

1. Show $(\partial C_V/\partial V)_T = 0$ for
- a van der Waals gas
 - a gas obeying the equation $p = RT/(V_m - b)$
2. a) In addition to the isothermal compressibility (κ), there is the adiabatic compressibility (κ_S)

$$\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T \qquad \kappa_S = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_S$$

Prove the two compressibilities are related by $\kappa = \gamma \kappa_S$ where $\gamma = C_p/C_V$.

- b) Calculate κ_S and κ for helium (assumed to be an ideal gas) at 300 K and 5.00 bar. Explain qualitatively (in words) why κ_S is smaller than κ .
3. Zzzzzz ... Why should anyone care about adiabatic compressibilities? Good question. One important application, among very many (such as the operation of engines), is the relation

$$\kappa_S = \frac{1}{\rho c^2}$$

between the adiabatic compressibility, density, and the speed of sound (c)

- Calculate the speed of sound in helium (assumed to be an ideal gas) at 300 K and 1 bar.
 - Calculate the speed of sound in air at 300 K and 1 bar. Assume air is 80 mol % N_2 ($C_{pm} = 29.1 \text{ J K}^{-1} \text{ mol}^{-1}$) and 20 mol % O_2 ($C_{pm} = 29.4 \text{ J K}^{-1} \text{ mol}^{-1}$).
 - Can you use the answers for **a** and **b** to explain why the voice of deep-sea divers breathing He/ O_2 mixtures sounds “strange”? (Also, why do deep-sea divers breathe He/ O_2 mixtures?)
 - Can you suggest why the adiabatic compressibility – not the isothermal compressibility – is used to calculate the speed of sound?
 - Does the speed of sound in a gas increase with **i**) temperature? **ii**) pressure?
4. a) For liquids and solids, why is it generally much easier to measure C_p than C_V ?
- b) Prove $C_p = C_V + \frac{TV\beta^2}{\kappa}$
- c) C_{pm} for liquid water is $75.3 \text{ J K}^{-1} \text{ mol}^{-1}$ at 25 °C and 1 bar. Calculate C_{Vm} . Data for liquid water at 25 °C and 1 bar: density = $0.99707 \text{ g cm}^{-3}$, $\kappa = 45.9 \times 10^{-6} \text{ bar}^{-1}$, $\beta = 2.04 \times 10^{-4} \text{ K}^{-1}$.
- d) Show $C_{pm} = C_{Vm} + R$ for an ideal gas.

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5. a) $(\partial p/\partial T)_V = \beta/\kappa$ is used to study changes in pressure with temperature for systems at constant volume. For adiabatic processes at constant entropy, prove

$$\left(\frac{\partial p}{\partial T}\right)_S = \frac{C_p}{\beta TV} \quad \text{Hint! Use the cyclic rule and a Maxwell relation.}$$

b) Calculate $(\partial p/\partial T)_S$ for helium (assumed to be an ideal gas) at 298 K and 1.00 bar.

c) Calculate $(\partial p/\partial T)_S$ for solid aluminum at 298 K and 1.00 bar. Data for aluminum at 25 °C and 1 bar: density = 2.70 g cm^{-3} , $\beta = 69.3 \times 10^{-6} \text{ K}^{-1}$, $C_{pm} = 24.4 \text{ J K}^{-1} \text{ mol}^{-1}$

d) Aluminum initially at 25 °C and 1 bar is struck and shaped by a hydraulic ram, increasing the pressure to 500 bar. Assuming the process is adiabatic and reversible, calculate the final temperature of the aluminum. (Hint: Because the temperature change is small, $(\partial p/\partial T)_S = \Delta p/\Delta T$ is a good approximation.)

