

1. 5.00 moles of liquid water initially at 20 °C is heated at 1.00 atm constant pressure to form water vapor at 100 °C (the normal boiling point of water). Calculate q , w , ΔU , ΔH and ΔS .

- [5] *Suggestions:* Divide the process into two steps: **i)** heating $\text{H}_2\text{O}(l)$ from 20 °C to 100 °C, **ii)** vaporizing $\text{H}_2\text{O}(l)$ at 100 °C. Ignore the small volume of $\text{H}_2\text{O}(l)$ in the work calculation.

$$\text{Data: } C_{p,m}(\text{H}_2\text{O}, l) = 75.29 \text{ J K}^{-1} \text{ mol}^{-1} \quad \Delta H_{\text{vap},m}(\text{H}_2\text{O}, l) = 48.15 \text{ kJ mol}^{-1}$$

2. The **isothermal compressibility** $\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T$ gives the negative fractional change in volume with pressure at fixed T .

The **adiabatic compressibility** defined as $\kappa_{\text{ad}} = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_{\text{ad}}$ is similar, but gives the negative fractional change in volume with pressure *under adiabatic conditions* ($q = 0$). The two compressibilities are related by $\kappa = \gamma \kappa_{\text{ad}}$ where $\gamma = C_p/C_V$, the heat capacity ratio.

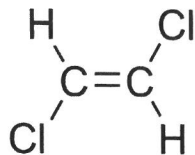
- [2] **a)** For He (assumed to be an ideal gas), show $\kappa_{\text{ad}} = 3/(5p)$. *Hint:* Recall $\kappa = 1/p$ for ideal gases.
b) For N_2 gas molecules that are translating and rotating, but not vibrating, show $\kappa_{\text{ad}} = 5/(7p)$.

3. **a)** Suggest why κ_{ad} might be more useful than κ for the analysis of sound waves. *Hint:* Sound is a series of fast compression/expansion waves propagating through a system.
b) The **speed of sound** c and the adiabatic compressibility are related by $c = \sqrt{1/(\rho \kappa_{\text{ad}})}$ where $\rho = M/V_m$ is the density. Does the speed of sound increase with temperature for an ideal gas? Justify your answer.
 [5] **c)** Does the speed of sound increase with pressure for an ideal gas? Justify your answer.
d) Calculate the speed of sound in air at 1.00 bar and 300 K. Assume air is an ideal gas mixture of N_2 (mol fraction 0.800) + O_2 (mole fraction 0.200) with $C_{V,m} = 5R/2$.

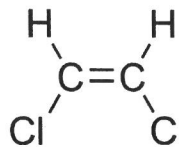
4. The wavelength (λ) and frequency (ν = number of waves per second) of sound are related by $c = \lambda \nu$. Most people can hear sound at frequencies from about 20 to 20,000 Hz. (1 Hz = 1 s⁻¹).
a) Using $c = 340 \text{ m s}^{-1}$ for the speed of sound, calculate the wavelength
i) at $\nu = 20 \text{ Hz}$ **ii)** at $\nu = 20,000 \text{ Hz}$.

- [3] **b)** What is **ultrasonic imaging**?
c) Ultrasonic imaging employs sound waves with much higher frequencies than audible sound, up to several GHz. Why?

5. This question refers to the relative stabilities of



trans-1,2-dichloroethylene



cis-1,2-dichloroethylene

- a) According to organic chemistry and the rules of steric hindrance, which isomer is likely to be more stable? Explain.
- [4] b) Calculate q and ΔS at 25 °C and 1.00 bar for conversion of the *cis* isomer to the *trans* isomer.



Data at 25 °C: $\Delta H_{\text{fm}}^\circ(\textit{trans}\text{-1,2-DCE, }l) = -23.14 \text{ kJ mol}^{-1}$ $S_{\text{m}}^\circ(\textit{trans}\text{-1,2-DCE, }l) = 195.85 \text{ J K}^{-1} \text{ mol}^{-1}$
 $\Delta H_{\text{fm}}^\circ(\textit{cis}\text{-1,2-DCE, }l) = -27.60 \text{ kJ mol}^{-1}$ $S_{\text{m}}^\circ(\textit{cis}\text{-1,2-DCE, }l) = 198.41 \text{ J K}^{-1} \text{ mol}^{-1}$

- c) According to the Second Law of thermodynamics, the entropy of an isolated system can never decrease. Use the Second Law to decide which isomer is more stable. *Hint*: The reaction is not isolated, so be careful to include the entropy changes of the isomers *and the surroundings*.
6. Question 5 shows that one of the isomers of 1,2-dichloroethylene is unstable. Yet pure *trans*-1,2-dichloroethylene and pure *cis*-1,2-dichloroethylene can be purchased from chemical companies!
- [1] How is this possible?

