

P. (5.20) 1st Excited State Energy Level of Hydrogen atom
 $U = 10.2 \text{ eV}$
 [Atom's Ground State Energy = 0]
 1st Excited state is really 4 independent states,
 $E_1 = -13.6 \text{ eV}$
 $E_2 = -3.4 \text{ eV}$
 $E_3 = -1.51 \text{ eV}$
 Multiplicity = 4
 cell with same energy.

Temp? for which Minimum Free Energy F of Hydrogen atom in 1st Excited level is positive, and ... is negative.
 Hint: $F = 0$ for ground state
 So if F is negative of any state, atom will spontaneously go to that state since F must be minimum.
 For small system, however, the answer is probabilistic & random fluctuations will be large.

Soln

$$F = U - TS$$

for 1st Excited state $U = 10.2 \text{ eV}$
 $S = k \ln 4$
 $F = 10.2 \text{ eV} - T \cdot k \ln 4$

* If T is low, F is +ve \Rightarrow Atom will be in ground state, where $F = 0$.
 * At high T, F is -ve, therefore atom will most probably be in excited state.
 Transition temp can be obtained by

$$F = 0 = U - TS$$

$$\Rightarrow T = \frac{U}{S} = \frac{10.2 \text{ eV}}{k \ln 4}$$

where $S = k \ln 4$
 $k = 8.62 \times 10^{-5} \text{ eV/K}$
 $T = \frac{10.2 \text{ eV}}{(8.62 \times 10^{-5} \text{ eV/K} \cdot \ln 4)}$
 $\Rightarrow T = 8.5 \times 10^4 \text{ K}$

If $T < 8.5 \times 10^4 \text{ K} \Rightarrow$ Hydrogen atom will be in ground state
 If $T > 8.5 \times 10^4 \text{ K}$, ... in 1st excited state

Assignment

P. 5.2, 5.5, 5.14, 5.16 & 5.22

P. (5.2) Production of Ammonia
 $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$

at $T = 298 \text{ K}$, $P = 1 \text{ bar} = 1 \times 10^5 \text{ Pa}$
 Form ΔH and S tabulated at the end of book, compute ΔG for the reaction and check its consistency with values given in the table.

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta H = 2\Delta H(\text{NH}_3) - \Delta H(\text{N}_2) - 3\Delta H(\text{H}_2)$$

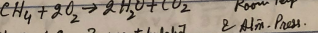
$$\Rightarrow \Delta H = 2(-46.11 \text{ kJ}) - 0 - 3(0) = -92.22 \text{ kJ}$$

and $\Delta S = 2\Delta S(\text{NH}_3) - \Delta S(\text{N}_2) - 3\Delta S(\text{H}_2)$
 $= 2(192.45 \text{ J/K}) - 191.61 \text{ J/K} - 3(130.68 \text{ J/K})$
 $\Rightarrow \Delta S = -198.75 \text{ J/K}$

Now $\Delta G = \Delta H - T\Delta S = -92.22 \text{ kJ} - (298 \text{ K})(-198.75 \text{ J/K})$
 $\Rightarrow \Delta G = -32.99 \text{ kJ}$ for 2 moles of ammonia

ΔG of 1 mol of ammonia $= \frac{1}{2}(-32.99 \text{ kJ}) = -16.495 \text{ kJ}$
 Tabulated value for ΔG of 1 mol of $\text{NH}_3(\text{g})$ is -16.45 kJ

P. (5.5) Fuel Cell using Methane (natural gas) Good Agreement



(a) ΔH & ΔG ? use tabulated values.
 $\Delta H = 2\Delta H(\text{H}_2\text{O}) + \Delta H(\text{CO}_2) - \Delta H(\text{CH}_4) - 2\Delta H(\text{O}_2)$
 $= 2(-285.83 \text{ kJ}) + (-393.51 \text{ kJ}) - (-74.81 \text{ kJ}) - 2(0)$
 $\Rightarrow \Delta H = -890.36 \text{ kJ}$

and $\Delta G = 2\Delta G(\text{H}_2\text{O}) + \Delta G(\text{CO}_2) - \Delta G(\text{CH}_4) - 2\Delta G(\text{O}_2)$
 $= 2(-237.13 \text{ kJ}) + (-394.36 \text{ kJ}) - (-50.72 \text{ kJ}) - 2(0)$
 $\Rightarrow \Delta G = -817.90 \text{ kJ}$