6. The equation $\text{dln}K/\text{d}T = \Delta H_R^\circ/RT^2$ is important for calculating equilibrium constants as a function of temperature. Derive the corresponding expression for $\text{dln}K/\text{d}p$.
7. The equilibrium constant of a chemical reaction doubles for every 10 °C increase in temperature under ambient conditions ($\approx 20 \text{ }^\circ\text{C}$). Estimate ΔH_R° for the reaction.
8. A gas mixture contains N_2 , H_2 and NH_3 at the respective partial pressures 5.00 bar, 2.00 bar and 0.02 bar at 400 °C. Is the mixture at equilibrium? At 400 °C the equilibrium constant for the reaction $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) = 2\text{NH}_3(\text{g})$ is $0.000160 \text{ bar}^{-2}$.
9. a) Calculate the equilibrium constant at 25 °C for the dissociation reaction $\text{N}_2\text{O}_4(\text{g}) = 2\text{NO}_2(\text{g})$. Data at 25 °C: $\Delta G_{\text{fm}}^\circ(\text{N}_2\text{O}_4, \text{g}) = 99.8 \text{ kJ mol}^{-1}$, $\Delta G_{\text{fm}}^\circ(\text{NO}_2, \text{g}) = 51.3 \text{ kJ mol}^{-1}$
- b) At a given total pressure $p = p_{\text{NO}_2} + p_{\text{N}_2\text{O}_4}$, show that the fraction of N_2O_4 dissociated at equilibrium (α) is given by
$$K = \frac{4\alpha^2}{1-\alpha^2} p$$
- c) Calculate α at 25 °C and $p = 0.100 \text{ bar}$. Also, show that α increases as the pressure drops.
10. Oxygen, an unwanted impurity in many industrial gases, can be removed using hot (to speed up the reaction) copper powder (large reactive surface area): $4\text{Cu}(\text{s}) + \text{O}_2(\text{g}) = 2\text{Cu}_2\text{O}(\text{s})$.
- a) Calculate the equilibrium constant K at 500 K. The pressures of Cu and Cu_2O are not included in the equilibrium expression $K = 1/p_{\text{O}_2}$. Have Cu and Cu_2O been ignored?
- b) What is the partial pressure of oxygen in equilibrium with Cu(s) and $\text{Cu}_2\text{O}(\text{s})$ at 500 K?
- Data at 25 °C: $\Delta H_{\text{fm}}^\circ(\text{Cu}_2\text{O}, \text{s}) = -169 \text{ kJ mol}^{-1}$, $\Delta G_{\text{fm}}^\circ(\text{Cu}_2\text{O}, \text{s}) = -146 \text{ kJ mol}^{-1}$

(background)

① $C_V = \left(\frac{\partial U}{\partial T} \right)_V$ why? at constant volume:
 $dU_V = dq_V - p_{\text{ext}} dV \rightarrow 0$

$$C_V = \frac{dq_V}{dT} = \frac{dU_V}{dT} = \left(\frac{\partial U}{\partial T} \right)_V$$

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

order of differentiation doesn't matter

know $\left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial p}{\partial T} \right)_V - p$

thermodynamic equation of state

the "Plan":

so if $T \left(\frac{\partial p}{\partial T} \right)_V - p = 0$, then $\left(\frac{\partial C_V}{\partial V} \right)_T = 0$

a) $p = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \rightarrow \left(\frac{\partial p}{\partial T} \right)_V = \frac{\partial}{\partial T} \left(\frac{RT}{V_m - b} - \frac{a}{V_m^2} \right)_V$

$$T \left(\frac{\partial p}{\partial T} \right)_V - p = \frac{RT}{V_m - b} - \left(\frac{RT}{V_m - b} - \frac{a}{V_m^2} \right) = \frac{a}{V_m^2}$$

$$\left(\frac{\partial C_V}{\partial V} \right)_T = \left[\frac{\partial}{\partial T} \left(\frac{\partial U}{\partial V} \right)_T \right]_V = \left(\frac{\partial}{\partial T} \frac{a}{V_m^2} \right)_V = 0$$

b) $\left(\frac{\partial C_V}{\partial V} \right)_T = \left[\frac{\partial}{\partial T} \left(\frac{\partial U}{\partial V} \right)_T \right]_V = \left[\frac{\partial}{\partial T} \left(T \left(\frac{\partial p}{\partial T} \right)_V - p \right) \right]_V = \left(\frac{\partial}{\partial T} \left(\frac{TR}{V_m - b} - p \right) \right)_V$

