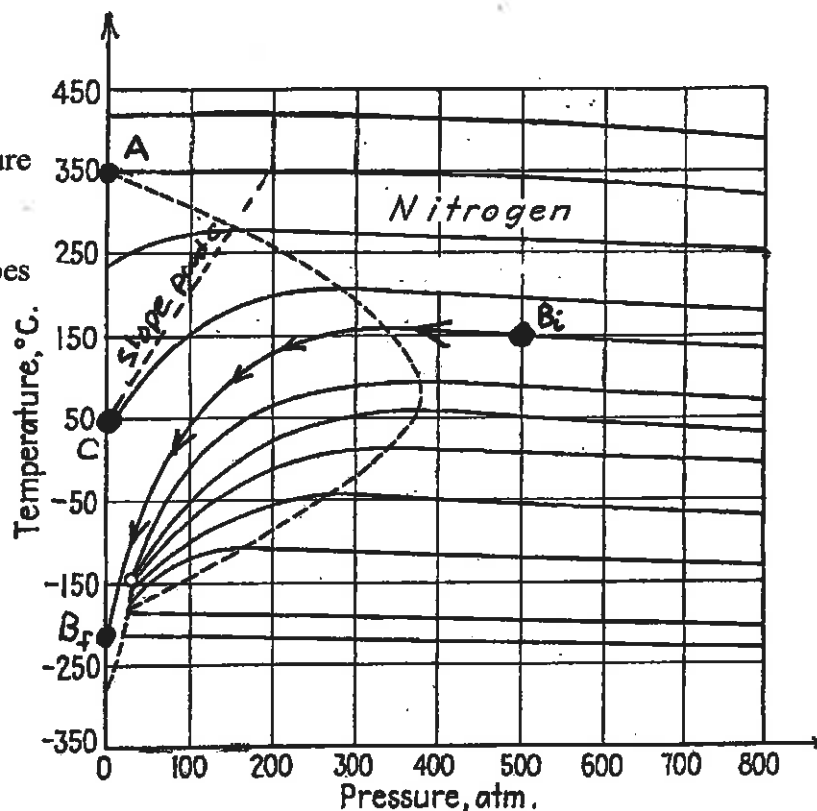


1. Use the data for the Joule-Thomson (JT) expansion of  $N_2$  plotted below to answer this question.

[4]

- Give the maximum JT inversion temperature of  $N_2$ .
- $N_2$  initially at 500 atm and 150 °C undergoes a JT expansion into a vacuum ( $p_f = 0$ ). Estimate the final temperature of the gas.
- Estimate the Joule-Thomson coefficient ( $\mu_{JT}$ , in units of  $K \text{ atm}^{-1}$ ) of  $N_2$  at 50 °C and 1 atm.
- Can liquid  $N_2$ , an important cryogen, be produced by the JT expansion of  $N_2$  gas? Explain. (Liquid  $N_2$  boils at 1 atm and  $-196$  °C.)



- Natural gas (mostly methane) is an important industrial and residential fuel. It is widely available, easily transported, and clean-burning. Assuming natural gas is pure methane, how many kilograms of natural gas must be burned to produce 1.00 GJ ( $10^9$  J) of heat? (Use  $-891 \text{ kJ mol}^{-1}$  for the heat of combustion of methane.)

[7]

- Coal (a highly variable mixture of partially oxidized aromatics and many other compounds) is also an important fuel. Assuming coal is pure phenol ( $C_6H_5OH$ ), how many kilograms of coal must be burned to produce 1.00 GJ of heat? (Use  $-3054 \text{ kJ mol}^{-1}$  for the heat of combustion of phenol.)
- Carbon dioxide released into the atmosphere by the combustion of fossil fuels is a possible cause of climate change due to the "greenhouse effect". Give a brief explanation of the "greenhouse effect".
- For every GJ of heat produced, use your answers from parts b) and c) to estimate how many kilograms of  $CO_2$  are released by burning: i) natural gas, ii) coal.
- From the point of view of climate change, which is the better fuel: natural gas or coal? Why?
- In addition to  $CO_2$ , what other potentially harmful substances are released by burning coal?