P. (5.5) Continued next page b, c, & d.

Continued P.5.5

(b) Assume ideal performance
Electric work? obtained from this cell.
for each mole of methane

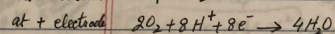
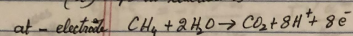
Total cond. all decrease in ΔG in above
reaction comes out as Electric work
Electric work out = $(817.90 \text{ KJ}) \sim 818 \text{ KJ}$

(c) Waste heat produced?

$$\text{Heat waste} = \Delta H - \Delta G = 890.36 - 817.90 \text{ KJ}$$

$$\Delta H \text{ decrease is sum of electric \& heat work} \approx 72 \text{ KJ}$$

(d) Steps in reaction is



Voltage of cell?

For each molecule of methane 8 electrons are

pushed around the circuit

$$\text{Voltage} = \frac{\text{Electric work done}}{\text{Total charge}}$$

$$\approx \frac{818 \text{ KJ}}{8(1.6 \times 10^{-19} \text{ C})(6.022 \times 10^{23})}$$

Total charge $8 \times 10^{-19} \text{ C}$ molecules

$$\Rightarrow \text{Voltage} = 1.06 \text{ V}$$

For 1 mole of methane

P.5.14 Relationship b/w C_p & C_v

(a) From P.3.33 \rightarrow heat capacity expression

1st consider $S(T, V)$

Express dS in partial derivatives

$$\left(\frac{\partial S}{\partial T}\right)_V \text{ and } \left(\frac{\partial S}{\partial V}\right)_T$$

As $S(T, V)$

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \quad I$$

As in P.3.33

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

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

(b) Consider $V(T, P) \Rightarrow dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP$

plugging into eq I.

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T \left[\left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP \right]$$

Set $dP = 0$ to find C_p

$$[\text{for constant } P] \quad dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P dT$$

$$= \frac{dS}{dT}$$

$$\Rightarrow \left(\frac{dS}{dT}\right)_P = \left(\frac{\partial S}{\partial T}\right)_V + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

Parallel

$$\frac{1}{T} C_p = \frac{C_v}{T} + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

$$\frac{dT}{dT} [C_p - C_v] = T \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

(c) use results of P.1.46 Maxwell relation

Specifically Helmholtz Free Energy.

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{P}{T} \quad \text{while}$$

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

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

Hence

$$C_p - C_v = T \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$$

$$\begin{aligned} dU &= TdS - PdV \\ TdS &= PdV \\ \left(\frac{\partial S}{\partial V}\right)_T &= \frac{P}{T} \end{aligned}$$

P. 5.14 continued

$$\left(\frac{\partial C_p}{\partial T}\right)_P = \left(\frac{\partial C_p}{\partial T}\right)_V + \left(\frac{\partial C_p}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_P$$

P. 1.46 part (c) $\Rightarrow \left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial V}\right)_T$

Hence $C_p - C_v = T \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$

$$= -T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_P = -T \left(\frac{\partial V}{\partial T}\right)_P^2 \left(\frac{\partial P}{\partial V}\right)_T$$

Co-efficient of expansion

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P$$

isothermal compressibility $\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T$

$$C_p - C_v = -T V \alpha^2 / \kappa_T = T V \alpha^2 / \kappa_T$$

Book uses P for coeff. of expansion (rather than α)

$$C_p - C_v = T V \frac{\alpha^2}{\kappa_T} \quad \text{or } T V \beta^2 / \kappa_T$$

(d) check for an ideal gas

ideal gas

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{T}$$

$$\Rightarrow \alpha = \frac{1}{T}$$

For ideal gas

while

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

Hence as part (c),

$$C_p - C_v = T V \frac{\alpha^2}{\kappa_T} = T V \left[\frac{1/T^2}{1/P}\right] = T V \frac{P}{T} = \frac{V P}{T} = N k$$

$$\Rightarrow C_p - C_v = N k$$

which agrees with what we had in Eq. (1.48) Ch. 2.

(e) Argue C_p can't be less than C_v .