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

$$= 0$$

κ , isothermal compressibility

κ_s , adiabatic compressibility

2. a) Prove $\kappa = \gamma \kappa_s$

$$\left(-\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = -\gamma \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_S \right)$$

from equation sheet:

$$dS = \frac{C_v}{T} dT + \frac{\beta}{\kappa} dV \quad \text{and} \quad dS = \frac{C_p}{T} dT - \beta V dp$$

at constant S ($dS=0$):

$$-\frac{\beta}{\kappa} dV_S = \frac{C_v}{T} dT_S \quad \text{I}$$

$$\beta V dp_S = \frac{C_p}{T} dT_S \quad \text{II}$$

$$\frac{-\frac{\beta}{\kappa} dV_S}{\beta V dp_S} = \frac{C_v}{C_p} \quad (\text{eq. I} \div \text{eq. II}) \Rightarrow -\frac{1}{\kappa} \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_S = \frac{C_v}{C_p}$$

$$\frac{\kappa_s}{\kappa} = \frac{C_v}{C_p} = \frac{1}{\gamma}$$

$$\boxed{\kappa = \gamma \kappa_s}$$

useful equations:

$$C_p = T \left(\frac{\partial S}{\partial T} \right)_P$$

$$C_v = T \left(\frac{\partial S}{\partial T} \right)_V$$

$$\left(\frac{\partial P}{\partial T} \right)_V = \frac{\beta}{\kappa}$$

or: $\kappa_s \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_S$

(cyclic rule)

$$\kappa_s = +\frac{1}{V} \left(\frac{\partial V}{\partial S} \right)_P \left(\frac{\partial S}{\partial P} \right)_V$$

$$= \frac{1}{V} \frac{\left(\frac{\partial S}{\partial P} \right)_V \left(\frac{\partial T}{\partial P} \right)_V}{\left(\frac{\partial S}{\partial V} \right)_P \left(\frac{\partial T}{\partial V} \right)_P} = \frac{1}{V} \frac{\frac{C_v}{T} \frac{\kappa}{\beta}}{\frac{C_p}{T} \frac{1}{V\beta}}$$

$$\boxed{\kappa_s = \frac{C_v}{C_p} \kappa = \frac{1}{\gamma} \kappa}$$

$$\boxed{\kappa = \gamma \kappa_s}$$

$$\frac{1}{V\beta}$$

(2 cont.)

b) He (ideal gas): $C_{vm} = \frac{3}{2}R$ (3 trans. @ $\frac{R}{2}$ each)

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

$$pV = nRT$$

$$\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T = -\frac{1}{V} \left[\frac{\partial}{\partial p} \left(\frac{nRT}{p} \right) \right]_T = \left(-\frac{1}{V} \right) \left(-\frac{nRT}{p^2} \right)$$

$$\kappa = \frac{nRT}{pV} \frac{1}{p}$$

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

$$\gamma = \frac{C_p}{C_v} = \frac{C_{p/n}}{C_{v/n}} = \frac{C_{pm}}{C_{vm}} = \frac{\frac{5}{2}R}{\frac{3}{2}R} = \frac{5}{3}$$

$$\kappa_s = \frac{1}{\gamma} \kappa = \frac{3}{5} \kappa$$

$\kappa_s < \kappa$ because the gas is more "difficult" to compress adiabatically because T increases (not isothermal) increasing the pressure

at 5.00 bar: $\kappa = \frac{1}{p} = \frac{1}{5.00 \text{ bar}} = 0.200 \text{ bar}^{-1}$