... page 2

3. a) Early steam engines used water boiling at about 1 atm and 100 °C ( $T_H = 373$  K). For every GJ of heat produced by burning fuel, calculate the maximum work obtainable from these engines. (Assume  $T_C = 293$  K)

[2]

- b) Modern steam engines (such as steam turbines that generate about 90% of the electricity used in Canada) use water boiling at high pressures, well above 1 atm. Why?

4. Calculate  $\Delta S$  for heating 1.00 kg of argon gas (assumed to be ideal) from 25 °C to 100 °C

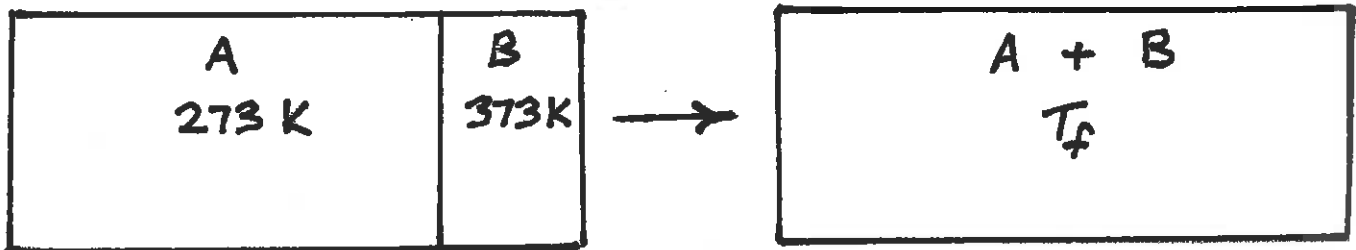
- a) at constant volume

[4]

- b) at constant pressure.

5. Two blocks of metal at different temperatures are brought into thermal contact and reach a final equilibrium temperature.

[3]



Block A (heat capacity  $C_{VA} = 300 \text{ J K}^{-1}$ ) is initially at 273 K. Block B (heat capacity  $C_{VB} = 100 \text{ J K}^{-1}$ ) is initially at 373 K. The two blocks are insulated from the surroundings and form an isolated system with negligible volume change.

- a) Show that the final temperature of the blocks is 298 K.

- b) Use the Second Law to show that the process is spontaneous (and the reverse process is impossible!).

(1) a) maximum inversion temperature

max.  $T$  when  $\frac{d\mu_{JT}}{dT} = 0$  zero slope  
of isenthalpic  
curve  
(constant  $H$ )

read about  $350^\circ\text{C}$  ( $623\text{ K}$ ) from graph  
(see point A on graph)

b) start at point  $B_i$  on graph, ( $500\text{ atm}$ ,  $150^\circ\text{C}$ )  
finish at point  $B_f$  on the isenthalpic curve  
 $P_f = 0$ , and approximately  $-220^\circ\text{C}$  (about  $50\text{ K}$ )

c) Joule-Thomson coefficient at  $50^\circ\text{C}$ ,  $1\text{ atm}$ :

estimate the slope of the isenthalp  
at point C on the graph  
(slope of dashed line, "eyeballed")

$$\frac{\Delta T}{\Delta P} \approx \frac{350 - 50\text{ K}}{200 - 0\text{ atm}} = 1.5 \frac{\text{K}}{\text{atm}}$$

d) **yes!** e.g. start at  $50^\circ\text{C}$ ,  $100\text{ atm}$   
and expand to  $P_f \approx 0$

e.g., part b

(In practice - even more important - air can be  
liquefied by JT expansion, then fractionally  
distilled to produce pure liquid  $\text{N}_2$  (mostly for  
 $\text{NH}_3$  production) and pure liquid  $\text{O}_2$ )

