

① a). A state function is a function that only depends on the initial and final state
 → it is independent of the path $\oint dx = 0$

6) i) I: reversible, isothermal expansion $(p_1, v_1, T_1) \rightarrow (p_2, v_2, T_1)$.
 perfect gas.

$$du = dq_{rev} + dw_{rev} \quad du = 0 \leftrightarrow \text{isothermal \& perfect gas}$$

$$\Delta u = 0 \quad (u = \frac{3}{2} nRT)$$

So: $dq_{rev} = -dw_{rev} = +pdv$ ($p = p_{ex}$ as reversible)

$$= \frac{nRT_1}{v} dv$$

$$q_{rev} = \int_{v_1}^{v_2} \frac{nRT_1}{v} dv = nRT_1 \ln \frac{v_2}{v_1}$$

$$w_{rev} = -q_{rev} = -nRT_1 \ln \frac{v_2}{v_1}$$

II: reversible, adiabatic expansion $(p_1, v_1, T_1) \rightarrow (p_2, v_2, T_2)$, perfect gas

[3]

→ adiabatic: $dq_{rev} = 0 \rightarrow q_{rev} = 0 \rightarrow du = dw_{rev}$
 (→ can't integrate $-pdv = -\frac{nRT}{v} dv$, as both T & v change).

so: $C_v = \left(\frac{\partial u}{\partial T} \right)_v \stackrel{p.g.}{=} \frac{\partial}{\partial T} \left(\frac{3}{2} nRT \right) = \frac{3}{2} nR$ (= constant!).

$$du = C_v dT \rightarrow \Delta u = w_{rev} = C_v \int_{T_1}^{T_2} dT = C_v (T_2 - T_1)$$

III: reversible heating at constant V $(p_1, v_2, T_2) \rightarrow (p_2, v_2, T_1)$

[3]

$$du = dq_{rev} + dw_{rev}, \text{ but } dv=0 \rightarrow w_{rev} = -\int p dv = 0$$

$$du = dq_{rev} = C_v dT \rightarrow \Delta u = q_{rev} = C_v \int_{T_2}^{T_1} dT = C_v (T_1 - T_2)$$

① b) ii) [3]

1 st path = I :	2 nd path = II + III	same as 1 st path?
$\Delta U = 0$	$\Delta U = C_V(T_2 - T_1) + C_V(T_1 - T_2) = 0$	yes
$W_{rev} = -nRT_1 \ln \frac{V_2}{V_1}$	$W_{rev} = C_V(T_2 - T_1) + 0 = C_V(T_2 - T_1)$	no ①
$Q_{rev} = nRT_1 \ln \frac{V_2}{V_1}$	$Q_{rev} = 0 + C_V(T_1 - T_2) = C_V(T_1 - T_2)$	no

So: $\rightarrow \Delta U$ is the same for both paths,
 so it is independent of the path $\rightarrow \Delta U$ is a state function ①
 $\rightarrow W_{rev}$ & Q_{rev} are not the same for both paths,
 so not independent of path $\rightarrow W_{rev}$ & Q_{rev} are not state functions. ①

c) $n=1$, perfect gas. reversible, adiabatic expansion, $V_2 = 100V_1$,
 $T_1 = 298\text{K}$.

[4]
$$\left. \begin{aligned} du &= dq_{rev} + dw_{rev} = 0 - pdv \\ du &= C_V dT \end{aligned} \right\} C_V dT = -pdv$$

$\Rightarrow C_V$ for perfect gas = $\frac{3}{2}nR \xrightarrow{n=1} C_V = \frac{3}{2}R$ (= constant)
 (see part b) i) II).