$$\kappa_s = \frac{3}{5} \kappa = 0.120 \text{ bar}^{-1}$$

③ a) He (ideal gas) at 300 K, 1 bar

1 bar = 10^5 Pa	1 g = $\frac{1 \text{ kg}}{1000}$ m ³
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$$\kappa_s = \frac{3}{5} \kappa = \frac{3}{5} \frac{1}{p} = \frac{3}{5} \frac{1}{1.00 \text{ bar}} = 0.600 \text{ bar}^{-1}$$

$$\rho = \frac{\text{mass}}{\text{volume}} = \frac{M}{V_m} = \frac{M}{\frac{RT}{p}} = \frac{Mp}{RT}$$

$$\rho = \frac{(4.003 \frac{\text{g}}{\text{mol}})(1.00 \text{ bar})}{(0.08314 \text{ L bar K mol}^{-1})(300 \text{ K})} = 0.160 \frac{\text{g}}{\text{L}}$$

need to convert to SI units

$$c = \sqrt{\frac{1}{\rho \kappa_s}} = \sqrt{\frac{1}{(0.160 \frac{\text{g}}{\text{L}} \frac{10^{-3} \text{ kg}}{\text{g}} \frac{10^3 \text{ L}}{\text{m}^3})(0.600 \text{ bar}^{-1}) \frac{10^5 \text{ bar}}{\text{Pa}}}} =$$

1021 $\frac{\text{m}}{\text{s}}$	He
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(3 cont.)

$$\begin{aligned} b) \quad C_{pm} &\approx 0.800 C_{pm}(N_2) + 0.200 C_{pm}(O_2) \\ &= 0.800(29.1) + 0.200(29.4) \\ &= 29.16 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

$$C_{vm} = C_{pm} - R = 20.85 \text{ J K}^{-1} \text{ mol}^{-1} \quad (\text{ideal gas}) \quad \text{why?}$$

$$\gamma = \frac{C_{pm}}{C_{vm}} = \frac{29.16}{20.85} = 1.398$$

$$\kappa = \frac{1}{p} (\text{ideal gas}) = \frac{1}{1.00 \text{ bar}} = 1.00 \text{ bar}^{-1}$$

$$\kappa_s = \frac{1}{\gamma} \kappa = \frac{1.00 \text{ bar}^{-1}}{1.398} = 0.715 \text{ bar}^{-1} = 0.715 \times 10^{-5} \text{ Pa}^{-1}$$

$$p = \frac{M_{N_2} P_{N_2}}{RT} + \frac{M_{O_2} P_{O_2}}{RT}$$

$$= \frac{28.02(0.800 \text{ bar})}{0.08314(300)} + \frac{32.00(0.200)}{0.08314(300)} = 0.8880 + 0.2566$$

$$p = 1.145 \frac{\text{g}}{\text{L}} = 1.145 \frac{\text{kg}}{\text{m}^3}$$

$$c = \frac{1}{\sqrt{\rho \kappa_s}} = \frac{1}{\sqrt{(1.145 \frac{\text{kg}}{\text{m}^3})(0.715 \times 10^{-5} \text{ Pa}^{-1})}} =$$

slower!

$$= \boxed{349 \frac{\text{m}}{\text{s}}}$$

Air

c) vocal cords vibrating at a given frequency (ν) in helium produce sound with longer wavelength (λ) [compared to sound waves in air ($c = \lambda \nu$)] not in resonance with voice box [Divers breathe He/O₂ to avoid absorbing N₂ in bloodstreams (causing "nitrogen narcosis" - the bends)] (He is almost insoluble.)

d) sound waves change pressure very rapidly (thousands of times per second) - no time for heat flow to maintain isothermal conditions \therefore adiabatic

(3 cont.)

$$e) \quad c = \sqrt{\frac{1}{\rho \kappa_s}}$$

$$\rho = \frac{Mp}{RT}$$

- i) heating a gas at constant pressure reduces the density, increasing the speed of sound
- ii) pressurizing a gas at constant temperature increases the density, reducing the speed of sound
-

