

- please answer all **5 questions** in the spaces provided
- this is a **two hour test**
- a calculator and the equation sheets provided may be used

- all questions are of equal value
- no books or notes are allowed
- no marks for unreadable answers

1. a) This question refers to the reaction $\text{CH}_4(\text{g}) + 2\text{H}_2\text{O}(\text{g}) = \text{CO}_2(\text{g}) + 4\text{H}_2(\text{g})$ used to make hydrogen from methane. Without checking data, why would you expect a positive entropy change for this reaction?

3 moles of reactant gases \rightarrow 5 moles of product gases
(larger entropy)
 $\Delta n_{\text{gas}} = +2 \text{ mol}$

- b) Calculate ΔH° , ΔG° and ΔS° for the reaction at 25 °C. Data at 25 °C:

	$\Delta H_{\text{fm}}^\circ / \text{kJ mol}^{-1}$	$\Delta G_{\text{fm}}^\circ / \text{kJ mol}^{-1}$	$S_{\text{m}}^\circ / \text{J K}^{-1} \text{ mol}^{-1}$
$\text{CH}_4(\text{g})$	-74.81	-50.72	186.26
$\text{H}_2\text{O}(\text{g})$	-241.82	-228.57	188.82
$\text{CO}_2(\text{g})$	-393.51	-394.36	213.74
$\text{H}_2(\text{g})$	0	0	130.68

$$\Delta H^\circ = -393.51 + 4(0) - (-74.81) - 2(-241.82) = 164.94 \text{ kJ mol}^{-1}$$

$$\Delta G^\circ = -394.36 + 4(0) - (-50.72) - 2(-228.57) = 113.50 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ = 213.74 + 4(130.68) - 186.26 - 2(188.82) = 172.56 \text{ J K}^{-1} \text{ mol}^{-1}$$

- c) Explain why the production of hydrogen from methane is not feasible at 25 °C.

ΔG° large and positive: non-spontaneous reaction

$$K = \frac{P_{\text{CO}_2} P_{\text{H}_2}^4}{P_{\text{CH}_4} P_{\text{H}_2\text{O}}^2} = \exp\left(-\frac{\Delta G^\circ}{RT}\right) = \exp(-45.79) = 1.302 \times 10^{-20}$$

(K very small)

- d) Is the production of hydrogen from methane feasible at 1000 °C? Justify your answer.

$$T_1 = 298.15 \text{ K} \quad T_2 = 1000 + 273.15 = 1273.15 \text{ K}$$

$$\ln K_2 = \ln K_1 - \frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$= -45.79 - \frac{164940}{8.314} \left(\frac{1}{1273.15} - \frac{1}{298.15} \right)$$

$$= -45.79 + 50.96$$

$$= 5.167$$

$$K_2 = e^{5.167} = 175.4$$

(favorable)

$$\text{at } T_2: \Delta G_2^\circ = -RT_2 \ln K_2 = -54.69 \text{ kJ mol}^{-1} \text{ at } 1000^\circ\text{C}$$

2. 20.0 L of helium (assumed to be an ideal gas) at 300 K and 5.00 bar expands isothermally against a constant external pressure of 1.00 bar to a final volume of 100.0 L.

a) Calculate w , q , ΔU , ΔH and ΔS .

isothermal ideal gas = $\Delta U = 0$, $\Delta H = 0$

work $w = -\int P_{\text{ext}} dV = -P_{\text{ext}} \int dV = -P_{\text{ext}} (V_f - V_i)$

$$w = -(1.00 \text{ bar})(100.0 \text{ L} - 20.0 \text{ L})$$

$$= -80.0 \text{ L bar}$$

$$= -(80.0 \text{ L bar})(100 \text{ J L}^{-1} \text{ bar}^{-1})$$

$$w = -8000 \text{ J}$$

$$q = \Delta U - w$$

$$q = 0 - w$$

$$q = 8000 \text{ J}$$

$$dS = \frac{C_v}{T} dT + \frac{nR}{V} dV$$

$$\Delta S = \int dS = nR \int_{V_i}^{V_f} \frac{1}{V} dV$$

$$= nR \ln(V_f/V_i)$$

$$= (4.001 \text{ mol}) 8.314 \frac{\text{J}}{\text{K mol}} \ln \frac{100.0 \text{ L}}{20.0 \text{ L}}$$

$$\Delta S = 53.5 \text{ J K}^{-1}$$

$$n = \frac{P_i V_i}{RT} = 4.001 \text{ mol}$$

$$= \frac{(5.00 \text{ bar})(20.0 \text{ L})}{(0.08314 \text{ L bar K}^{-1} \text{ mol}^{-1})(300 \text{ K})}$$

b) Use the entropy (not your equation sheet!) to prove the expansion is irreversible.