Although α (called β in book) can be negative but it appears as square in $C_p - C_v = T V \frac{\alpha^2}{\kappa_T}$

But κ can never be negative

$\Rightarrow C_p - C_v$ will always be +ve. α is negative for rubbers or polymers - number a problem.

or $C_p > C_v$ (always)

or $C_p - C_v = 0$ only if $\alpha = 0$

(f) For mercury $C_p - C_v = ?$ (Use data)

$$C_p - C_v = T V \frac{\alpha^2}{\kappa_T} = (298 \text{ K}) (10^{-6} \text{ m}^3) \left[\frac{2.57 \times 10^{-4} \text{ K}^{-1}}{4.52 \times 10^{-10} \text{ Pa}^{-1}} \right]^2$$

$$C_p - C_v = T V \beta^2 / \kappa_T$$

For mercury

$$\alpha \text{ (or } \beta \text{ in book)} = 2.57 \times 10^{-4} \text{ K}^{-1}$$

$$\kappa_T = 4.52 \times 10^{-10} \text{ Pa}^{-1}$$

we get

$$C_p - C_v = 0.0435 \text{ J/K}$$

Using data for P. 405 $\Rightarrow C_p - C_v = 3.58 \text{ J/K}$ for 1 mol of mercury

(g) Temp. dependence

$$C_p - C_v \text{ is } T \alpha^2 \text{ or } T \beta^2$$

Since V & κ_T of Solids are weakly dependent on T .

$\alpha \rightarrow 0$ as $T \rightarrow 0$

Therefore as $T \rightarrow 0$

$$C_p - C_v \rightarrow 0 \text{ or } C_p \rightarrow C_v$$

At high Temp: $\alpha(T)$ is relatively constant

Therefore $(C_p - C_v) \propto T$

P. 5.16

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

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \text{ and } \kappa_S = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_S$$

Isobaric compressibility

$$\kappa_T = \kappa_S + \frac{TV\beta^2}{C_p}$$

and check against ideal gas.

$$\text{As } V(P, T) \Rightarrow dV = \left(\frac{\partial V}{\partial P} \right)_T dP + \left(\frac{\partial V}{\partial T} \right)_P dT$$

$$-V\kappa_T = \left(\frac{\partial V}{\partial P} \right)_T dP + \left(\frac{\partial V}{\partial T} \right)_P dT$$

$$\text{Consider } T(S, P) \Rightarrow dT = \left(\frac{\partial T}{\partial P} \right)_S dP + \left(\frac{\partial T}{\partial S} \right)_P dS$$

$$\text{Set } dS = 0 \Rightarrow dT = \left(\frac{\partial T}{\partial P} \right)_S dP$$

For constant entropy (Adiabatic process)

$$dV = \left(\frac{\partial V}{\partial P} \right)_T dP + \left(\frac{\partial V}{\partial T} \right)_P \left(\frac{\partial T}{\partial P} \right)_S dP$$

$$\Rightarrow \left(\frac{\partial V}{\partial P} \right)_S = \left(\frac{\partial V}{\partial P} \right)_T + \left(\frac{\partial V}{\partial T} \right)_P \left(\frac{\partial T}{\partial P} \right)_S$$

$$\text{Similarly } -V\kappa_S = -V\kappa_T + V\beta \left(\frac{\partial T}{\partial P} \right)_S$$

$$\kappa_T - \kappa_S = \beta \left(\frac{\partial T}{\partial P} \right)_S$$

$$\kappa_T - \kappa_S = \beta \left(\frac{\partial T}{\partial P} \right)_S$$

From Helmholtz $\Rightarrow dH = TdS + VdP$ (for fixed N)

$$\text{From results of P. 5.12 (P. 5.8) } \left(\frac{\partial T}{\partial P} \right)_S = \left(\frac{\partial V}{\partial S} \right)_P$$

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

$$\therefore \kappa_T - \kappa_S = \beta \left(\frac{\partial V}{\partial T} \right)_P \left(\frac{\partial T}{\partial S} \right)_P$$

Now

$$\kappa_T - \kappa_S = \beta \cdot V \cdot \beta \left(\frac{\partial T}{\partial S} \right)_P$$

$$= V\beta^2 \left(\frac{\partial T}{\partial S} \right)_P$$

$$\text{but } \left(\frac{\partial T}{\partial S} \right)_P = \frac{1}{C_p}$$

$$\text{We know } \left(\frac{\partial S}{\partial T} \right)_P = \frac{1}{C_p}$$

$$\kappa_T = \kappa_S + \frac{TV\beta^2}{C_p}$$

Always

$\kappa_T > \kappa_S$ since if β is negative, C_p can't be negative. β is squared.