So: $\frac{3}{2}R dT = -\frac{nR}{v} dv \rightarrow \frac{3}{2}R \int_{T_1}^{T_2} \frac{1}{T} dT = -R \int_{V_1}^{V_2} \frac{1}{v} dv$

$\frac{3}{2} \ln \frac{T_2}{T_1} = -\ln \frac{V_2}{V_1} \rightarrow \ln \frac{T_2}{T_1} = -\frac{2}{3} \ln \frac{V_2}{V_1}$ ①

$T_2 = T_1 \cdot \exp\left(-\frac{2}{3} \cdot \ln \frac{V_2}{V_1}\right)$

$= 298 \cdot \exp\left(-\frac{2}{3} \cdot \ln 100\right) (= T_1 \cdot 0.0464)$

$= 13.8\text{K}$ ①

Some remember $\frac{V_2}{V_1} = \left(\frac{T_1}{T_2}\right)^{3/2}$ ②
 $\rightarrow T_2 = T_1 \left(\frac{V_2}{V_1}\right)^{-2/3} = 298 \cdot 100^{-2/3} = 13.8\text{K}$ ②



① d).

[3]

$$dA = -SdT - pdV$$

$$\text{Fund. Eq.: } dA = \underbrace{\left(\frac{\partial A}{\partial T}\right)_V}_{-S} dT + \underbrace{\left(\frac{\partial A}{\partial V}\right)_T}_{-p} dV \quad (1)$$

$$\text{so: } \left(\frac{\partial p}{\partial T}\right)_V = \frac{\partial}{\partial T}(\bar{p})_V = \frac{\partial}{\partial T} \left(-\left(\frac{\partial A}{\partial V}\right)_T \right)_V$$

\uparrow
 $p = -\left(\frac{\partial A}{\partial V}\right)_T$

$$-\frac{\partial}{\partial T} \left(\left(\frac{\partial A}{\partial V}\right)_T \right)_V \stackrel{(1)}{=} -\frac{\partial}{\partial V} \left(\left(\frac{\partial A}{\partial T}\right)_V \right)_T = \frac{\partial}{\partial V} \left(-\left(\frac{\partial A}{\partial T}\right)_V \right)_T$$

$+S$

$A = \text{state function}$
order of diff. does not matter

$$\text{so: } \left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T \quad (1)$$

for sub in $S = -\left(\frac{\partial A}{\partial T}\right)_V$
from F.E. to get answer.

(2) a). First Law: $dU = dq_{rev} + dw_{rev}$

[4] Thermo-def of entropy: $dS = \frac{dq_{rev}}{T}$ (or $dS \geq \frac{dq}{T}$).

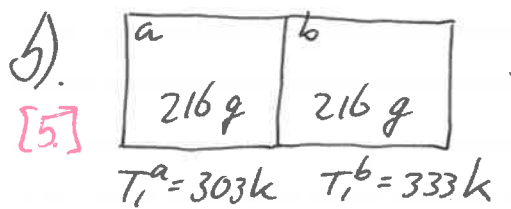
• reversible change in S , closed system, $dV=0$.

$\left. \begin{array}{l} \hookrightarrow p = p_{ex} \\ dV = 0 \end{array} \right\} dw_{rev} = -pdV = 0.$

or directly via $dq = C_v dT, p.T.O$

so: $dU = dq_{rev} + dw_{rev} = TdS + 0 = TdS$
 also: $C_v = \left(\frac{\partial U}{\partial T}\right)_V \rightarrow dU = C_v dT$

$\Rightarrow TdS = C_v dT \quad (\rightarrow dS = \frac{C_v}{T} dT).$



- constant $V \rightarrow C_v$
 - isolated from surroundings \rightarrow no heat exchange with surroundings

$\Delta S_{surr} = 0.$

$T_2 = \frac{303 + 333}{2} = 318\text{K}$ (equal amounts of water)

from a): $dS = \frac{C_v}{T} dT \rightarrow \Delta S = C_v \int \frac{1}{T} dT$ $C_v = \text{constant}$

$\Delta S = \Delta S_a + \Delta S_b = C_v \int_{T_1^a}^{T_2} \frac{1}{T} dT + C_v \int_{T_1^b}^{T_2} \frac{1}{T} dT$

$= C_v \ln \frac{T_2}{T_1^a} + C_v \ln \frac{T_2}{T_1^b} = C_v \ln \left(\frac{T_2^2}{T_1^a T_1^b} \right)$