notice $\int \frac{dq}{T} = \frac{1}{T} \int dq = \frac{q}{T} = \frac{8000 \text{ J}}{300 \text{ K}} = 26.7 \frac{\text{J}}{\text{K}} \neq \Delta S$

$$\therefore q \neq q_{\text{rev}} \quad q = q_{\text{irrev}}$$

$$\Delta S_{\text{sys}} + \Delta S_{\text{sur}} \Big|_{\text{isolated overall}} = 53.5 \frac{\text{J}}{\text{K}} + \frac{-8000 \text{ J}}{300 \text{ K}}$$

$$= 53.5 \frac{\text{J}}{\text{K}} - 26.7 \frac{\text{J}}{\text{K}}$$

$$\Delta S_{\text{total}} = 26.8 \frac{\text{J}}{\text{K}} (> 0 \text{ for the universe})$$

\therefore irrev.

3. a) For the Carnot cycle explain why:

reversible

i) $q_H + q_C + w$ must equal zero *First Law for one engine cycle.*

$$\oint_i^i dU = U_i - U_i = 0 = q_H + q_C + w = \text{total heat} + \text{total work per cycle}$$

(U is a state function)

ii) $q_H/T_H + q_C/T_C$ must equal zero

$$\oint_i^i \frac{dq}{T} = \oint_i^i \frac{dq_{rev}}{T} = \oint_i^i ds = S_i - S_i = 0 = \frac{q_H}{T_H} + \frac{q_C}{T_C}$$

(S is a state function)

b) Calculate the maximum efficiency of an atmospheric steam engine operation with $T_C = 290 \text{ K}$ and $T_H = 373 \text{ K}$.

$$\epsilon = 1 - \frac{T_C}{T_H} = 1 - \frac{290 \text{ K}}{373 \text{ K}} = \boxed{0.222}$$

c) Modern steam engines use high pressure steam at temperatures up to ⁸⁰⁰500 K. High-pressure steam engines are much more expensive to build than atmospheric engines. Why are they used?

$\epsilon = 1 - \frac{T_C}{T_H}$ *increasing T_H increases the efficiency, requiring lower fuel costs to justify the more costly high-pressure engines*

d) A house is kept warm by using a heat pump with $T_H = 293 \text{ K}$ (inside the house) and $T_C = 270 \text{ K}$ (outside the house). If electrical work $w = 1.00 \text{ MJ}$ is used to run the pump, calculate the maximum amount of heat that can be pumped into the house.

$$w = 1.00 \text{ MJ}$$

$$\epsilon = \frac{-w}{q_H} = 1 - \frac{T_C}{T_H} = 0.0785$$

$$q_H = \frac{-w}{1 - \frac{T_C}{T_H}}$$

$$= \frac{-1.00 \text{ MJ}}{1 - \frac{270 \text{ K}}{293 \text{ K}}}$$

$$= \boxed{-12.73 \text{ MJ}}$$

+12.73 MJ pumped into house (for 1.00 MJ work)

4. a) Starting with the equation $dH = TdS + Vdp$ for the enthalpy, show

$$\left(\frac{\partial H}{\partial p}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_p + V$$

hint: use a Maxwell relation

$$dH = Tds + vdp \quad (\div dP_T)$$

$$\left(\frac{\partial H}{\partial p}\right)_T = T\left(\frac{\partial s}{\partial p}\right)_T + v$$

$$= -T\left(\frac{\partial v}{\partial T}\right)_p + v$$

from $dG = -SdT + Vdp$
Maxwell relation:
$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$$

- b) Use the result from part a to prove $(\partial H/\partial p)_T = 0$ for an ideal gas. $v = nRT/p$

$$\left(\frac{\partial H}{\partial p}\right)_T = -T\left(\frac{\partial}{\partial T} \frac{nRT}{p}\right)_p + v = -T \frac{nR}{p} \left(\frac{\partial T}{\partial T}\right)_p + v$$

$$= -\frac{nRT}{p} + v = -v + v = 0$$

- c) 2.00 moles of pure O₂ and 8.00 moles of pure N₂ (assumed to be ideal gases) mix at 300 K and 1.00 bar. Prove this process is spontaneous.