4. a) The pressure increases very significantly if solids and liquids are heated at constant V

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{\beta}{\kappa} \quad \text{requiring thick-walled vessels to keep } V \text{ constant}$$

$$b) \quad dU = dq + dw \stackrel{-P_{\text{ext}} dV}{=} \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$dq \stackrel{C_V}{=} \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV + P_{\text{ext}} dV$$

at constant pressure:

$$dq_p = C_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV + p dV$$

$$\left(\frac{dq_p}{dT} = C_p\right)$$

$$\div dT_p$$

$$C_p = \frac{dq_p}{dT_p} = C_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p + p \left(\frac{\partial V}{\partial T}\right)_p$$

$$= C_V + \left[T \left(\frac{\partial p}{\partial T}\right)_V - p \right] \left(\frac{\partial V}{\partial T}\right)_p + p \left(\frac{\partial V}{\partial T}\right)_p = C_V + T \left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_p$$

$$C_p = C_V + \frac{TV\beta^2}{\kappa}$$

(4 cont.)

$$(1 \text{ bar} = 10^5 \text{ Pa})$$

$$c) \quad C_{vm} = C_{pm} - \frac{TV_m\beta^2}{\kappa}$$

$$C_{pm} = 75.3 \text{ J K}^{-1} \text{ mol}^{-1} \quad T = 298.15 \text{ K}$$

$$\beta = 2.04 \times 10^{-4} \text{ K}^{-1} \quad \kappa = 45.9 \times 10^{-6} \text{ bar}^{-1} \\ = 45.9 \times 10^{-11} \text{ Pa}^{-1}$$

$$V_m = \frac{M}{\rho} = \frac{18.015 \frac{\text{g}}{\text{mol}}}{0.99707 \frac{\text{g}}{\text{cm}^3}} = 18.07 \frac{\text{cm}^3}{\text{mol}} = 18.07 \times 10^{-6} \frac{\text{m}^3}{\text{mol}}$$

$$C_{vm} = C_{pm} - \frac{TV_m\beta^2}{\kappa} = C_{pm} - \frac{(298.15)(18.07 \times 10^{-6})(2.04 \times 10^{-4})^2}{45.9 \times 10^{-11}} \\ = C_{pm} - 0.488 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$C_{vm} = 74.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

! notice!

$$C_{vm} \neq C_{pm} - R$$

$$\frac{0.488 \text{ J}}{\text{K mol}} = 0.059R$$

not an ideal gas
H₂O(l)

$$d) \text{ ideal gas } \beta = \frac{1}{T} \quad \kappa = \frac{1}{P}$$

$$C_{pm} - C_{vm} = \frac{TV_m\beta^2}{\kappa}$$

$$= \frac{TV_m \frac{1}{T^2}}{\frac{1}{P}} \quad (\text{ideal gas}) \\ PV_m = RT$$

$$= \frac{PV_m}{T} = R$$

$$\textcircled{5} \text{ a) } \left(\frac{\partial P}{\partial T} \right)_S = - \left(\frac{\partial P}{\partial S} \right)_T \left(\frac{\partial S}{\partial T} \right)_P = \frac{\left(\frac{\partial S}{\partial T} \right)_P}{-\left(\frac{\partial S}{\partial P} \right)_T}$$

$$\beta \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$$

note: $C_p = T \left(\frac{\partial S}{\partial T} \right)_P \left(= \frac{dq_p}{dT} \right)$

and $\left(\frac{\partial S}{\partial P} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_P$

