

1. a) For an ideal gas ( $dU = C_V dT$ ) undergoing a reversible process ( $dw_{\text{rev}} = -pdV$ ), the First Law  $dU = dq + dw$  gives

$$dq_{\text{rev}} = C_V dT + pdV$$

- [4] Use the test for an exact differential to show the function  $q_{\text{rev}}(T, V)$  does not exist, which means  $q_{\text{rev}}$  is path-dependent. *Hints:*  $C_V = (\partial U / \partial T)_V$  and for an ideal gas  $(\partial U / \partial V)_T = 0$ .

- b) Dividing  $dq_{\text{rev}}$  by  $T$  gives  $\frac{dq_{\text{rev}}}{T} = \frac{C_V}{T} dT + \frac{p}{T} dV$ . Show  $dS$  defined by  $dS = dq_{\text{rev}}/T$  is an exact differential, illustrating the important result that the entropy state function  $S(T, V)$  exists.

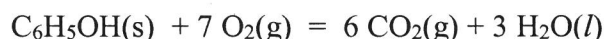
2. 20.0 L of He (assumed to be an ideal gas with  $C_{V,m} = 3R/2$ ) initially at 400 K and 2.00 bar expands adiabatically into an evacuated 20.0 L flask ( $p_{\text{external}} = 0$ ), doubling its volume.

- [6] a) Calculate  $q$ ,  $w$ ,  $\Delta U$ ,  $\Delta H$  and  $\Delta S$ .  
b) Is the expansion reversible? Justify your answer.

3. a) Calculate  $q$  for the combustion of one mole of methane at 25 °C and 1 bar.



- [2] b) Calculate  $q$  for the combustion of one mole of phenol at 25 °C and 1 bar.



$$\begin{array}{ll} \text{Data: } \Delta H_{\text{fm}}^\circ(\text{CH}_4, \text{g}) = -74.81 \text{ kJ mol}^{-1} & \Delta H_{\text{fm}}^\circ(\text{CO}_2, \text{g}) = -393.51 \text{ kJ mol}^{-1} \\ \Delta H_{\text{fm}}^\circ(\text{C}_6\text{H}_5\text{OH}, \text{s}) = -165.0 \text{ kJ mol}^{-1} & \Delta H_{\text{fm}}^\circ(\text{H}_2\text{O}, \text{l}) = -285.83 \text{ kJ mol}^{-1} \end{array}$$