$= 75.5 \cdot \ln \left(\frac{318^2}{303 \cdot 333} \right) = 0.160 \text{ J mol}^{-1} \text{ K}^{-1}$

(integration).

but, we have $\frac{216\text{g}}{18\text{g mol}^{-1}} = 12$ moles water in ^{both} a & b:

$\Delta S = 12 \cdot 0.160 = 2.02 \text{ J K}^{-1}$

$\Delta S_{tot} = \Delta S + \Delta S_{surr} = 2.02 + 0 = 2.02 \text{ J K}^{-1} > 0$

So in agreement with 2nd Law, as this happens spontaneously



(2) a) variation: $du = dq_{rev} + dw_{rev}$ (1)

$$ds = \frac{dq_{rev}}{T}$$

also, $c_{st} v$: $dq_{rev} = C_v dT$ (2)

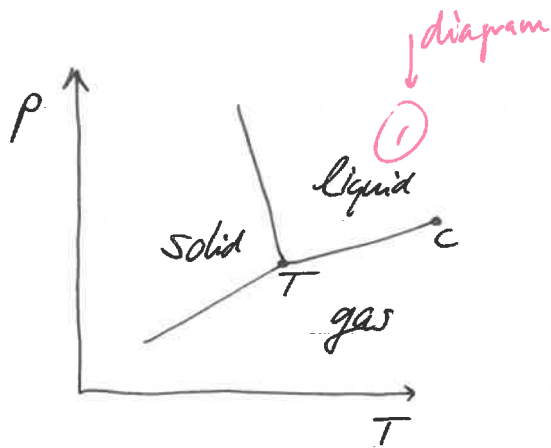
($du = dq_{rev} + dw_{rev}$
@ $c_{st} v$)

$$ds = \frac{C_v dT}{T}$$

↓

$$T ds = C_v dT$$
 (1)

(2) c. [2]



T: triple point, (where all three phases co-exist.)

labels
↓
①

c: critical point (where the boundary between the liquid and gas phases stops to exist.)

$$d). \frac{dp}{dT} = \frac{\Delta S_m}{\Delta V_m}$$

i). s-l boundary: $\Delta S_m = S_m^l - S_m^s > 0$, as $S_m^l > S_m^s$ ①

but $\Delta V_m = V_m^l - V_m^s < 0$, as ice floats on water, in other words \rightarrow density of ice $<$ density of water
 $\rightarrow V_m^s > V_m^l$

so: $\frac{dp}{dT} = \frac{\Delta S_m}{\Delta V_m} < 0$ for ice-water boundary. ①

ii). s-g vs. l-g boundary:

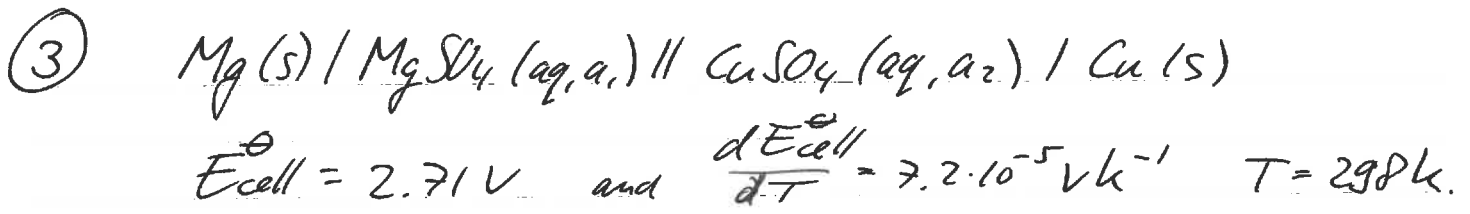
[2]

\rightarrow in both cases $\Delta S_m > 0$, as $\begin{cases} \rightarrow \text{s-g: } S_m^g > S_m^s \\ \rightarrow \text{l-g: } S_m^g > S_m^l \end{cases}$

