Rotational specific heat of para-H_2, ortho-H_2, high temperature mixture, and equilibrium mixture of the two modifications

$Na \equiv 6.0221367 \cdot 10^{23}$ **[mol^{-1}]**

Rotational constant of H_2: [m^{-1}] $B := 5932.2$

$h \equiv 6.6260755 \cdot 10^{-34}$ **[J s]**

(seeVP_OH2.mcd) $\theta r := \frac{h \cdot c \cdot B}{k}$

$k \equiv 1.380658 \cdot 10^{-23}$ **[J K^{-1}]**

Rotational temperature of H_2 [K] $\theta r = 85.351$

$c \equiv 2.99792458 \cdot 10^{8}$ **[m s^{-1}]**

$R \equiv 1.9872156$ **[cal mol^{-1} K^{-1}]**

H has nuclear spin 1/2 h/2π

Rotational partition function for: $i := 0..400$ $T_i := i + 1$ **[K]**
Temperature vector

Index of quantum numbers: $j := 0..5$ **corresponds to J = 0 to 11**

We first compute the thermal ortho-para equilibrium; the common energy base is J=0:

$$M_{j,i} := (4 \cdot j + 1) \cdot \exp\left[-2 \cdot j \cdot (2 \cdot j + 1) \cdot \frac{\theta r}{T_i}\right]$$

Population matrix p-H_2
J = 0,2,4,6,8,10,... only even J's allowed

$$N_{j,i} := (4 \cdot j + 3) \cdot \exp\left[-(2 \cdot j + 1) \cdot (2 \cdot j + 2) \cdot \frac{\theta r}{T_i}\right]$$

Population matrix o-H_2
J = 1,3,5,7,9,11,... only odd J's allowed

$Qrotp_i := \sum M^{\langle i \rangle}$ $Qrotr_i := \sum N^{\langle i \rangle}$

Sum over populations at temperature T_i gives the partition functions of each modification with J=0 reference

$Kp_i := \frac{3 \cdot Qrotr_i}{Qrotp_i}$ $x_i := \frac{Kp_i}{1 + Kp_i}$

$xp := 1 - x$

Equilibrium constant:
x molefraction of o-H_2
xp or 1-x molefraction of p-H_2

Qroto for Cpo calculation: Energy base is now J=1; Population matrix for ortho-H2 (-(-2) in exponent!):

$$P_{j,i} := (4 \cdot j + 3) \cdot \exp\left[-[(2 \cdot j + 1) \cdot (2 \cdot j + 2) - 2] \cdot \frac{\theta r}{T_i}\right] \quad Qroto_i := \sum P^{\langle i \rangle}$$

$lnQp := \overrightarrow{\ln(Qrotp)}$ $lnQo := \overrightarrow{\ln(Qroto)}$

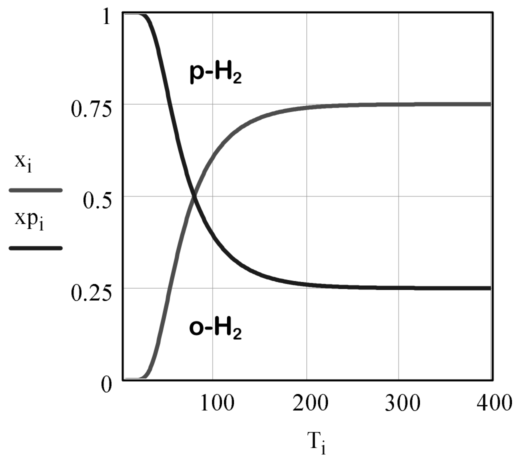
$k := 0..399$ $l := 0..398$

First and second derivative of lnQ(T) for p- and o-H_2:

$dlnQp_k := lnQp_{k+1} - lnQp_k$ $dlnQo_k := lnQo_{k+1} - lnQo_k$

$ddlnQp_l := dlnQp_{l+1} - dlnQp_l$ $ddlnQo_l := dlnQo_{l+1} - dlnQo_l$

mole fractions at equilibrium



Rotational specific heat Cp per Mol for p- and o-H_2:

$pp_l := R \cdot T_l \cdot (2 \cdot dlnQp_l + T_l \cdot ddlnQp_l)$ $po_l := R \cdot T_l \cdot (2 \cdot dlnQo_l + T_l \cdot ddlnQo_l)$

$pm := 0.25 \cdot pp + 0.75 \cdot po$ **'frozen' high temperature mixture of p-H_2/o-H_2 = 1/3, normal hydrogen**

$pc := 0.95 \cdot pp + 0.05 \cdot po$ **Clusius & Hiller had a mixture of 95% p-H2 and 5% o-H2, see below**

For equilibrium we have to add the enthalpy change for the p-o conversion to the rot. spec. heat dx/dT :
Cp = (1-x)Cpp + xCpo + dx/dT*ΔHr.

