From: Nikolai Piskunov <piskunov@astro.uu.se>
Subject: **Re: H2+ partition func and equilibrium constant**
Date: 24 January 2007 15:37:35 CET
To: Paul Barklem <barklem@astro.uu.se>

Hi Paul,

Here is the complete "default" list of molecules in EOS.
I would suggest that we concentrate on 2-atom creatures first
and cover the range between 0 and 12000 K. I will work out
the polynomial fit which is smooth but takes care of the kink.

Thanks, Nik

'H2','CO','H2O','OH','N2','SiO','HS','H2S','NH','SiH',
'CH','H2+','NO','MgH','HCl','SiS','AlOH','NH2','AlH',
'CN','CO2','SO','TiO','S2','FeH','NH3','HCN','HCO',
'O2','CH2','HF','H3+','CaH','Al2O','AlO','CH3','SiH2',
'MgO','C2','TiO2','VO2','NaH','AlCl','AlF','VO','CS',
'MgOH','PO2','CaOH','PH2','C2H','ScO','AlO2H','AlS',
'FeO','CrO','CH4','NS','SO2','SiN','OH-','ZrO','NO+',
'ZrO2','BO','SiO2','HBO','SiC','YO2','TiS','HBO2',
'C2H2','OCS','ZrO+','NaOH',
'CaCl','AlOF','YO','NaCl','C2O','CHP','HS-','H2-',
'TiH','PH3','MgS','TiO+','LaO2','Si2','SiH4','BH2',
'AlOCl','LaO','C2N','AlBO2','KCl','SiH-','CaF',
'CaO2H2','KOH','CN-','Al2O2','BaOH','SrOH','BO2',
'SiF','CH-','C3','C2-','MgO2H2','BeOH','HBS','SiC2',
'FeO2H2','CrO2','BeH2O2','BH3','NaCN','BeH2','Si2N',
'CaCl2','NaBO2','C3H','OBF','CS2','LiOH','Al2','LiCl',
'TiOCl','C2H4','CHCl','TiCl','AlOF2','KBO2','Si2C',
'CHF','BO-','AlO2','BaO2H2','OTiF','CS-','C2N2',
'SrO2H2','ClCN','AlClF','KCN','AlCl2','BaCl2','AlF2',
'MgCl2',
'FeO-','BO2H2','SiH3Cl','FeCl2','Si3','SiH3F','CH3Cl',
'SrCl2','CaF2','TiF2','LiBO2','MgClF','BeBO2','C2HCl',
'TiCl2','C4','H3BO3','MgF2','BaClF','BeF2','C2HF',
'BeCl2','TiOCl2','ZrCl2','BaF2','BeC2','Be2O','SrF2',
'ZrF2','FeF2','P4','SiH2F2','H3O+','C5','TiF3',
'TiCl3','ZrCl3','Na2Cl2','Na2O2H2','Be3O3','K2Cl2',
'K2O2H2','ZrCl4','Na2C2N2','ZrF4','Li2O2H2',

+ CH^+, CrH, SiH^+ } unlike

C_2^+ me

Not in S&T
FeH
CH^-

Not in S&T but no data in mine
ZrO+
TiH
TiO+
TiCl
BO^-
FeO^-

For Ulrike

CrH ✓

CH^+ (not in NIST, but in Huber & Herzberg's book!)

SiH^+ ✓

Negative ions, as in SLT.

data avail and used for C_2^-

data avail for OH^- but only extracts so use OH.

limited data for CH^-, use CH.

$$Q = e^{cE_0/T} \sum_e e^{-cT_e/T} \sum_v e^{-cG_v/T}$$

$$\times \underbrace{\sum_S e^{-cA_v \Lambda \Sigma/T}}_{2S+1} \sum_N (2N+1) g_{\Lambda hk} e^{-cF/T}$$

$$c = \frac{hc}{k}$$

$$= \exp\left[\frac{c}{T} E_0\right] \cdot \sum_e \sum_v \sum_N g_{\Lambda, hfs} (2S+1)(2N+1)$$

$$\cdot \exp\left[-\frac{c}{T}\left(G_v + T_e + F_N\right)\right]$$

$$F_v(N) = B_v J(J+1) - D_v [J(J+1)]^2 + \cdots$$

$$B_v = B_e - \alpha_e\left(v+\tfrac{1}{2}\right) + \gamma_e\left(v+\tfrac{1}{2}\right)^2 + \cdots$$