For ideal gas

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

$$PV = NkT \Rightarrow \left(\frac{\partial V}{\partial P} \right)_T = -\frac{V}{P}$$

$$\text{and } \kappa_S = \frac{1}{\gamma P} \text{ since } \frac{C_p}{C_v} = \gamma$$

$$(P = 1.39 \text{ ch. 1.}) \text{ also } \kappa_T = \gamma \kappa_S$$

$$\kappa_T - \kappa_S = \frac{TV\beta^2}{C_p} \text{ for ideal gas}$$

$$\downarrow \frac{1}{P} - \frac{1}{\gamma P} = \frac{1}{P} \left(1 - \frac{1}{\gamma} \right) = \frac{1}{P} \left(\frac{\gamma - 1}{\gamma} \right)$$

$$= \frac{1}{P} \left(\frac{f+2}{f} - 1 \right) = \frac{1}{P} \left(\frac{2}{f+2} \right)$$

$$\text{While } \beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = \frac{1}{V} \frac{\partial}{\partial T} \left(\frac{NkT}{P} \right) = \frac{Nk}{PV} = \frac{1}{T}$$

$$C_p = \frac{f}{2} Nk + Nk = \left(\frac{f+2}{2} \right) Nk$$

$$\therefore \frac{TV\beta^2}{C_p} = \frac{T \cdot V \cdot \left(\frac{1}{T} \right)^2}{\left(\frac{f+2}{2} \right) Nk} = \frac{V}{TNk \left(\frac{f+2}{2} \right)}$$

$$= \frac{1}{P} \left(\frac{2}{f+2} \right)$$

Therefore $\kappa_T = \kappa_S + \frac{TV\beta^2}{C_p}$ works for ideal gas. Same as $\kappa_T - \kappa_S$.

P 5.22 show Eq. 5.40 is in agreement with the explicit formula for μ of a monoatomic ideal gas -- (Section 3.5)
 Show how to calculate μ° for monoatomic gas.

$$N\mu = G \quad \text{or} \quad \mu = \frac{G}{N} \quad \frac{\partial \mu}{\partial P} = \frac{1}{N} \frac{\partial G}{\partial P}$$

$$\frac{\partial \mu}{\partial P} = \frac{V}{N} \quad \text{since } \left(\frac{\partial G}{\partial P} \right)_{T,N} = V$$

$$= \frac{kT}{P} \quad \text{for ideal gas} \quad PV = NkT$$

$$\therefore d\mu = kT \frac{\partial P}{P} \Rightarrow \mu(T, P) = kT \int \frac{\partial P}{P}$$

keeping T constant $\int_{P_0}^P d\mu(T, P) = kT \int_{P_0}^P \frac{\partial P}{P} \Rightarrow \mu(T, P) - \mu_0(T, P_0) = kT \ln\left(\frac{P}{P_0}\right)$

or $\mu(T, P) = \mu_0(T) + kT \ln\left(\frac{P}{P_0}\right)$

(Eq. 5.40) ← μ_0 is at room Temp & at $P_0 = 1 \text{ atm} = 10^5 \text{ Pa}$
 we can replace $\frac{V}{N} = \frac{kT}{P}$

From Section 3.5, we have $\mu = -kT \ln \left[\frac{V}{N} \left(\frac{2\pi m k T}{h^2} \right)^{3/2} \right]$

Multiplying P_0 inside the ln term

$$\mu = -kT \ln \left[\frac{P_0}{P} \cdot \frac{kT}{P} \left(\frac{2\pi m k T}{h^2} \right)^{3/2} \right]$$

$$= -kT \ln \left[\frac{kT}{P_0} \left(\frac{2\pi m k T}{h^2} \right)^{3/2} \right] + kT \ln\left(\frac{P}{P_0}\right) \quad (\text{note})$$

This is similar to Eq. 5.40 when

$$\mu_0(T) = -kT \ln \left[\frac{kT}{P_0} \left(\frac{2\pi m k T}{h^2} \right)^{3/2} \right]$$

we can write $\mu(T, P) = \mu_0(T) + kT \ln\left(\frac{P}{P_0}\right)$ ✓
 same as Eq. 5.40