2. a) 1.00 mol  $\text{CH}_4$  releases 891 kJ heat when burned

$$\begin{aligned} \text{number of moles} &= \frac{1.00 \text{ GJ}}{891 \text{ kJ mol}^{-1}} = \frac{1.00 \times 10^9 \text{ J}}{8.91 \times 10^5 \text{ J mol}^{-1}} \\ \text{for 1.00 GJ heat} & \\ &= 1122 \text{ mol} \end{aligned}$$

$$\begin{aligned} \text{methane} &= (1122 \text{ mol}) \left( 16.04 \frac{\text{g}}{\text{mol}} \right) = 1.80 \times 10^4 \text{ g} = \boxed{18.0 \text{ kg}} \\ \text{mass} & \end{aligned}$$

b) 1.00 mol phenol releases 3054 J heat when burned

$$\begin{aligned} \text{number of moles} &= \frac{1.00 \text{ GJ}}{3054 \text{ kJ mol}^{-1}} = 327.4 \text{ mol} \\ \text{for 1.00 GJ heat} & \end{aligned}$$

$$\begin{aligned} \text{phenol} &= (327.4 \text{ mol}) \left( 94.11 \frac{\text{g}}{\text{mol}} \right) = 3.08 \times 10^4 \text{ g} = \boxed{30.8 \text{ kg}} \\ \text{mass} & \end{aligned}$$

c)  $\text{N}_2$  and  $\text{O}_2$  (the main components of air) are "infrared inactive", meaning these molecules do not absorb IR radiation (Why? From quantum mechanics, IR absorption requires a molecular vibration with a changing electric dipole moment — impossible for  $\text{N} \equiv \text{N}$  or  $\text{O} = \text{O}$ )

$\text{CO}_2$  molecules have bending vibrations and asymmetric stretching vibrations that change the molecular dipole moment and are therefore infrared active



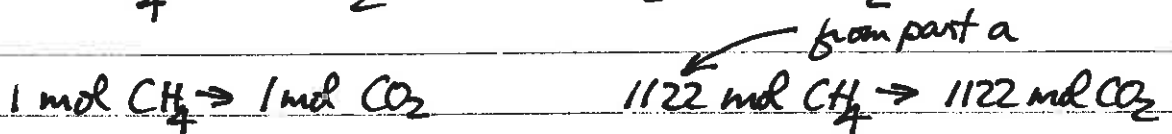
(2 c cont.)

Atmospheric  $N_2$  and  $O_2$  do not absorb IR radiation  
→ heat radiation escapes to outer space

Atmospheric  $CO_2$  strongly absorbs IR radiation,  
warming the atmosphere, as in a greenhouse under glass

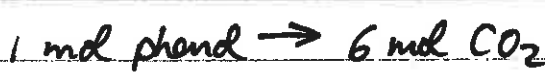
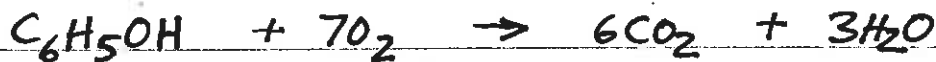
( $CH_4$ ,  $H_2O$  are also greenhouse gases)

d) i) methane combustion, balanced reaction:



$$\text{mass } CO_2 = (1122 \text{ mol}) \left( \frac{44.01 \text{ g}}{\text{mol}} \right) = 4.94 \times 10^5 \text{ g} = \boxed{49.4 \text{ kg}}$$

ii) phenol combustion, balanced reaction:



$$\text{mass } CO_2 = (1962 \text{ mol}) \left( \frac{0.04401 \text{ kg}}{\text{mol}} \right) = \boxed{86.3 \text{ kg}}$$

e)  $CH_4$  is better! Burning coal ( $\approx$  phenol) produces  
75% more  $CO_2$  to produce the same amount of heat

f) = sulfur oxides, mercury and other toxic heavy metals,  
fly ash

3. a) max. efficiency  $\epsilon = 1 - \frac{T_C}{T_H} = 1 - \frac{293\text{ K}}{373\text{ K}} = \boxed{0.214}$

(21.4%)