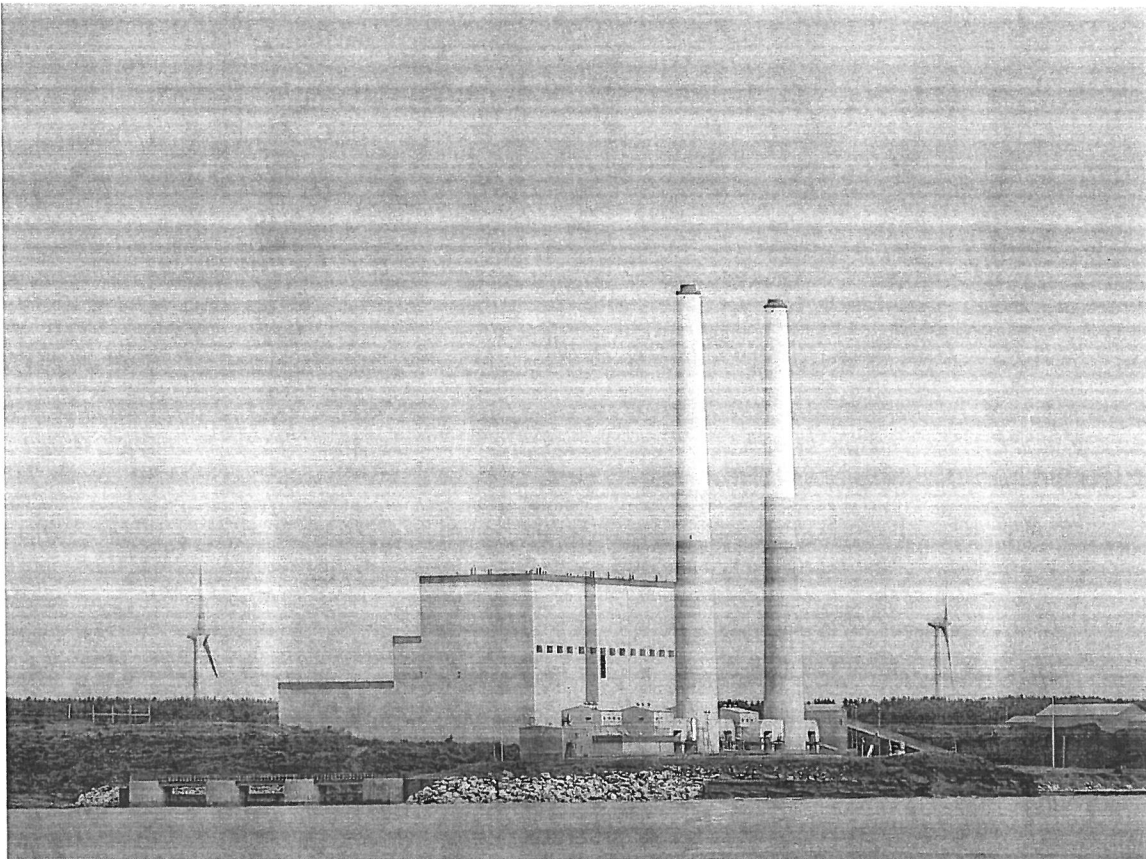
4. a) Assuming natural gas is pure methane ( $16.0 \text{ g mol}^{-1}$ ), a good approximation here, calculate the number of kilograms of natural gas that must be burned to produce 1.00 GJ heat. Also calculate the number of kilograms of  $\text{CO}_2$  ( $44.0 \text{ g mol}^{-1}$ ) produced.
- [4] b) Coal is a mineral of variable composition containing carbon, hydrogen, oxygen and smaller amounts of sulfur, nitrogen and other elements. Assuming coal is pure phenol ( $94.1 \text{ g mol}^{-1}$ ), a good approximation here, calculate the number of kilograms of coal that must be burned to produce 1.00 GJ heat. Also calculate the number of kilograms of  $\text{CO}_2$  produced.
- c) Global warming caused by increasing levels of atmospheric  $\text{CO}_2$  from burning fossil fuels is believed to be a major crisis facing humanity. From this point of view, which fuel is better: natural gas or coal? Explain.

5. The **Lingan Generating Station** near Sydney, Cape Breton, provides about 25 % of the electricity used in Nova Scotia. Bituminous coal is burned to produce steam at 350 °C and 170 bar. The high-pressure steam spins gas turbines to run 600 MW electrical generators.
- a) Use 350 °C for the temperature of the hot reservoir and 15 °C for the cold reservoir (the seawater coolant) to calculate the Carnot efficiency ( $\epsilon$ ) of the station.
- [4] b) The actual efficiency of the station (34 %) is significantly lower than the Carnot efficiency calculate in a. Why?
- c) Calculate the (electrical) work produced per year by the station.
- d) Burning one tonne of bituminous coal produces about 30 GJ of heat. Estimate the number of tonnes of coal burned at the station per year.

$$1 \text{ tonne} = 1000 \text{ kg}$$

$$600 \text{ MW} = 6.00 \times 10^8 \text{ J s}^{-1}$$

$$1 \text{ year} = 3.15 \times 10^7 \text{ s}$$



(Q1) a)  $dq_{\text{rev}} = C_v dT + p dV$

for an ideal gas undergoing a reversible process.