According to Gibbs-Helmholtz dlnKp/dT = ΔHr/RT² · Since Kp = x/(1-x), dlnKp/dx = 1/(x(1-x)).

Hence dx/dT = (dlnKp/dT) / (dlnKp/dx) = x(1-x)ΔHr/RT²

Energy of the rotator per J=1: $\varepsilon := B \cdot h \cdot c \cdot \frac{Na}{4.184}$ **[cal mol⁻¹]**

$Ep_{j,i} := M_{j,i} \cdot 2 \cdot j \cdot (2 \cdot j + 1) \cdot \varepsilon$ $\qquad ep_i := \sum Ep^{\langle i \rangle}$ $\qquad$ **$M_j \varepsilon_j$ for all T_i**

$Eo_{j,i} := P_{j,i} \cdot [(2 \cdot j + 1) \cdot (2 \cdot j + 2) - 2] \cdot \varepsilon$ $\qquad eo_i := \sum Eo^{\langle i \rangle}$

$\Delta H_l := eo_l - ep_l + 2 \cdot \varepsilon$ $\qquad \Delta H_1 = 339.22$ **cal/mol** **This is the enthalpy/mol for the reaction of 1 mol p-H_2 at temperature T_l to 1 mol o-H_2**

$z_l := R \cdot x_l \cdot (1 - x_l) \cdot \left(\frac{\Delta H_l}{R \cdot T_l} \right)^2$ **add this term to Cp because of the p-o conversion in dT:**
$dx/dT*\Delta H_l = Rx(1-x)*(\Delta H_l/RT)^2$

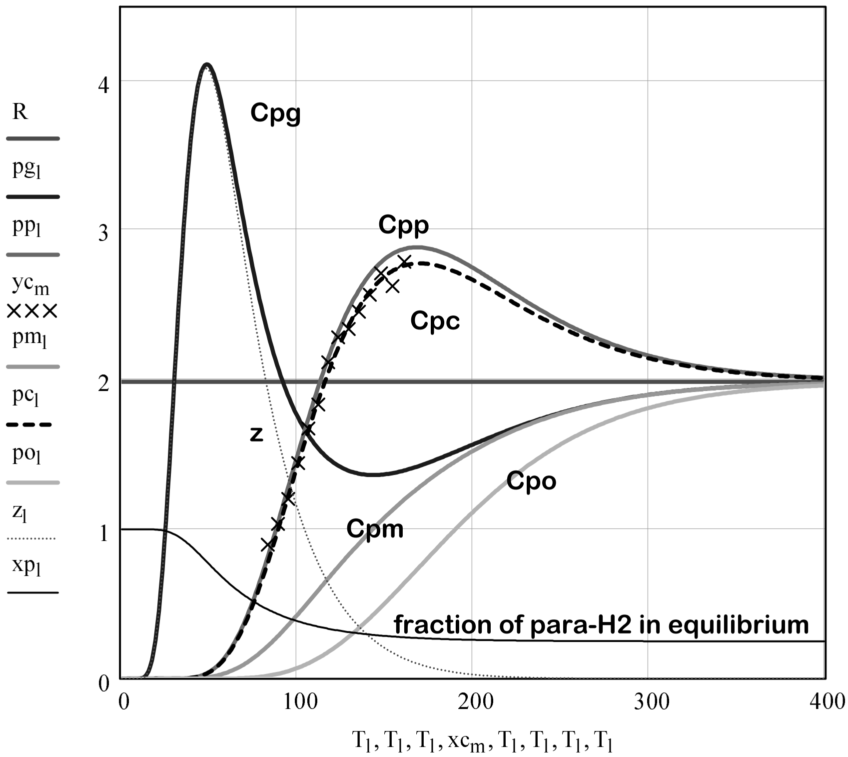
$pg_l := (1 - x_l) \cdot pp_l + x_l \cdot po_l + z_l$ **Cpg for equilibrium o-/p-H_2 mixture**

$ht_l := R$ **asymptote for all Cp's at high temperature**

$xc := xcc \qquad yc := ycc \qquad m := 0 .. 13$ **data vectors on right page ->**

crosses are 14 datapoints from K.Clusius & K.Hiller, Z.Phys.Chem. B4(1929)158 for 95% p-H_2

Specific Heat Cp of the Rotators o-/p-H_2: [cal mol⁻¹ K⁻¹]



From left to right: Cpg equilibrium, z, Cpp, datapoints, Cpc, Cpm of the hightemperature mixture, and Cpo.