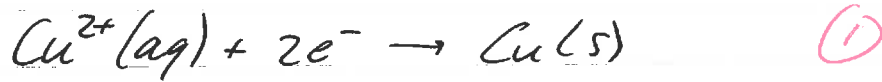
but $\Delta S_m^{\text{s-g}} > \Delta S_m^{\text{l-g}}$, as $S_m^l > S_m^s$ ①

$\rightarrow \Delta V_m$ is roughly the same for both phase boundaries, as $\Delta V_m \approx V_{m,g}$ because $V_{m,g} \gg V_{m,l}$ ①

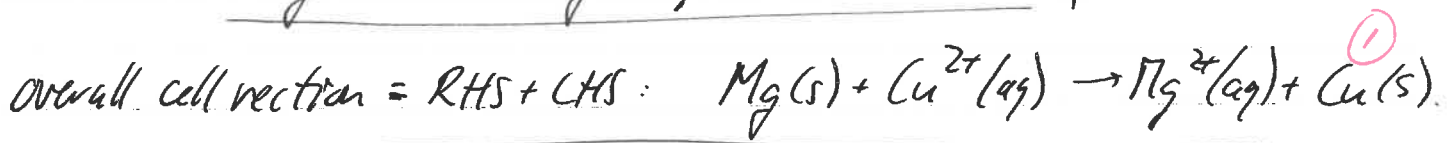
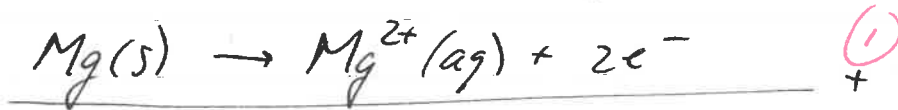
so: $\frac{dp}{dT} = \frac{\Delta S_m}{\Delta V_m}$ is always larger for s-g boundary.



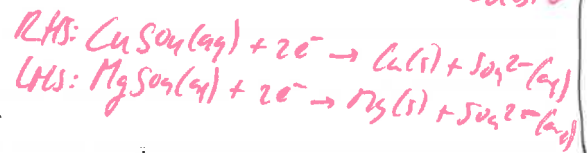
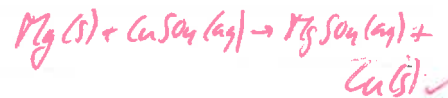
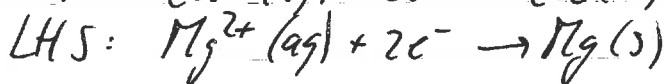
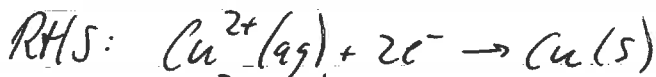
a). RHS: cathode: reduction of oxidizing agent:



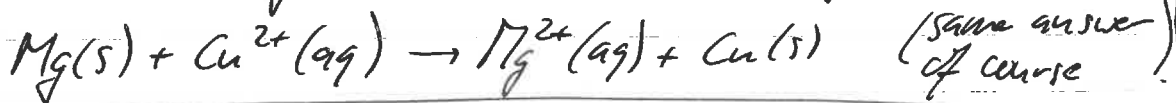
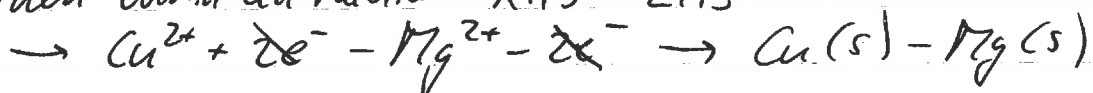
LHS: anode: oxidation of reducing agent:



note: also full marks if half-reaction are written as reductions:



but then overall cell reaction = RHS - LHS



b). $\Delta_r G^{\ominus} = -\nu F E_{cell}^{\ominus} = -2 \cdot 96480 \cdot 2.71 = -523 \text{ kJ mol}^{-1}$ (1)