Q1

step I

 $\text{H}_2\text{O}(l)$
at 20 °C, 1 atm $\text{H}_2\text{O}(l)$
at 100 °C, 1 atm(assume
 $\Delta V = 0$
no gases
(yet))

$$w = -\int p_{\text{ext}} dV \quad (p \text{ constant}) = -p \int dV$$

$$w = -p \Delta V \approx p(0) = 0$$

(the volume change ΔV is negligibly small for liquids)heat at
constant pressure

$$C_p = \frac{dq_p}{dT} \text{ so } dq_p = C_p dT$$

$$q_p = \Delta H = \int C_p dT = \int n C_{pm} dT$$

(constant p)

$$= n C_{pm} \int dT = n C_{pm} \Delta T$$

$$= (5.00 \text{ mol})(75.29 \text{ J K}^{-1} \text{ mol}^{-1})(373.15 - 293.15) \text{ K}$$

$$q = \Delta H = 30.12 \text{ kJ}$$

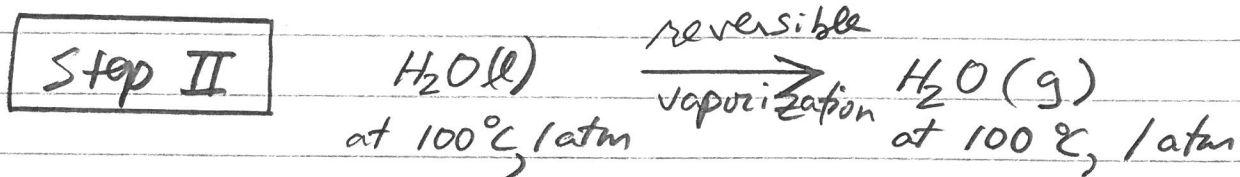
$$\Delta U = q + w = 30.12 \text{ kJ}$$

$$\Delta S = \int \frac{dq_{\text{rev}}}{T} = \int \frac{C_p dT}{T} = C_p \int \frac{1}{T} dT = n C_{pm} \ln\left(\frac{T_f}{T_i}\right)$$

$$= (5.00 \text{ mol})(75.29 \text{ J K}^{-1} \text{ mol}^{-1}) \ln\left(\frac{373.15 \text{ K}}{293.15 \text{ K}}\right)$$

$$\Delta S = 90.83 \text{ J K}^{-1}$$

(Q1 cont.)



$$q = \Delta H = n \Delta H_{\text{vap},m} = (5.00 \text{ mol})(43.15 \text{ kJ mol}^{-1}) = 215.8 \text{ kJ}$$

$$w = -\int P_{\text{ext}} dV = -P \int dV = -P \Delta V$$
$$= -P(V_g - V_l) \approx -PV_g = -P \frac{nRT}{P} = -nRT$$
$$= -(5.00 \text{ mol})(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(373.15 \text{ K})$$

$$w = -15.51 \text{ kJ}$$

$$\Delta U = q + w$$
$$\Delta U = 200.3 \text{ kJ}$$

$$\Delta S = \int \frac{dq_{\text{rev}}}{T} = \frac{q_{\text{rev}}}{T} = \frac{215800 \text{ J}}{373.15 \text{ K}}$$

$$\Delta S = 578.3 \text{ J K}^{-1}$$

	Step I	Step II	Total (Step I + Step II)
q	30.12 kJ	215.8 kJ	245.9 kJ
w	0	-15.51 kJ	-15.51 kJ
ΔU	30.12 kJ	200.3 kJ	230.4 kJ
ΔH	30.12 kJ	215.8 kJ	245.9 kJ
ΔS	90.83 J K ⁻¹	578.3 J K ⁻¹	669.1 J K ⁻¹

Q2 a) helium 3 translations (x, y, z) @ $\frac{R}{2}$ each:

$$C_{vm} = \frac{3}{2} R$$

$$C_{pm} = C_{vm} + R \quad (\text{ideal gas})$$
$$= \frac{3}{2} R + R$$

$$\gamma = \frac{C_{pm}}{C_{vm}} = \frac{(5/2) R}{(3/2) R}$$

$$C_{pm} = \frac{5}{2} R$$

$$\gamma = \frac{5}{3}$$

$$\kappa_{ad} = \frac{1}{\gamma} \kappa$$

$$(\kappa = \frac{1}{p})$$

$$= \frac{1}{5/3} \frac{1}{p}$$

$$\boxed{\kappa_{ad} = \frac{3}{5p}}$$

b) N_2 3 translations @ $\frac{R}{2}$ each } $C_{vm} = \frac{3}{2} R + \frac{2R}{2}$
2 rotations @ $\frac{R}{2}$ each } $C_{vm} = \frac{5}{2} R$

$$C_{pm} = C_{vm} + R = \frac{7}{2} R$$

$$\gamma = \frac{C_{pm}}{C_{vm}} = \frac{(7/2) R}{(5/2) R} = \frac{7}{5}$$

$$\kappa_{ad} = \frac{1}{\gamma} \kappa$$

$$= \frac{1}{7/5} \frac{1}{p}$$

$$\boxed{\kappa_{ad} = \frac{5}{7p}}$$

Q3 a) sound waves are "fast" compressions/expansions

no time for heat transfer $\rightarrow \therefore$ adiabatic!