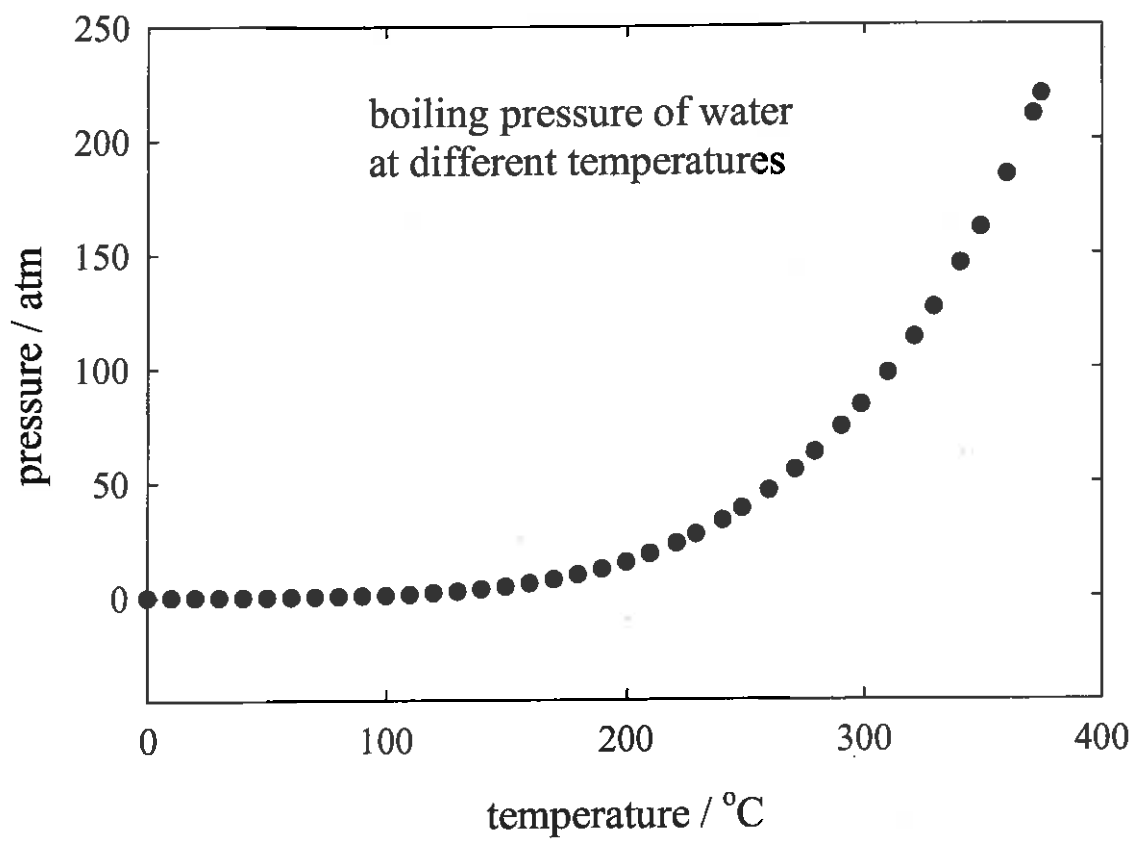
$$\epsilon = \frac{-W}{Q_H} \quad 0.214 = \frac{-W}{1.00\text{ GJ}} \quad -W = 0.214\text{ GJ}$$

(done on surroundings)

b) The boiling temperature of liquid water increases rapidly (almost exponentially!) with the pressure (Why - Chapter 8!) (e.g. 1 atm @ 100°C, but 200°C @ 15.3 atm)

As the boiling temperature and pressure increase, so does  $T_H$  and the max. engine efficiency  $1 - \frac{T_C}{T_H}$