$$D_v = D_e - \beta_e\left(v+\tfrac{1}{2}\right) + \cdots$$

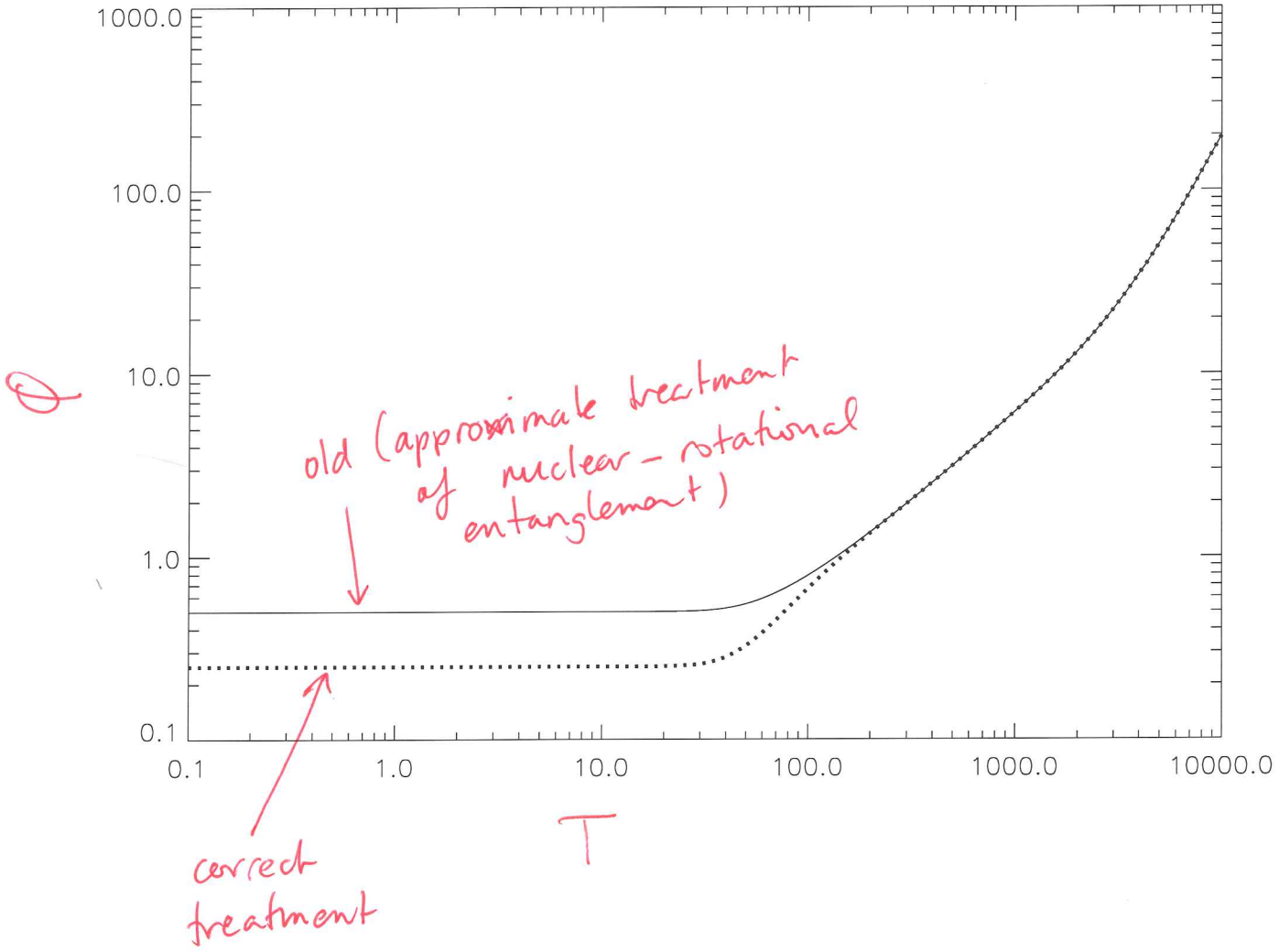
$$G(v) = \omega_e\left(v+\tfrac{1}{2}\right) - \omega_e x_e\left(v+\tfrac{1}{2}\right)^2 + \omega_e y_e\left(v+\tfrac{1}{2}\right)^3 + \omega_e z_e\left(v+\tfrac{1}{2}\right)^4$$