(Maxwell relation from $dG = -SdT + VdP$)

$$\left(\frac{\partial P}{\partial T} \right)_S = \frac{\left(\frac{\partial S}{\partial T} \right)_P}{-\left(\frac{\partial S}{\partial P} \right)_T} = \frac{\frac{C_p}{T}}{\left(\frac{\partial V}{\partial T} \right)_P} = \frac{\frac{C_p}{T}}{\beta V} = \frac{C_p}{\beta T V}$$

b) $C_{pm} = C_{vm} + R = \frac{3}{2}R + R = \frac{5}{2}R$ for He (ideal gas)

$$\beta = \frac{1}{T}$$

$$P V_m = RT$$

$$\left(\frac{\partial P}{\partial T} \right)_S = \frac{C_p}{\beta T V} = \frac{C_p/n}{\beta T V/n} = \frac{C_{pm}}{\beta T V_m}$$

$$= \frac{\frac{5}{2}R}{\frac{1}{T} V_m} = \frac{5}{2} \frac{R}{V_m} = \frac{5}{2} \frac{R}{\frac{RT}{P}} = \frac{5}{2} \frac{P}{T}$$

$$\left(\frac{\partial P}{\partial T} \right)_S = \frac{5}{2} \frac{1.00 \text{ bar}}{298 \text{ K}} = 0.00839 \frac{\text{bar}}{\text{K}}$$

c) A(s) $C_{pm} = 24.4 \text{ J K}^{-1} \text{ mol}^{-1}$ $\beta = 69.3 \times 10^{-6} \text{ K}^{-1}$

$$T = 298.15 \text{ K} \quad V_m = \frac{M}{\rho} = \frac{26.98 \frac{\text{g}}{\text{mol}}}{2.70 \frac{\text{g}}{\text{cm}^3}} = 9.992 \frac{\text{cm}^3}{\text{mol}}$$

$$V_m = 9.992 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$$

(5 c cont.)

(all SI units)

$$\left(\frac{\partial p}{\partial T}\right)_s = \frac{C_p}{\beta TV} = \frac{C_{pm}}{\beta TV_m} = \frac{24.4}{(69.3 \times 10^{-6})(298.15)(9.992 \times 10^{-6})}$$

$$= 1.182 \times 10^8 \frac{\text{Pa}}{\text{K}}$$

($10^5 \text{ Pa} = 1 \text{ bar}$)

$$\left(\frac{\partial p}{\partial T}\right)_s = 1182 \frac{\text{bar}}{\text{K}}$$

$$d) \quad 1182 \frac{\text{bar}}{\text{K}} = \frac{\Delta p}{\Delta T} = \frac{499 \text{ bar}}{\Delta T}$$

$$\Delta T \approx \frac{499 \text{ bar}}{1182 \text{ bar/K}} = \boxed{0.42 \text{ K}}$$

6. Trick question! $K(T)$ depends only on T !

$p = p^0 = 1 \text{ bar}$
(fixed)

$$\ln K(T) = -\Delta G^0 / RT$$

$$\frac{d \ln K}{dp} = 0$$

equilibrium
"constant"
at fixed T

$$7. \quad \frac{d \ln K}{d \frac{1}{T}} = -\frac{\Delta H^0}{R}$$

$\approx 20^\circ \text{C}$

$T \approx 293 \text{ K}$

$$\boxed{\frac{K(T_2)}{K(T_1)} = 2}$$

use $\Delta T = 10 \text{ K}$

use $T_1 = 288 \text{ K}$

$T_2 = 298 \text{ K}$

$$\Delta H^0 \approx -R \frac{\ln K_2 - \ln K_1}{\frac{1}{T_2} - \frac{1}{T_1}}$$

$$= -R \frac{\ln \left(\frac{K_2}{K_1}\right)}{\frac{1}{T_2} - \frac{1}{T_1}} = -8.314 \left(\frac{\text{J}}{\text{K mol}}\right) \frac{\ln 2}{\frac{1}{298 \text{ K}} - \frac{1}{288 \text{ K}}}$$

$$\boxed{\Delta H^0 = 49400 \text{ J mol}^{-1}}$$

8.



$$Q = \frac{(\text{P}_{\text{NH}_3}/\text{P}^\circ)^2}{(\text{P}_{\text{N}_2}/\text{P}^\circ)(\text{P}_{\text{H}_2}/\text{P}^\circ)^3} = \frac{0.02^2}{5.00(2.00)^3} = 1.00 \times 10^{-5}$$

$$K = 1.6 \times 10^{-4}$$

$Q < K$ forward reaction spontaneous

9.