See graph - next page



4. a) heat argon from 25 °C to 100 °C at constant volume (1,000 g)  $(C_{pm} - C_{vm} = R)$  ideal gas

assumed to be ideal  
 $C_{vm} = \frac{3}{2} R$      $C_{pm} = \frac{5}{2} R$

$$dU_v = dq_v - P_{ext} dV \overset{0}{=} dq_v = C_v dT$$

$$dS = \frac{dq_v}{T} = \frac{C_v dT}{T}$$

$$n = \frac{\text{mass}}{M} = \frac{1000 \text{ g}}{39.95 \frac{\text{g}}{\text{mol}}} = 25.03 \text{ mol}$$

$$\Delta S = \int_{S_i}^{S_f} dS = \int_{T_i}^{T_f} C_v \frac{dT}{T} = C_v \int \frac{dT}{T} = n C_{vm} \int d \ln T$$

$$\Delta S = n \frac{3}{2} R (\ln T_f - \ln T_i) = n \frac{3}{2} R \ln \left( \frac{T_f}{T_i} \right)$$

$$= (25.03 \text{ mol}) \frac{3}{2} (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \left( \frac{373 \text{ K}}{298 \text{ K}} \right)$$

$$\Delta S_v = \boxed{70.1 \text{ J K}^{-1}}$$

b) heat argon (1,000 g) from 25 °C to 100 °C at constant pressure

$$dq_p = dH = C_p dT$$

$$dS = \frac{dq_p}{T} = \frac{C_p dT}{T} = n C_{pm} \frac{dT}{T}$$

$$\Delta S = \int n C_{pm} \frac{dT}{T} = \int n \frac{5}{2} R \frac{dT}{T} = n \frac{5}{2} R \int d \ln T$$

$$= n \frac{5}{2} R \ln \left( \frac{T_f}{T_i} \right) = (25.03 \text{ mol}) \frac{5}{2} 8.314 \frac{\text{J}}{\text{K mol}} \ln \left( \frac{373 \text{ K}}{298 \text{ K}} \right)$$

$$\Delta S_p = \boxed{116.7 \text{ J K}^{-1}}$$



initially:

5. a)

Block A $C_{VA} = 300 \frac{J}{K}$ $T_{Ai} = 273K$	Block B $C_{VB} = 100 \frac{J}{K}$ $T_{Bi} = 373K$
----------------------------------------------------------	----------------------------------------------------------

final temperature  $T_f$

isolated system:  $q = 0 = q_A + q_B$

$$0 = q_A + q_B$$

$$= \int_{T_{Ai}}^{T_f} C_{VA} dT + \int_{T_{Bi}}^{T_f} C_{VB} dT = C_{VA}(T_f - T_{Ai}) + C_{VB}(T_f - T_{Bi})$$

$$C_{VA}T_f + C_{VB}T_f = C_{VA}T_{Ai} + C_{VB}T_{Bi} \quad T_f = \frac{C_{VA}T_{Ai} + C_{VB}T_{Bi}}{C_{VA} + C_{VB}}$$

$$T_f = \frac{300(273) + 100(373)}{300 + 100} K$$

$$T_f = 298K$$

$$\begin{aligned} b) \Delta S &= \Delta S_A + \Delta S_B = \int_{T_{Ai}}^{T_f} \frac{dq_{revA}}{T} + \int_{T_{Bi}}^{T_f} \frac{dq_{revB}}{T} \\ &= \int_{T_{Ai}}^{T_f} \frac{C_{VA} dT}{T} + \int_{T_{Bi}}^{T_f} \frac{C_{VB} dT}{T} \end{aligned}$$

$$= C_{VA} \ln\left(\frac{T_f}{T_{Ai}}\right) + C_{VB} \ln\left(\frac{T_f}{T_{Bi}}\right)$$

$$= \left(300 \frac{J}{K}\right) \ln\left(\frac{298}{273}\right) + \left(100 \frac{J}{K}\right) \ln\left(\frac{298}{373}\right)$$

$$= 26.29 \frac{J}{K} - 22.45 \frac{J}{K}$$

$$\Delta S = +3.84 \frac{J}{K}$$

important  
for an isolated system,  $\therefore$  spont. process