$K_p = \exp\left(-\frac{\Delta_r G^{\ominus}}{RT}\right) = \exp\left(\frac{+523 \cdot 10^3}{8.314 \cdot 298}\right) = 4.6 \cdot 10^{91}$ (1) [err-FW]

K_p is huge \rightarrow equilibrium very far to the right. (1) [err-FW]

[note $\Delta_r G^{\ominus} = -\nu F E_{cell}^{\ominus}$ not in formula sheet; alternative via Nernst eq:

$E_{cell} = E_{cell}^{\ominus} - \frac{RT}{\nu F} \ln Q \rightarrow @ \text{ eqm: } E_{cell} = 0 \quad E_{cell}^{\ominus} = \frac{RT}{\nu F} \ln K_p$ (1) ($Q = K_p$)

via $\ln K_p = \frac{\nu F E_{cell}^{\ominus}}{RT} \rightarrow K_p = \exp\left\{\frac{\nu F E_{cell}^{\ominus}}{RT}\right\} = 4.6 \cdot 10^{91}$ + remark (1)

$\Delta_r G^{\ominus} = -RT \ln K_p = -523 \text{ kJ mol}^{-1}$ (1)

$$③ \text{ c.) } \rightarrow \Delta_r S^\ominus = \nu F \left(\frac{dE^\ominus}{dT} \right)$$

from $dg = -SdT + vdp \rightarrow S = -\left(\frac{\partial G}{\partial T}\right)_p$ & using $\Delta_r G^\ominus = -\nu F E_{\text{cell}}^\ominus$
not required in answer

$$\Delta_r S^\ominus = \nu F \left(\frac{dE^\ominus}{dT} \right) = 2 \cdot 96480 \cdot 7.2 \cdot 10^{-5} = 13.89 \text{ J mol}^{-1} \text{ K}^{-1} \quad ①$$

$\rightarrow \Delta_r H^\ominus$: from $G = H - TS \rightarrow H = G + TS$
so at constant T: $\Delta_r H^\ominus = \Delta_r G^\ominus + T \Delta_r S^\ominus$

$$\Delta_r H^\ominus = -523 \cdot 10^3 + 298 \cdot 13.89 = -519 \text{ kJ mol}^{-1} \quad ① \quad [\text{err-FW}]$$

d). Nernst equation: $E_{\text{cell}} = E_{\text{cell}}^\ominus - \frac{RT}{\nu F} \ln Q$ $Q = \prod_i a_i^{\nu_i}$

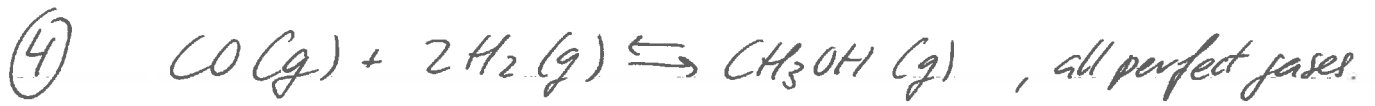
$$Q = \frac{a_{\text{Ag}^{2+}} \cdot a_{\text{Cu}(s)}}{a_{\text{Ag}(s)} \cdot a_{\text{Cu}^{2+}}} = \frac{10^{-4} \cdot 1}{1 \cdot 10^{-2}} = 10^{-2} \quad ①$$

$\left. \begin{array}{l} a_{\text{Ag}^{2+}} = a_1 \\ a_{\text{Cu}^{2+}} = a_2 \\ a_{\text{Cu}(s)} = a_{\text{Ag}(s)} = 1 \end{array} \right\}$

$$E_{\text{cell}} = 2.71 - \frac{8.314 \cdot 298}{2 \cdot 96480} \cdot \ln 10^{-2}$$

$$= 2.77 \text{ V}$$

① [err-FW]
v & alpha



a) $\Delta_r G^\ominus = -RT \ln K_p$ ①

$$\Delta_r G^\ominus = \sum_i \nu_i \Delta_f G^\ominus(i) = \Delta_f G^\ominus(\text{CH}_3\text{OH}) - \Delta_f G^\ominus(\text{CO}) - 2 \cdot \Delta_f G^\ominus(\text{H}_2)$$