a) at 25 °C $\Delta G^\circ = 2\Delta G_{\text{fm}}^\circ(\text{NO}_2, \text{g}) - \Delta G_{\text{fm}}^\circ(\text{N}_2\text{O}_4, \text{g})$

$$\Delta G^\circ = 2(51.3) - 99.8 = 2.8 \text{ kJ mol}^{-1}$$

$$K = \exp\left(-\frac{\Delta G^\circ}{RT}\right) = \exp\left(-\frac{2800}{8.314(298.15)}\right)$$

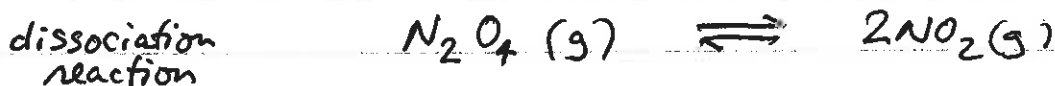
$$K = \exp(-1.129)$$

$K = 0.323$

convenient variable:
 $\alpha =$ fraction of total N_2O_4 that dissociates

b) $P = P_{\text{NO}_2} + P_{\text{N}_2\text{O}_4}$

start with pure N_2O_4 ($\alpha = 0$)



initially: 1 mol 0 mol

from stoichiometry:

at equilibrium $(1-\alpha)$ mol 2α mol

(9 cont.)

ideal gases $P_i = y_i P = \left(\begin{matrix} \text{mole fraction} \\ \text{of gas } i \end{matrix} \right) \left(\begin{matrix} \text{total} \\ \text{pressure} \end{matrix} \right)$

b) cont.

$$K = \frac{(P_{NO_2}/P^0)^2}{(P_{N_2O_4}/P^0)} = \frac{(y_{NO_2}P/P^0)^2}{(y_{N_2O_4}P/P^0)}$$

$$y_{NO_2} = \frac{\text{mole fraction } NO_2}{n_{N_2O_4} + n_{NO_2}} = \frac{2\alpha}{1-\alpha + 2\alpha} = \frac{2\alpha}{1+\alpha}$$

$$y_{N_2O_4} = \frac{\text{mole fraction } N_2O_4}{n_{N_2O_4} + n_{NO_2}} = \frac{1-\alpha}{1-\alpha + 2\alpha} = \frac{1-\alpha}{1+\alpha}$$

$$K = \frac{(y_{NO_2}P/P^0)^2}{y_{N_2O_4}P/P^0} = \frac{\left(\frac{2\alpha}{1+\alpha} P/P^0\right)^2}{\frac{1-\alpha}{1+\alpha} P/P^0} = \frac{4\alpha^2}{(1-\alpha)(1+\alpha)} \frac{P}{P^0}$$

$$K = \frac{4\alpha^2}{1-\alpha^2} \frac{P}{P^0}$$

Why do this? The fraction of total N_2O_4 dissociated is a convenient (and dimensionless) variable, easy to understand

$\alpha = 0 \rightarrow$ no dissociation

$\alpha = 1 \rightarrow$ complete dissociation

c) at $p = 1.00$ bar and $25^\circ C$ $0.323 = \frac{4\alpha^2}{1-\alpha^2} \frac{1.5\text{bar}}{1.5\text{bar}}$

$$0.323 - 0.323\alpha^2 = 4\alpha^2 \quad 0.323 = 4.323\alpha^2$$

$$\alpha^2 = 0.07472$$

$$\alpha = 0.273$$

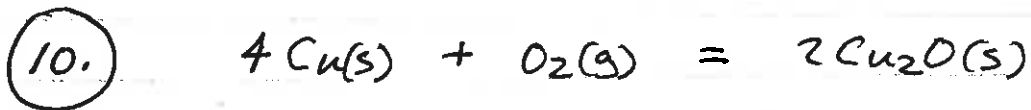
27.3% dissociation of N_2O_4

$$K = 0.323 \text{ (constant)}$$

if $p \rightarrow 0$ in the expression $K = \frac{4\alpha^2}{1-\alpha^2} \frac{P}{P^0}$

then $\frac{4\alpha^2}{1-\alpha^2}$ must go to ∞ to keep $\frac{4\alpha^2}{1-\alpha^2} \frac{P}{P^0}$