$dq_{\text{rev}}$  is an exact differential and the function

$q_{\text{rev}}(T, V)$  exists if  $\left(\frac{\partial C_v}{\partial V}\right)_T \stackrel{(?)}{=} \left(\frac{\partial p}{\partial T}\right)_T$

[Hints:  $C_v = \left(\frac{\partial U}{\partial T}\right)_V$  and for an ideal gas  $\left(\frac{\partial U}{\partial V}\right)_T = 0$ ]

$\left(\frac{\partial C_v}{\partial V}\right)_T = \left[ \frac{\partial}{\partial V} \left( \frac{\partial U}{\partial T} \right)_V \right]_T \stackrel{\text{switch order of differentiation}}{=} \left[ \frac{\partial}{\partial T} \left( \frac{\partial U}{\partial V} \right)_T \right]_V = 0$

$\left(\frac{\partial p}{\partial T}\right)_V = \left( \frac{\partial}{\partial T} \frac{nRT}{V} \right)_V = \frac{nR}{V} \left( \frac{\partial T}{\partial T} \right)_V = \frac{nR}{V}$

$0 \neq \frac{nR}{V} \Rightarrow$

the function  $q_{\text{rev}}(T, V)$  does not exist

This means:  $dq_{\text{rev}}$  is not an exact differential

$q_{\text{rev}}$  is not a state function

$q_{\text{rev}}$  is path-dependent

(Q1 cont.)

$$b) \quad dS = \frac{C_V}{T} dT + \frac{P}{T} dV$$

for an ideal gas undergoing a reversible process.

$dS$  is an exact differential and the function

$S(T, V)$  exists if  $\left(\frac{\partial \frac{C_V}{T}}{\partial V}\right)_T$  equals  $\left(\frac{\partial \frac{P}{T}}{\partial T}\right)_V$

$$\left(\frac{\partial \left(\frac{C_V}{T}\right)}{\partial V}\right)_T = \frac{1}{T} \left(\frac{\partial C_V}{\partial V}\right)_T = \frac{1}{T} \left[\frac{\partial}{\partial V} \left(\frac{\partial U}{\partial T}\right)_V\right] = \frac{1}{T} \left[\frac{\partial}{\partial T} \left(\frac{\partial U}{\partial V}\right)_T\right] = 0$$

(ideal gas:  $PV = nRT$        $\frac{P}{T} = \frac{nR}{V}$ )

$$\left(\frac{\partial \frac{P}{T}}{\partial T}\right)_V = \left(\frac{\partial}{\partial T} \frac{nR}{V}\right)_V = \left(\frac{\partial}{\partial T} \text{constant}\right)_V = 0$$

$$0 = 0 \Rightarrow$$

the function  
 $S(T, V)$  exists

This means:  $dS$  is an exact differential

$S(T, V)$  is a state function

$\Delta S$  is path-independent

Q2 20.0 L of He at 400 K and 2.00 bar expands adiabatically into a vacuum ( $P_{\text{external}} = 0$ ) to a final volume of 40.0 L

a)  $q = 0$  (adiabatic)

$$w = - \int P_{\text{external}} dV = - \int (0) dV = 0$$

$$\Delta U = q + w = 0 + 0 = 0$$

for an ideal gas (assumed here), the internal energy  $U(T)$  depends only on the temperature

if  $\Delta U = 0$ , then  $\Delta T = 0$  ( $T_f = T_i = 400 \text{ K}$ )

$$\begin{aligned} H &= U + pV \\ \Delta H &= \Delta U + \Delta(pV) = \Delta U + \Delta(nRT) \\ &= \Delta U + nR\Delta T \\ &= 0 + nR(0) \end{aligned}$$

$$\Delta H = 0$$

(enthalpy  $H$  also depends only on  $T$  for an ideal gas)

from Q1,  $ds = \frac{C_v}{T} dT + \frac{P}{T} dV$

here,  $T$  is constant ( $dT = 0$ ) and  $ds = \frac{P}{T} dV = \frac{nR}{V} dV$

