water caused a temperature rise in the calorimeter of 0.667 K. What was the mol percent of CH_4 in the original mixture? [ΔH_{comb} for $CH_4(g) = -210.8$ kcal/mol.]



2) $CH_4 + O_2 = 2L$

$T = 25°C = 298$ K

$P = 740$ torr $= 740/760$ atm $\left\{ \frac{x \text{ torr}}{760} = y \text{ atm} \right\}$

$S = 1260$ cal/K

Total No. of moles of gas $= \frac{PV}{RT} = \frac{740}{760} \times \frac{1}{0.0821 \times 298}$

$= 3.98 \times 10^{-2}$ Moles

$\Delta H = 1260 \times 0.667$ K ($\Delta H =$ Mass $\times S \times \Delta T$)

$= 840.4$ cal

No. of Moles $= \frac{\text{Heat produced by } CH_4}{\text{Heat produced in 1 Mole}} = \frac{840.4 \text{ cal}}{210.8 \times 10^3}$

$= 3.99 \times 10^{-3}$ Moles

% of Moles : $\frac{3.94\times10^{-3}}{3.98\times10^{-3}}$ {moles of CH_4}

= 10 %

3. Calculate the heat of following gaseous reaction $CH_4 + 4F_2 \rightarrow CF_4 + 4HF$ the bond energy of C –H, F– F, C–F and H–F bonds are 99.3, 38, 116 and 135 KCal/mole respectively

3) $CH_4 + 4F_2 \rightarrow CF_4 + 4HF$

	K cal/Mole
C – H	99.3
F – F	38
C – F	116
H – F	135

Heat is absorbed To break bonds Hence (+ve)

Heat is released to form bonds hence (–ve)

$+ 99.3\times4 + 4\times38 - 4\times(116) - 4\times(135$

$\boxed{= -454.8 \text{ K cal/Mole}}$

4. The heat of reaction for $N_2 + 3H_2 \longrightarrow 2NH_3$ at 27°C is -91.94 KJ. What will be its value at 50°C? The molar heat capacities at constant pressure and 27°C for N_2, H_2 and NH_3 are 28.45, 28.32 and 37.07 joule respectively.