= 0!

$$= -162.0 - -137.2 = -24.8 \text{ kJ mol}^{-1}$$
 ①

$$K_p = \exp\left(-\frac{\Delta_r G^\ominus}{RT}\right) = \exp\left(\frac{+24.8 \cdot 10^3}{8.314 \cdot 298}\right) = 2.22 \cdot 10^4$$
 ① [err fw from $\Delta_r G^\ominus$]

b) $\Delta_r G^\ominus = -RT \ln K_p \rightarrow \ln K_p = -\frac{\Delta_r G^\ominus}{RT}$

$$\Rightarrow \frac{\partial \ln K_p}{\partial T} \stackrel{\text{① writing derivative}}{=} -\frac{1}{R} \frac{\partial}{\partial T} \left(\frac{\Delta_r G^\ominus}{T} \right) \stackrel{\text{① applying Gibbs-Helmholtz}}{=} -\frac{1}{R} \frac{-\Delta_r H^\ominus}{T^2} = \frac{\Delta_r H^\ominus}{RT^2}$$

using Gibbs-Helmholtz (given $\left(\frac{\partial(G/T)}{\partial T}\right)_p = \frac{-H}{T^2}$)

$$\Rightarrow \int_{\ln K_1}^{\ln K_2} d \ln K_p \stackrel{\text{① sep. var.}}{=} \frac{\Delta_r H^\ominus}{R} \int_{T_1}^{T_2} \frac{1}{T^2} dT \rightarrow \text{assuming } \Delta_r H^\ominus \text{ is independent of } T$$
 ①

$$\ln \frac{K_2}{K_1} = \frac{\Delta_r H^\ominus}{R} \left[-\frac{1}{T} \right]_{T_1}^{T_2} = \frac{\Delta_r H^\ominus}{R} \left[-\frac{1}{T_2} + \frac{1}{T_1} \right]$$
 ② doing integral

$$\ln \frac{K_2}{K_1} = -\frac{\Delta_r H^\ominus}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$

(4) c). $T_2 = 600 \text{ K}$, $\Delta_r H^\ominus$ independent of $T \rightarrow$ use Van't Hoff eq.
 $T_1 = 298 \text{ K}$ & $k_1 = 2.22 \cdot 10^{-4}$ (from part a)

$$\Delta_r H^\ominus = \sum_i \nu_i \Delta_f H^\ominus(i) = \Delta_f H^\ominus(\text{CH}_3\text{OH}) - \Delta_f H^\ominus(\text{CO}) - 2 \cdot \Delta_f H^\ominus(\text{H}_2)$$

$= 0!$

$$= -200.7 - -110.5 = -90.2 \text{ kJ mol}^{-1} \quad (1)$$

$$\ln \frac{k_2}{k_1} = - \frac{\Delta_r H^\ominus}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) = - \frac{-90.2 \cdot 10^3}{8.314} \left(\frac{1}{600} - \frac{1}{298} \right) =$$
$$= -10.32$$

$$k_2 = k_1 \cdot \exp(-10.32) = 2.44 \cdot 10^{-4} \quad (1) \quad [\text{err. F.W. from } \Delta_r H^\ominus \text{ and } k_1]$$

so $k_2 < k_1$ as $T \uparrow$, which is consistent with Le Chatelier as this states that for an exothermic reaction ($\Delta_r H^\ominus < 0$, as here), an increase in temperature, shifts the equilibrium to reactants, i.e.

$$\left(\frac{d \ln k_p}{dT} = \frac{\Delta_r H^\ominus}{RT^2} < 0, \text{ so } T \uparrow, k_p \downarrow \right).$$

$k_p \downarrow$. (2)
[only def. LC: (1)]

(4) d). $\text{CO} + 2\text{H}_2 \rightleftharpoons \text{MeOH}$ (but $\text{MeOH} = \text{CH}_3\text{OH}$)