$$\Delta S = \int ds = nR \int_{V_i}^{V_f} \frac{1}{V} dV = nR \ln\left(\frac{V_f}{V_i}\right) = \frac{P_i V_i}{T} \ln\left(\frac{V_f}{V_i}\right)$$

$$\Delta S = \frac{(2.00 \times 10^5 \text{ Pa})(20.0 \times 10^{-3} \text{ m}^3)}{400 \text{ K}} \ln\left(\frac{40.0 \text{ L}}{20.0 \text{ L}}\right) = 6.93 \frac{\text{J}}{\text{K}}$$

(Q2 cont.)

b) Is the expansion reversible?

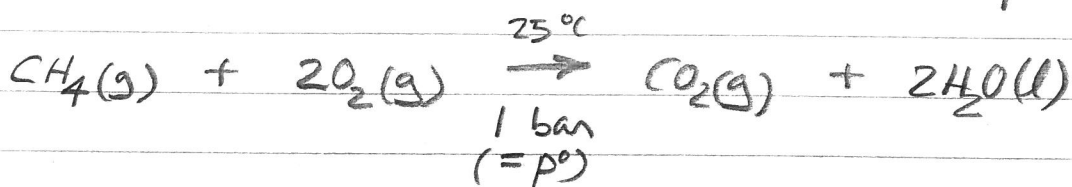
No, because  $P_{\text{external}} = P$  if reversible

here  $P_{\text{external}} < P \therefore$  irreversible

Also, notice  $\Delta S > 0$  for an isolated system.  
(and  $\Delta S \neq \frac{q}{T}$ , so  $q \neq q_{\text{rev}}$ ) ( $q=0, w=0$ )

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(Q3) a) Heat of combustion of one mole of methane:



$$q = \Delta H \quad (\text{constant pressure } p = p^\circ = 1 \text{ bar})$$

$$= \Delta H_f^\circ (\text{products}) - \Delta H_f^\circ (\text{reactants})$$

$$= \Delta H_{\text{fm}}^\circ (\text{CO}_2, \text{g}) + 2\Delta H_{\text{fm}}^\circ (\text{H}_2\text{O}, \text{l}) - \Delta H_{\text{fm}}^\circ (\text{CH}_4, \text{g}) - 2\Delta H_{\text{fm}}^\circ (\text{O}_2, \text{g})$$

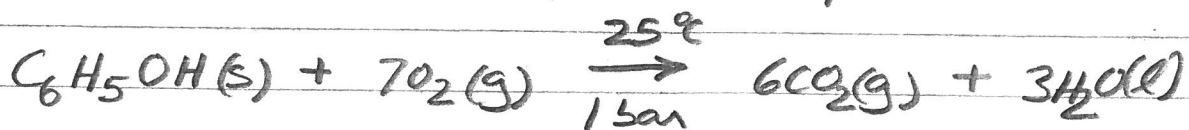
$$= -393.51 + 2(-285.83) - (-74.81) - 2(0)$$

$$q = -890.36 \text{ kJ}$$

(useful for Q4)

(Q3 cont.)

b) Heat of combustion of one mole of phenol =



$$q = \Delta H \quad (\text{constant pressure } p = p^\circ = 1 \text{ bar})$$

$$= \Delta H_f^\circ(\text{products}) - \Delta H_f^\circ(\text{reactants})$$

$$= 6\Delta H_{f,m}^\circ(\text{CO}_2, g) + 3\Delta H_{f,m}^\circ(\text{H}_2\text{O}, l) - \Delta H_{f,m}^\circ(\text{C}_6\text{H}_5\text{OH}, s)$$

$$- 7\Delta H_{f,m}^\circ(\text{O}_2, g)$$

$$= 6(-393.51) + 3(-285.83) - (-165.0) - 7(0)$$

$$q = -3053.55 \text{ kJ}$$

(useful for Q4)