b) speed of sound $c = \sqrt{\frac{1}{\rho \kappa_{ad}}} = \sqrt{\frac{\gamma}{\rho \kappa}}$

for ideal gases:

$$\kappa = \frac{1}{P} \quad \text{density } \rho = \frac{M}{V_m} = \frac{M}{RT/P} = \frac{MP}{RT}$$

$$c = \sqrt{\frac{\gamma}{\rho \kappa}} = \sqrt{\frac{\gamma}{\frac{MP}{RT} \frac{1}{P}}} = \boxed{\sqrt{\frac{\gamma RT}{M}} = c}$$

c is proportional to $T^{1/2} \Rightarrow$ increases with T

c) for an ideal gas, the speed of sound is independent of the pressure

d) for air (80 mol % N_2 + 20 mol % O_2):

$$\text{average } \bar{M} = 0.80 M_{N_2} + 0.20 M_{O_2}$$

$$\bar{M} = (0.80)(0.0280) + 0.20(0.0320) = 0.0288 \text{ kg mol}^{-1}$$

$$\gamma = 7/5 \quad (\text{see Q2 b}) \quad T = 300 \text{ K}$$

$$c = \sqrt{\frac{\gamma RT}{M}} = \sqrt{\frac{\frac{7}{5} (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (300 \text{ K})}{0.0288 \text{ kg mol}^{-1}}} \quad (\text{all SI units})$$

speed of sound in air at 300K = $c = 348 \text{ m s}^{-1}$

Q4 a) i) $\lambda = \frac{c}{\nu} = \frac{340 \text{ m s}^{-1}}{20 \text{ s}^{-1}} = \boxed{17.0 \text{ m}}$

ii) at 20,000 Hz $\lambda = \frac{340 \text{ m s}^{-1}}{20,000 \text{ s}^{-1}} = \boxed{0.0170 \text{ m}}$

b) ultrasonic imaging \approx "sonic radar"!
"sonography"

shoot sound waves at objects, and use the sound reflected back to a "microphone" to look for the internal structure of objects

* medical imaging

* sonar (detecting underwater objects)
Das Boot!

* detecting flaws (e.g., cracks or bad welds) in machine parts, pipes, tanks

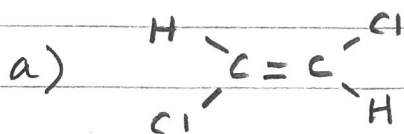
* bats use high-frequency chirps to locate bugs (food)

c) why use high frequencies ($\gg 20,000 \text{ Hz}$) for ultrasonic imaging

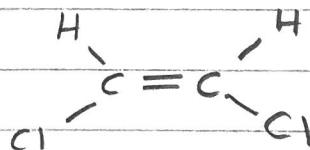
\Rightarrow higher frequencies give shorter wavelengths ($\lambda = c/\nu$) and higher resolution images

(e.g., $\lambda = 0.00034 \text{ m} = 0.34 \text{ m}$ at $\nu = 1 \text{ MHz}$)

(Q5)



trans
isomer



cis
isomer

the trans isomer has less "steric hindrance"

because the "big" chlorine atoms are

farther apart, repel each other less

strongly, leading to a **more stable trans isomer**

b) for the trans isomer \rightarrow cis isomer reaction:

$$\begin{aligned} \Delta H &= q &= \Delta H_{\text{fm}}^{\circ}(\text{cis}) - \Delta H_{\text{fm}}^{\circ}(\text{trans}) \\ (\text{constant pressure}) &&= -27.60 - (-23.14) = -4.46 \text{ kJ} \end{aligned}$$

$$\Delta S = S_{\text{m}}^{\circ}(\text{cis}) - S_{\text{m}}^{\circ}(\text{trans}) = 198.41 - 195.85 = 2.56 \text{ J K}^{-1}$$

c) for the trans \rightarrow cis reaction: ($q = q_{\text{system}} = -q_{\text{surroundings}}$)

$$\left(\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \right)_{\text{(isolated)}} = 2.56 + \frac{+4460 \text{ J}}{298.15 \text{ K}} = 17.5 \frac{\text{J}}{\text{K}}$$

$\Delta S > 0$ for an isolated system

spontaneous reaction \Rightarrow **cis isomer is more stable**

(Q6)

The trans isomer is unstable, but the rate of conversion of trans to cis is very slow, so pure trans-DCE (and pure cis-DCE) are available commercially