$$E_0 = G_0 + F_{e1,\, v=0}(N=1)$$

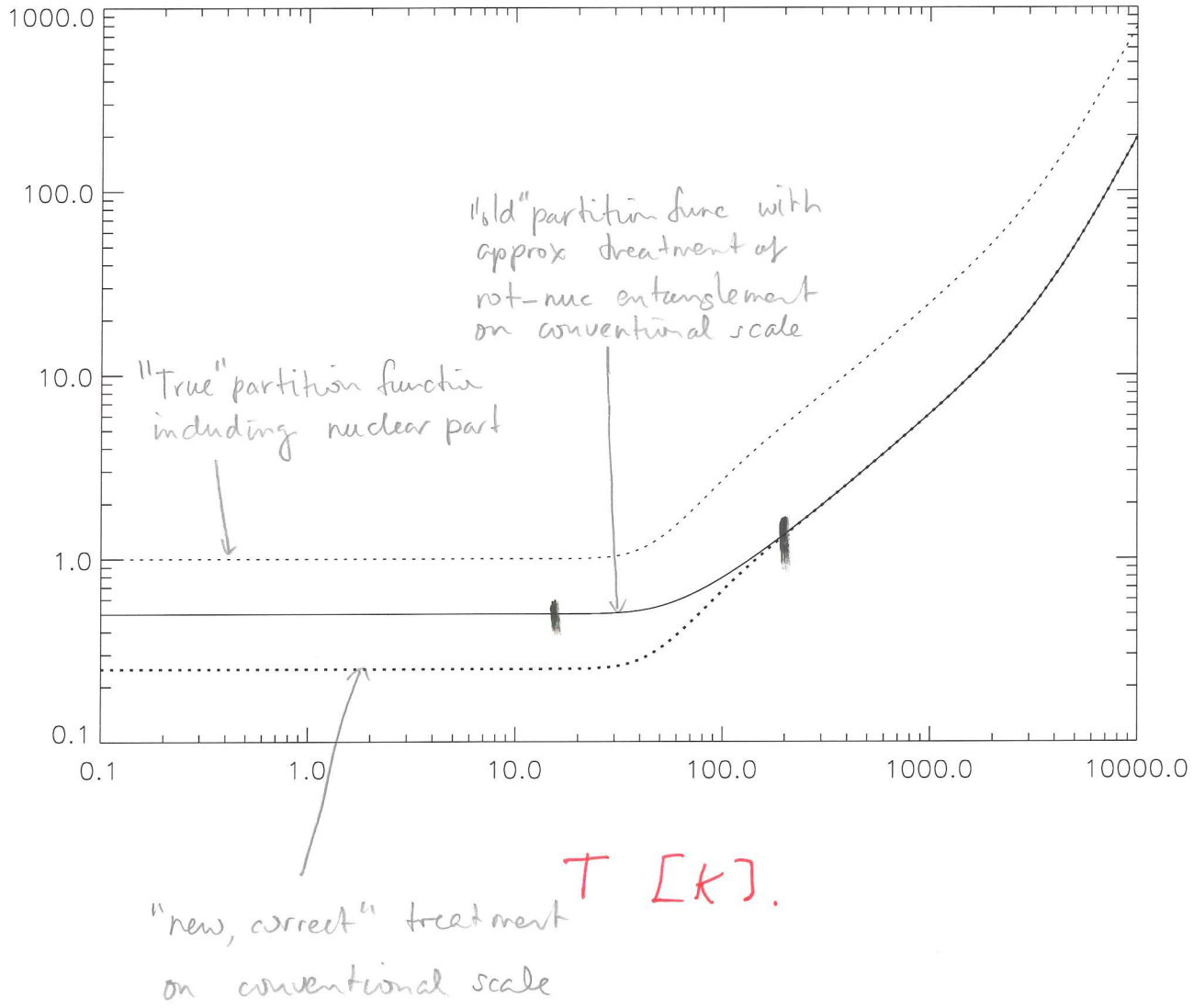
G_0: lowest vibrational energy

$F_{e1,\, v=0}(N=1)$: lowest rotational state.