$\frac{1}{1-\alpha^2} \rightarrow \frac{1}{0}$ if $\alpha \rightarrow 1$ (complete dissociation)



$$K = \frac{1}{P_{\text{O}_2}/P^0} = e^{-\Delta G^\circ/RT}$$

pure stable elements

a) at 25°C: $\Delta G^\circ = 2\Delta G_{\text{fm}}^\circ(\text{Cu}_2\text{O}, s) - 4\Delta G_{\text{fm}}^\circ(\text{Cu}, s) - \Delta G_{\text{fm}}^\circ(\text{O}_2, g)$

$$= 2(146 \text{ kJ mol}^{-1}) = -292 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ = 2\Delta H_{\text{fm}}^\circ(\text{Cu}_2\text{O}, s) - 4\Delta H_{\text{fm}}^\circ(\text{Cu}, s) - \Delta H_{\text{fm}}^\circ(\text{O}_2, g)$$

$$= 2(-169) - 4(0) - 0 = -338 \text{ kJ mol}^{-1}$$

$$T_1 = 298.15 \text{ K} \quad (25^\circ\text{C}) \quad T_2 = 500 \text{ K}$$

$$K(T_1) = e^{-\Delta G^\circ/RT_1} = e^{-(-292000)/(8.314 \times 298.15)}$$

$$K(T_1) = e^{117.8} = \boxed{1.44 \times 10^{51} = K_{25^\circ\text{C}}}$$

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

$$= +117.8 - \frac{(-338,000 \text{ J mol}^{-1})}{8.314 \text{ JK}^{-1}\text{mol}^{-1}} \left(\frac{1}{500 \text{ K}} - \frac{1}{298.15 \text{ K}} \right)$$

$$= +117.8 - 55.0 = +62.8$$

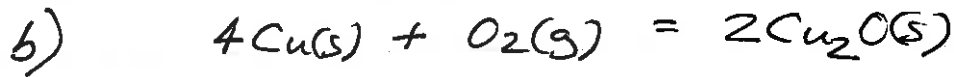
$$K(T_2) = e^{62.8} = \boxed{1.88 \times 10^{27} = K_{500\text{K}}}$$

notice K decreases as T increases

→ exothermic reaction ($\Delta H^\circ < 0$)

as T increases from 298 K to 500 K (68% increase)
 K decreases by about 24 orders of magnitude (! wow!)

(10 cont.)



$$K = \frac{1}{P_{\text{O}_2}/P^\circ} = 1.88 \times 10^{27} \quad \text{at } 500 \text{ K}$$

$$\begin{array}{l} \text{equilibrium} \\ \text{oxygen pressure} \end{array} = \frac{P^\circ}{K} = 5.32 \times 10^{-28} \text{ bar}$$

very small P_{O_2}

$$\begin{array}{l} \text{equilibrium O}_2 \\ \text{concentration} \end{array} = \frac{n}{V} = \frac{P_{\text{O}_2}}{RT}$$

$$= \frac{5.32 \times 10^{-28} \text{ bar}}{(0.08314 \text{ L bar mol}^{-1} \text{ K}^{-1})(500 \text{ K})}$$

$$= 1.28 \times 10^{-29} \frac{\text{mol}}{\text{L}}$$

$$= 7.70 \times 10^{-6} \frac{\text{O}_2 \text{ molecules}}{\text{L}}$$

only 1 O₂ molecule per 128 m³!