(Q4) a) burning 1.00 mole methane (16.0 g) produces 890.36 kJ heat

to produce 1.00 GJ = 1000 MJ = 1,000,000 kJ heat =

$$\text{burn } (16.0 \text{ g}) \frac{1,000,000 \text{ kJ}}{890.36 \text{ kJ}} = (16.0 \text{ g}) 1123$$

$$= 17,970 \text{ g methane}$$

$$= 17.97 \text{ kg methane}$$

(1123 moles of  $\text{CH}_4$ )

(Q4 a) cont.)



burning 1.00 mole  $\text{CH}_4$  produces 1.00 mole  $\text{CO}_2$

burning 1123 moles  $\text{CH}_4$  produces 1123 mole  $\text{CO}_2$

$$\text{mass of CO}_2 = (1123 \text{ mol}) \left(44.0 \frac{\text{g}}{\text{mol}}\right) = 49,412 \text{ g} = \boxed{49.412 \text{ kg CO}_2}$$

b) burning 1.00 mole phenol ( $94.1 \text{ g mol}^{-1}$ )  
produces 3053.55 kJ heat

to produce 1.00 GJ heat = 1,000 MJ =  $10^6$  kJ

$$\text{burn } (94.1 \text{ g}) \frac{1,000,000 \text{ kJ}}{3053.55 \text{ kJ}} = (94.1 \text{ g}) 327.49$$

$$= 30,816 \text{ g phenol}$$

$$= \boxed{30.816 \text{ kg phenol}}$$



burning 1.00 mole phenol produces 6.00 mole  $\text{CO}_2$

burning 327.49 mole phenol gives  $(6.00)(327.49)$   
 $= 1964.9$  mole  $\text{CO}_2$

$$\text{mass CO}_2 = (1964.9 \text{ mol}) \left(44.0 \frac{\text{g}}{\text{mol}}\right) = 86,457 \text{ g} = \boxed{86.457 \text{ kg CO}_2}$$



(Q4 cont.)

c) producing 1.00 GJ heat by burning natural gas ( $\approx$  methane) releases 49.4 kg CO<sub>2</sub>

producing 1.00 GJ heat by burning coal ( $\approx$  phenol) releases 86.4 kg CO<sub>2</sub>

replacing coal with natural gas as a fuel releases  $\frac{49.4}{86.4} = 57\%$  of the

CO<sub>2</sub> from burning coal, a significant 43% reduction

Q5

a) Carnot efficiency of a heat

engine with  $T_H = 623 \text{ K}$  ( $350^\circ\text{C}$ )

and  $T_C = 288 \text{ K}$  ( $15^\circ\text{C}$ )

$$\varepsilon = 1 - \frac{T_C}{T_H} = 1 - \frac{288 \text{ K}}{623 \text{ K}}$$

$$= \boxed{0.537} \quad (\approx 54\%)$$

(Q5 cont.)

b) The actual efficiency of the station

$$= \frac{\text{actual work done}}{\text{heat input at } T_H}$$

$$= 0.34 \text{ for a real non-reversible engine}$$

(friction, heat losses, expansions/compressions not reversible)

The Carnot efficiency of the station

$$= \frac{\text{work done}}{\text{heat input at } T_H} \text{ for a reversible engine}$$

(idealized, not real)

$$= 0.54 \text{ and more efficient than a real engine}$$

c) work performed by the Lingen Station  
per year

$$= (\text{power})(\text{time})$$

$$\left( \text{power} = \frac{\text{energy}}{\text{time}} \right)$$

$$= (600 \text{ MW})(1 \text{ year})$$

$$= (600 \times 10^6 \text{ J s}^{-1})(3.15 \times 10^7 \text{ s})$$

$$\text{work done} = \boxed{1.89 \times 10^{16} \text{ J per year}}$$