H_2 partition function



H_2 partition function



conventional scale means

$$q = \frac{q_{\text{"true"}}}{\sum_{\text{atoms}} q_{nuc}}$$

eg molecule AB

$$q = \frac{q_{elec}\, q_{vib}\, q_{rot}\, q_{nucl}}{q_{nuc}^{A}\; q_{nuc}^{B}}$$

$q_{nuc}^{A} = (2I_A + 1)$, etc.

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A Stellar Journey

Check of low T behaviour, and then of g_Λ, hfs..

$J_{min} = 1$

H_2 $I = 0.5$, $^1\Sigma_g^+$, $J = 0 \rightarrow g_\alpha = \frac{0.5}{2} = \frac{1}{4}$ ✓

Li_2 $I = 1.5$, $^1\Sigma_g^+$ $J = 0 \rightarrow g_\alpha = \frac{1.5}{4} = \frac{3}{8} = 0.375$ ✓

B_2 $I = 1.5$, $^3\Sigma_g^-$ $J = 0 \rightarrow g_\sigma = \frac{2.5}{4} = \frac{5}{8} = 0.625$

$(2S+1) \times 0.625 = 1.875$ ✓

C_2 $I = 0$, $^1\Sigma_g^+$ $J = 0 \rightarrow g_\sigma = \frac{1}{1} = 1$ ✓

N_2 $I = 1$, $^1\Sigma_g^+$ $J = 0 \rightarrow g_\sigma = \frac{2}{3} = 0.667$ ✓

O_2 $I = 0$, $^3\Sigma_g^-$ $J = 0 \rightarrow g_\alpha = 0$ ✓

Si_2 $I = 0$ $^3\Sigma_g^-$ $J = 0 \rightarrow g_\alpha = 0$ ✓

H_2^+ $I = 0.5$ $^2\Sigma_g^+$ $J = 0 \rightarrow g_\alpha = \frac{1}{4}$

$(2S+1) \times \frac{1}{4} = \frac{1}{2}$ ✓

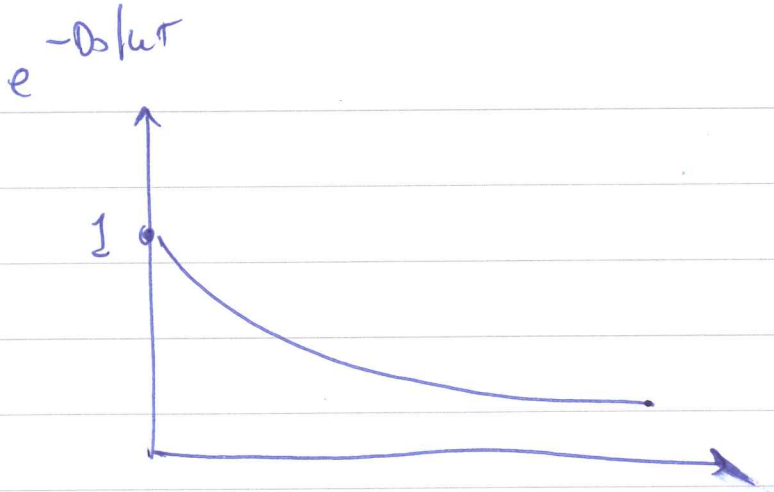
He_2^+ $I = 0$ $^2\Sigma_g^+$ $J = 0 \rightarrow g_\sigma = \frac{1}{1} = 1$

$(2S+1) \times 1 = 2$ ✓

O_2^+ $I = 0$ $^2\Pi_g$ $J = 1 \rightarrow g = 1$

$(2S+1)(2J+1) \times 1 = 6$ ✓

Ne_2^+ $I = 0$ $^2\Sigma_u^+$ $J = 0 \rightarrow g_\alpha = 0$ ✓



$$\frac{P_A P_B}{P_{AB}} = K_{AB} \propto e^{-D_0/kT}$$

$D_0 \downarrow \rightarrow K_{AB} \uparrow \rightarrow$ less molecules

$D_0 \uparrow \rightarrow K_{AB} \downarrow \rightarrow$ more molecules

eg. CO has $D_0^\circ \sim 11$ eV

so first to form in most situations

H_2^- has $D_0 \sim 1$ eV

never forms!