$t=0$	n	$2n$	0
equilibrium	$n(1-\alpha)$	$2n(1-\alpha)$	$n\alpha$
x_i	$\frac{1-\alpha}{3-2\alpha}$	$\frac{2(1-\alpha)}{3-2\alpha}$	$\frac{\alpha}{3-2\alpha}$

$n - n\alpha + 2n - 2n\alpha + n\alpha = 3n - 2n\alpha = n(3 - 2\alpha)$

$x_{\text{CH}_3\text{OH}} = x_{\text{MeOH}} = x_M = \frac{1}{4} = \frac{\alpha}{3-2\alpha} \rightarrow$ calculate α :

$4\alpha = 3 - 2\alpha \rightarrow 6\alpha = 3 \rightarrow \alpha = \frac{1}{2}$

So: $x_{\text{CO}} = \frac{1-\alpha}{3-2\alpha} = \frac{1-\frac{1}{2}}{3-2\cdot\frac{1}{2}} = \frac{\frac{1}{2}}{2} = \frac{1}{4}$

$x_{\text{H}_2} = \frac{2(1-\alpha)}{3-2\alpha} = \frac{2(1-\frac{1}{2})}{3-2\cdot\frac{1}{2}} = \frac{1}{2}$ (= $2 \cdot x_{\text{CO}}$ of course).

Now: $k_p = \prod_i a_i^{v_i}$ perfect gases $\Rightarrow k_p = \frac{\left(\frac{p_M}{p^\ominus}\right)}{\left(\frac{p_{\text{CO}}}{p^\ominus}\right) \left(\frac{p_{\text{H}_2}}{p^\ominus}\right)^2} \Rightarrow$ use $p_i = x_i p$

$k_p = \frac{(x_M \cdot p / p^\ominus)}{\left(\frac{x_{\text{CO}} \cdot p}{p^\ominus}\right) \left(\frac{x_{\text{H}_2} \cdot p}{p^\ominus}\right)^2} = \frac{x_M}{x_{\text{CO}} x_{\text{H}_2}^2} \cdot \left(\frac{p^\ominus}{p}\right)^2$

So, $k_p = 2.44 \cdot 10^{-4}$ @ $T = 600\text{K}$ & $x_M = x_{\text{CO}} = \frac{1}{4}$ & $x_{\text{H}_2} = \frac{1}{2}$

$\Rightarrow k_p = \frac{\frac{1}{4}}{\frac{1}{4} \left(\frac{1}{2}\right)^2} \cdot \left(\frac{p^\ominus}{p}\right)^2 = 4 \cdot \left(\frac{p^\ominus}{p}\right)^2 = 2.44 \cdot 10^{-4}$

$\frac{4}{2.44 \cdot 10^{-4}} = \left(\frac{p}{p^\ominus}\right)^2 \rightarrow p = p^\ominus \left(\frac{4}{2.44 \cdot 10^{-4}}\right)^{\frac{1}{2}} = 128 p^\ominus$

$p = 128 p^\ominus$. (= 128 bar).

[err FW]

(2)

answer when $K_2 = 3.0 \cdot 10^{-4}$ and is used:

$$K_p = 3.0 \cdot 10^{-4} \quad \text{and} \quad X_N = X_{CO} = \frac{1}{4} \quad \text{and} \quad X_{H_2} = \frac{1}{2}$$

$$P = P^\ominus \left(\frac{4}{3.0 \cdot 10^{-4}} \right)^{\frac{1}{2}} = 115.5 P^\ominus$$

$$P = 116 P^\ominus (= 116 \text{ bar}).$$

$$\text{also: } \left. \begin{array}{l} X_{CO} + X_{H_2} + X_N = 1 \\ X_N = \frac{1}{4} \quad \text{and} \quad X_{H_2} = 2 X_{CO} \end{array} \right\}$$

$$X_{CO} + 2X_{CO} + \frac{1}{4} = 1$$

$$X_{CO} = \frac{1}{4}$$

$$X_{H_2} = \frac{1}{2}.$$

fine
without
table

2