4) $\Delta H(T_2) = \Delta H(T_1) + C_p(T_2 - T_1)$

$C_p(NH_3)$: 37.07

$C_p(N_2)$: 28.45

$C_p(H_2)$: 28.32

$T_1 = 27°C$

$T_2 = 50°C$

$\Delta H(T_1) = -91.94 \text{ KJ mol}^{-1}$

$\Delta C_p = 2\times C_p(NH_3) - C_p(N_2) - C_p(H_2)\times3$

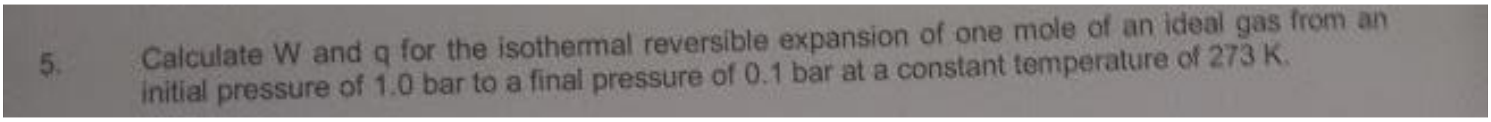
$= 2\times37.07 - 28.45 - 3\times28.32$

$= -39.27 \text{ KJ/mol} \times 10^{-3}$

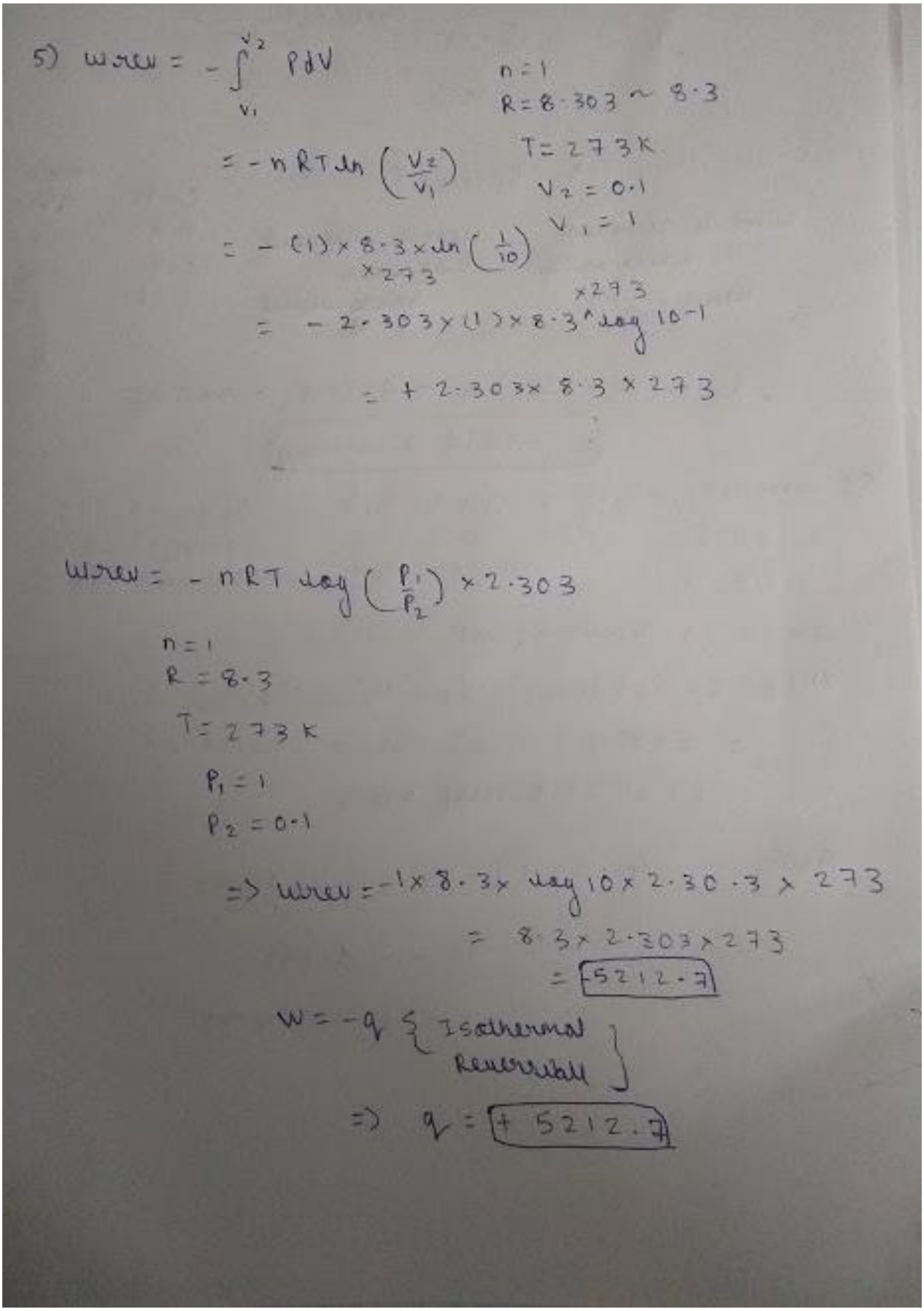
$\Delta H(T_2) = -91.94 + [-0.03927\times(50-27)]$

$= -91.94 - (0.90)$

$= -92.84 \text{ KJ mol}^{-1}$



5. Calculate W and q for the isothermal reversible expansion of one mole of an ideal gas from an initial pressure of 1.0 bar to a final pressure of 0.1 bar at a constant temperature of 273 K.



5) $w_{rev} = -\int_{V_1}^{V_2} P\,dV$

n = 1
R = 8.303 ~ 8.3
T = 273 K
$V_2 = 0.1$
$V_1 = 1$

$= -nRT\ln\left(\frac{V_2}{V_1}\right)$

$= -(1)\times 8.3\times \ln\left(\frac{1}{10}\right)\times 273$

$= -2.303\times(1)\times 8.3\overset{\times 273}{\wedge}\log 10^{-1}$

$= +2.303\times 8.3\times 273$

$w_{rev} = -nRT\log\left(\frac{P_1}{P_2}\right)\times 2.303$

n = 1
R = 8.3
T = 273 K
$P_1 = 1$
$P_2 = 0.1$

$\Rightarrow w_{rev} = -1\times 8.3\times \log 10\times 2.30\cdot 3\times 273$

$= 8.3\times 2.303\times 273$

$= \boxed{-5212.7}$

$w = -q$ { Isothermal Reversible }

$\Rightarrow q = \boxed{+5212.7}$