3/10/2014.

Energy & Entropy Problem Sheet 1.

Note — these solutions are only intended as a guide. To obtain full credit in an exam you should show your working.

1. a) i) $f(x,y) = y + x^2 + e^{xy}$

$$\frac{\partial f}{\partial x} = 2x + ye^{xy}$$

$$\frac{\partial f}{\partial y} = 1 + xe^{xy}$$

ii) $$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right) = e^{xy} + xye^{xy}$$

$$\frac{\partial^2 f}{\partial y \partial x} = \frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right) = e^{xy} + xye^{xy}$$

b) i) $$p = \frac{RT}{V} \Rightarrow \left.\frac{\partial p}{\partial V}\right|_T = -\frac{RT}{V^2}$$

$$\therefore K_T = -V\left.\frac{\partial p}{\partial V}\right|_T = \frac{RT}{V} = p.$$

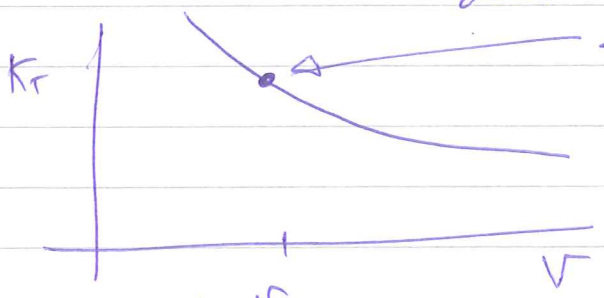
This tells us how difficult it is to change the volume of air.
If the volume changes by $\frac{\Delta V}{V}$, then the pressure changes by

$$K_T\left(\frac{\Delta V}{V}\right).$$

ii) $\frac{\partial K_T}{\partial V} = -\frac{RT}{V^2}$.

negative ⇒ harder to compress as volume decreases.

positive ⇒ easier to compress as volume decreases



Note: if this had a +ve slope then the gas would become easier to compress as its volume decreased — an unstable situation!

2.a) i) $dx = \underbrace{(10y + 6z)}_{A}dy + \underbrace{6y}_{B}dz$

$\frac{\partial (10y+6z)}{\partial z} = 6 = \frac{\partial (6y)}{\partial y} = 6.$

⇒ exact.

ii) $dx = (3y^2 + 4yz)dy + (2yz + y^2)dz$

$\frac{\partial}{\partial z}(3y^2 + 4yz) = 4y.$

$\frac{\partial}{\partial y}(2yz + y^2) = 2z + 2y$

} not exact.

b) i) $dU = dQ + dW$.

$dQ = \frac{3}{2} R dT$ for 1 mole of ideal gas.

$dW = -p dV$.

$\therefore dU = \frac{3}{2} R dT - p dV$.

$\Rightarrow \frac{\partial}{\partial V}\left(\frac{3R}{2}\right) = 0$ & $\frac{\partial}{\partial T}(-p) = 0$ (p constant)

$\therefore U$ is exact

& $U = \frac{3}{2} RT - pV$.

(function of state — only depends on start & end points)!

ii) $dS = \frac{dU}{T} + \frac{p}{T} dV = \frac{3R}{2T} dT - \frac{p dV}{T} + \frac{p dV}{T}$

$= \frac{3R}{2T} dT$.

$\therefore S$ is exact & $S = \frac{3R}{2} \ln T + S_0$.

3. a) Adiabatic processes obey $pV^\gamma = \text{const.}$

Ideal gas $\Rightarrow pV = RT$.

$\therefore p^{1-\gamma} T^\gamma = \text{const.}$

If $T_1 = 273K$ & $p_1 = 101.3 kPa$ (1 atm)
& $p_2 = 1013 kPa$ (10 atm)

$$\Rightarrow T_2 = \left(\frac{p_1}{p_2}\right)^{\frac{1}{\gamma}-1} T_1$$

$\gamma = 7/5$ for diatomic gas

$$\Rightarrow T_2 \simeq 527K.$$

b) The work done on the gas in isothermal compression is:

$$W = \int -p\,dV = \int -p\left(-\frac{RT}{p^2}\right)dp$$

$dV = \frac{\partial V}{\partial p}dp$.

$$= RT \ln \frac{p_2}{p_1} = RT \ln 10.$$

If it remains at the same temperature:

$$dU = dW + dQ = 0$$
$$\therefore dW = -dQ$$
$$Q = -RT \ln 10$$
$$= -5.2 kJ \text{ per mole of gas.}$$

4 a) The lake is large $\Rightarrow$ temperature unchanged.
The block cools from $T_1 = 100°C$ to $T_2 = 10°C$.