at constant T, p :

$$\Delta G_{T,p} = n_{O_2} RT \ln X_{O_2} + n_{N_2} RT \ln X_{N_2}$$

$$= (2.00 \text{ mol})(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(300 \text{ K}) \ln\left(\frac{2.00}{2.00+8.00}\right)$$

$$+ (8.00)(8.314)(300 \text{ K}) \ln\left(\frac{8.00}{2.00+8.00}\right)$$

$$= (-8028 - 4452) \text{ J}$$

$$\Delta G_{T,p} = -12480 \text{ J}$$

$\Delta G_{T,p} < 0 \therefore$ spontaneous

O₂, calculate
$$\Delta S = n_{O_2} R \ln X_{O_2} + n_{N_2} R \ln X_{N_2}$$

$$= -\frac{\Delta G}{T}$$

$$\Delta S = 41.6 \frac{\text{J}}{\text{K}} > 0$$

isolated system ($q=0$, $w=0$)

5. This question refers to the reaction: *trans*-1,2-dichloroethylene (g) = *cis*-1,2-dichloroethylene (g)

data at 25 °C:

trans-1,2-dichloroethylene (g)

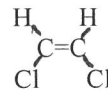
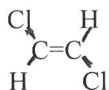
$$\Delta H_{\text{fm}}^{\circ} = 6.15 \text{ kJ mol}^{-1}$$

$$\Delta G_{\text{fm}}^{\circ} = 28.57 \text{ kJ mol}^{-1}$$

cis-1,2-dichloroethylene (g)

$$\Delta H_{\text{fm}}^{\circ} = 3.77 \text{ kJ mol}^{-1}$$

$$\Delta G_{\text{fm}}^{\circ} = 26.31 \text{ kJ mol}^{-1}$$



- a) To decide if *trans*-1,2-dichloroethylene is more stable than *cis*-1,2-dichloroethylene, why not buy a sample of *cis*-1,2-dichloroethylene and see if it spontaneously converts to the *trans*-isomer?

Reaction rate \approx zero! Too slow!

Won't see any isomerization (at 25 °C).

- b) According to organic chemistry, *trans*-1,2-dichloroethylene (less steric hindrance) is more stable than the *cis*-isomer. Use the data provided to show the *cis*-isomer is in fact more stable at 25 °C.

at 25 °C, 1 bar:

$$\boxed{\text{trans} = \text{cis}}$$

$$\Delta G^{\circ} = \Delta G_{\text{fm}}^{\circ}(\text{cis}) - \Delta G_{\text{fm}}^{\circ}(\text{trans})$$

$$= (26.31 - 28.57) \text{ kJ mol}^{-1}$$

$$\boxed{\Delta G^{\circ} = -2.26 \text{ kJ mol}^{-1} < 0}$$

cis product more stable

- c) 2.00 moles of *trans*-1,2-dichloroethylene are placed in a 50.0 tank at 25 °C. Calculate the number of moles of the *trans*-isomer and the number of moles of the *cis*-isomer present at equilibrium.

$$K = \frac{P_{\text{cis}}}{P_{\text{trans}}} = \frac{n_{\text{cis}} RT/V}{n_{\text{trans}} RT/V} = \frac{n_{\text{cis}}}{n_{\text{trans}}} = \exp\left[-\frac{-2260}{(8.314)(298.15)}\right]$$

$$0.9117$$

$$K = 0.9117 = 2.489 = \frac{n_{\text{cis}}}{n_{\text{trans}}}$$

$$n_{\text{cis}} = 2.489 n_{\text{trans}}$$

$$n_{\text{cis}} + n_{\text{trans}} = 2.00 \text{ mol}$$

$$2.489 n_{\text{trans}} + n_{\text{trans}} = 2.00 \text{ mol}$$

$$\boxed{n_{\text{trans}} = 0.573 \text{ mol} \quad n_{\text{cis}} = 1.427 \text{ mol}}$$

- d) *cis*-1,2-dichloroethylene is more stable than the *trans*-isomer. In part c, why doesn't 2.00 moles of the *trans*-isomer convert completely to 2.00 moles of the more-stable *cis*-isomer?

If the *trans* \rightarrow *cis* reaction went to 100% completion, a lower Gibbs energy can be reached by back-reacting the *cis* to form some *trans* due to the decrease in G caused by physically mixing the two isomers.

Q1
Q2
Q3
Q4
Q5