Vanghees

Problem II 7.1.

Need: New equilibrium composition of mixture

Given: Mixture of H_2, I_2, HI in equilibrium at $T = 675 K$

$(\mathcal{N}_{HI}^*)_1 = 9.664$ mole

$(\mathcal{N}_{H_2}^*)_1 = 0.168$ mole

$(\mathcal{N}_{I_2}^*)_1 = 0.168$ mole

1 mole I_2 added; V, T remain constant.

Solution:

From first equilibrium we can determine the equilibrium constant.

Assume the unit volume was 1 l.

Then $[HI]_1^* = 9.664$ mol/l

$[H_2]_1^* = 0.168$ mol/l $= [I_2]_1^*$.

Reaction:

$$2\,HI \rightleftharpoons H_2 + I_2$$

$$K_c(T) = \frac{[H_2]^*[I_2]^*}{[HI]^{*2}} = 3.022 \times 10^{-4} \quad \text{(dimensionless)}.$$

Immediately after one mole of iodine is added to the mixture (which is then no longer in equilibrium)

$(\mathcal{N}_{HI})_2 = 9.664$ mole

$(\mathcal{N}_{I_2})_2 = 1.168$ mole

$(\mathcal{N}_{H_2})_2 = 0.168$ mole

Using progress of reaction variable ξ ; $d\mathcal{N}_A = \nu_A\, d\xi$.

$d\mathcal{N}_{HI} = -2d\xi \qquad d\mathcal{N}_{H_2} = d\mathcal{N}_{I_2} = d\xi$.

$$\left.\begin{aligned}
(\mathcal{N}_{HI}^*)_2 &= (\mathcal{N}_{HI})_2 - 2\xi.\\
(\mathcal{N}_{H_2}^*)_2 &= (\mathcal{N}_{H_2})_2 + \xi.\\
(\mathcal{N}_{I_2}^*)_2 &= (\mathcal{N}_{I_2})_2 + \xi.
\end{aligned}\right\} \quad [X_A]_2^* = \frac{(\mathcal{N}_A)_2 + \nu_A \xi^*}{V}$$

At eqb'm

$$\frac{\left[(\mathcal{N}_{H_2})_2 + \xi^*\right]\left[(\mathcal{N}_{I_2})_2 + \xi^*\right]}{\left[(\mathcal{N}_{HI})_2 - 2\xi^*\right]^2}\,\frac{\cancel{V^2}}{\cancel{V^2}} = K_c(T) = 3.022 \times 10^{-4}.$$

Vaughan

So $$\frac{(0.168+\xi)(1.168+\xi)}{(9.664-2\xi)^2} = 3.022\times 10^{-4}$$

$$\xi^{*2} + 1.336\,\xi^{*} + 0.1962 = 1.209\times 10^{-3}\,\xi^{*2} - 1.168\times 10^{-2}\,\xi^{*} + 0.02822$$

i.e. $$0.9988\,\xi^{*2} + 1.348\,\xi^{*} + 0.168 = 0$$

$$\Rightarrow \xi^{*} = -1.210\,,\ -0.139$$

Now on general grounds we expect the addition of I_2 to shift the reaction to the left (as written), i.e. expect a negative value of ξ^*. Thus the negative values are not unexpected. However the value $\xi^* = -1.210$ can be discarded because $(N_{H_2}^*)_2 = 0.168 + \xi^* > 0$ is necessary for a physically reasonable solution.

So finally

$(N_{HI}^*)_2 = 9.942$ moles.

$(N_{I_2}^*)_2 = 1.029$ moles

$(N_{H_2}^*)_2 = 0.029$ moles.

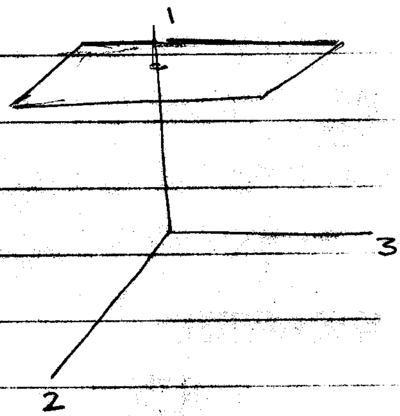
$\leftarrow$ New equilibrium composition

Supplementary Prob 4. Varghese

Given: Gas in equilibrium

Need: Fraction of the molecules striking wall with

$m C_x > m\bar{C}$; $\bar{C} = \left(\frac{8kT}{\pi m}\right)^{1/2}$



Solution:

Assume wall normal to x_1 axis,

Maxwell velocity distribution

Differential flux of molecules $= n C_1 f(C_i) dV_c$

Total flux of molecules $= \frac{n\bar{C}}{4}$ (from HW)

Need flux with $mC_1 > m\bar{C}$ i.e. $C_1 > \bar{C}$

$$\text{So} \quad F = \frac{4}{n\bar{C}} \int_{C_1=\bar{C}}^{\infty} \int_{C_2=0}^{\infty} \int_{C_3=0}^{\infty} n C_1 \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{mC^2}{2kT}} dC_1\, dC_2\, dC_3$$

Integration over C_2 & C_3 each give factors of $\left(\frac{2\pi kT}{m}\right)^{1/2}$

$$\text{So} \quad F = \frac{4}{\bar{C}} \int_{\bar{C}}^{\infty} C_1 \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-\frac{mC_1^2}{2kT}} dC_1$$

Letting $x = \frac{mC_1^2}{2kT}$ $\quad dx = \frac{m}{\cancel{2}kT} \cancel{2} C_1 dC_1$ $\quad C_1 = \bar{C} \Rightarrow x = \frac{m}{2kT} \frac{8kT}{\pi m} = \frac{4}{\pi}$

$$F = 4\left(\frac{\pi m}{8kT}\right)^{1/2}\left(\frac{m}{2\pi kT}\right)^{1/2} \frac{kT}{m} \int_{\frac{4}{\pi}}^{\infty} e^{-x} dx = -e^{-x}\Big|_{\frac{4}{\pi}}^{\infty}$$

$$F = e^{-4\pi} = 0.28$$

F

Supplementary Prob 5.

Need: (a) Temperature equivalent to 1eV

(b) T(K) of a 5 keV plasma

(c) $\bar{c}_e$, $\bar{c}_d$ in 5keV plasma

Given: $q_e = 1.602 \times 10^{-19}$ C.

$m_e = 9.108 \times 10^{-31}$ kg $\quad m_d = 3.343 \times 10^{-27}$ kg.

Solution:

$$1\,\text{eV} = q_e V = 1.602 \times 10^{-19}\ \text{J} = kT_{equiv}$$

$$\Rightarrow \quad T_{equiv} = \frac{1.602 \times 10^{-19}\ \text{J}}{1.3807 \times 10^{-23}\ \text{J/K}} = 1.1603 \times 10^4\ \text{K}$$

$$\approx 11{,}600\ \text{K}$$

$\longleftarrow$ $T_{eq}(1eV)$

So $T(5keV) = 5.8 \times 10^7$ K $\longleftarrow$ T(5keV)

$$\bar{c}_s = \left(\frac{8kT}{\pi m_s}\right)^{1/2}$$

so $\bar{c}_e = 4.73 \times 10^7$ m/s ($\approx$ 16% speed of light!)

$\therefore$ relativistic corrections important

$\bar{c}_d = 7.81 \times 10^5$ m/s ($\approx$ 0.26% of speed of light)

relativistic corrections not important.

Supplementary Problem 6

Given: Maxwellian molecules $\sigma_T = \frac{A}{g}$, Single species

Need: (a) Collision rate per molecule, θ

(b) $\mu\,(P,T)$

Solution.

As shown in class $\quad \theta = n\left(\frac{m^*}{2\pi kT}\right)^{3/2}\int_0^\infty e^{-\frac{m^* g^2}{2kT}}\, g\,\sigma_T\, 4\pi g^2\, dg$

For $\sigma_T = \frac{A}{g}$

$$\theta = nA\,\cancelto{1}{\left[\left(\frac{m^*}{2\pi kT}\right)^{3/2}\int_0^\infty e^{-\frac{m^* g^2}{2kT}}\, 4\pi g^2\, dg\right]}$$

$$= nA$$

$$\lambda = \frac{\bar{C}}{\theta} = \left(\frac{8kT}{\pi m}\right)^{1/2}\frac{1}{nA}$$

From chap 8

$$\mu \approx \frac{1}{2}\rho\,\bar{C}\lambda \approx \frac{1}{2}\, m\cancel{n}\left(\frac{8kT}{\pi m}\right)^{1/2}\left(\frac{8kT}{\pi m}\right)^{1/2}\frac{1}{\cancel{n}A}$$

$$\mu \approx \frac{1}{\cancel{2}}\cancel{m}\,\frac{\cancelto{4}{8}kT}{\pi \cancel{m}}\,\frac{1}{A} = \frac{4kT}{\pi A} \qquad \leftarrow \text{(a)}$$

So μ independent of p and $\mu \sim T$ $\qquad \leftarrow$ (b)