$$\Delta S_{block} = \int_{T_1}^{T_2} \frac{dQ}{T} = \int_{T_1}^{T_2} \frac{C_p\, dT}{T}$$

$$= C_p \ln\left(\frac{T_2}{T_1}\right)$$

$$= 150 \cdot \ln\left(\frac{283}{373}\right)$$

$$= -41.45\,JK^{-1}.$$

↑ T in kelvin

$$\Delta S_{lake} = \frac{Q}{T_{lake}} = \frac{\Delta T C_p}{T_{lake}}$$

↖ heat absorbed from block.

$$= \frac{90 \cdot 150}{283} = 47.7\,JK^{-1}$$

$$\therefore \Delta S_{universe} = \Delta S_{block} + \Delta S_{lake} = 6.3\,JK^{-1}.$$

b). $V = mgh = 100 \times 0.4 \times 9.81 = 392\,J$

potential energy ⇒ heat energy in lake

$$\therefore \Delta S_{LAKE} = \frac{392}{283} = 1.39\ JK^{-1}$$

$$\Delta S_{Block} = 0.$$

↑ ΔS_{UNI} change.

c) Block 1 $100^\circ C \rightarrow 50^\circ C$

Block 2 $0^\circ C \rightarrow 50^\circ C$

$$\therefore \Delta S_1 = \int_{373}^{323} \frac{C_p dT}{T} = C_p \ln \frac{323}{373}$$

Similarly $\Delta S_2 = C_p \ln \frac{323}{273}$ $\therefore \Delta S_{UNI} = 3.6\,JK^{-1}.$

5. $$\Delta S = \int_{T_0}^{T_1} \frac{C_p dT}{T} = \int_{T_0}^{T_1} \frac{aT}{T} dT$$

$$= a(T_1 - T_0)$$

$$\therefore \Delta S = 4.3 \text{ JK}^{-1} \text{mol}^{-1}.$$

6. $1 \to 2$ Gas is compressed
$2 \to 3$ Spark $\Rightarrow$ energy released & pressure rises
$3 \to 4$ Power stroke as gas expands
$4 \to 1$ Exhaust gases & heat released.

a) Work done is

$$W = Q_{23} - Q_{41}$$

(i.e. the heat in minus heat out is work).

Q_{23} heats gas & Q_{41} cools it

$$\therefore W = C_v(T_3 - T_2) - C_v(T_4 - T_1)$$

$$\eta = \frac{W}{Q_{23}} \qquad \left(\text{efficiency} = \frac{\text{work}}{\text{heat in}}\right)$$

$$= 1 - \frac{T_4 - T_1}{T_3 - T_2}.$$

But $pV = RT$ i.e. $p_1V_1 = RT_1$ etc.
$p_2 \; V_2 \; T_2$
$p_3 \; V_3 \; T_3$
$p_4 \; V_4 \; T_4$

$$\Rightarrow \quad \eta = 1 - \frac{p_4 V_1 - p_1 V_1}{p_3 V_2 - p_2 V_2}.$$

But $p_1 V_1^{\gamma} = p_2 V_2^{\gamma}$ on adiabatic heating

& $p_3 V_3^{\gamma} = p_4 V_4$

$V_3 = V_2$ & $V_4 = V_1$

$$\Rightarrow \quad \frac{p_1 V_1}{p_2 V_2} = \frac{V_2^{\gamma-1}}{V_1^{\gamma-1}}$$

&

$$\frac{p_4}{p_1} = \frac{p_3}{p_2}$$

$$\therefore \quad \eta = 1 - \left(\frac{V_2}{V_1}\right)^{\gamma-1} = 1 - r^{1-\gamma}$$

b) $\eta_{now} = 60\%$

If $\frac{V_1}{V_2} = \frac{11}{1} = 11 \Rightarrow \eta = 61.7\%$

$\therefore$ CO_2 reduced to $\frac{60}{61.7}$ of current

i.e. 3% reduction

10^7 cars producing 400kg CO_2/year

$\Rightarrow 4 \times 10^9$ kg yr^{-1} $\therefore$ reduction is 1.2×10^8 kg yr^{-1}

7.

$$dU = TdS + \gamma dA.$$

$$F = U - TS$$

$$\Rightarrow dF = dU - TdS - SdT$$

$$= -SdT + \gamma dA.$$

$$\therefore \left.\frac{\partial F}{\partial T}\right|_A = -S \quad \& \quad \left.\frac{\partial F}{\partial A}\right|_T = \gamma.$$

$$\Rightarrow \frac{\partial^2 F}{\partial A \partial T} = -\left.\frac{\partial S}{\partial A}\right|_T = \left.\frac{\partial \gamma}{\partial T}\right|_A.$$

If $dU = TdS + \gamma dA$

$$\Rightarrow \frac{dU}{dA} = \frac{TdS}{dA} + \gamma. \quad \text{(for small } dA\text{)}$$

$$\therefore u = \frac{T\partial S}{\partial A} + \gamma = \gamma - T\left.\frac{\partial \gamma}{\partial T}\right|_A$$

$\longrightarrow$ using maxwell relation