

AME 60636

Examination 1: Solution

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1. Consider the three species O , O_2 and O_3 . Initially, there is 1 *kmole* of O at $T = 6000\text{ K}$ and $P = 1.01 \times 10^6\text{ dyne/cm}^2$. The system equilibrates isothermally and isobarically. The reference pressure is $P_o = 1.01 \times 10^6\text{ dyne/cm}^2$. At $T = 6000\text{ K}$, one has the following thermodynamic data:

$$\begin{aligned}\bar{h}_O &= 0.370 \times 10^{13}\text{ erg/mole}, & \bar{s}_O^\circ &= 0.224 \times 10^{10}\text{ erg/mole/K}, \\ \bar{h}_{O_2} &= 0.224 \times 10^{13}\text{ erg/mole}, & \bar{s}_{O_2}^\circ &= 0.313 \times 10^{10}\text{ erg/mole/K}, \\ \bar{h}_{O_3} &= 0.471 \times 10^{13}\text{ erg/mole}, & \bar{s}_{O_3}^\circ &= 0.401 \times 10^{10}\text{ erg/mole/K},\end{aligned}$$

- (a) Find the equilibrium concentrations of O , O_2 , and O_3 .

Solution

Let us use the method of Lagrange multipliers as outlined in the course notes.

$$\bar{\mu}_{T,i}^\circ + \bar{R}T \ln \left(\frac{n_i P}{n P_o} \right) - \sum_{l=1}^L \lambda_l \phi_{li} = 0, \quad i = 1, \dots, N, \quad (1)$$

$$\sum_{i=1}^N \phi_{li} (n_{i_o} - n_i) = 0 \quad l = 1, \dots, L. \quad (2)$$

For this problem $P = P_o$, $N = 3$, $L = 1$. Take $i = 1$ for O , $i = 2$ for O_2 , and $i = 3$ for O_3 . This gives the four equations

$$\bar{\mu}_{6000,O}^\circ + \bar{R}T \ln \left(\frac{n_O}{n_O + n_{O_2} + n_{O_3}} \right) - \lambda = 0, \quad (3)$$

$$\bar{\mu}_{6000,O_2}^\circ + \bar{R}T \ln \left(\frac{n_{O_2}}{n_O + n_{O_2} + n_{O_3}} \right) - 2\lambda = 0, \quad (4)$$

$$\bar{\mu}_{6000,O_3}^\circ + \bar{R}T \ln \left(\frac{n_{O_3}}{n_O + n_{O_2} + n_{O_3}} \right) - 3\lambda = 0, \quad (5)$$

$$n_O + 2n_{O_2} + 3n_{O_3} = 1000. \quad (6)$$

Rearranging, one gets

$$\frac{\bar{\mu}_{6000,O}^\circ}{\bar{R}T} + \ln \left(\frac{n_O}{n_O + n_{O_2} + n_{O_3}} \right) - \frac{\lambda}{\bar{R}T} = 0, \quad (7)$$

$$\frac{\bar{\mu}_{6000,O_2}^\circ}{\bar{R}T} + \ln \left(\frac{n_{O_2}}{n_O + n_{O_2} + n_{O_3}} \right) - \frac{2\lambda}{\bar{R}T} = 0, \quad (8)$$

$$\frac{\bar{\mu}_{6000,O_3}^\circ}{\bar{R}T} + \ln \left(\frac{n_{O_3}}{n_O + n_{O_2} + n_{O_3}} \right) - \frac{3\lambda}{\bar{R}T} = 0, \quad (9)$$

$$n_O + 2n_{O_2} + 3n_{O_3} = 1000. \quad (10)$$

Rearranging further, one finds

$$\frac{n_O}{n_O + n_{O_2} + n_{O_3}} = \exp\left(\frac{\lambda}{\overline{RT}}\right) \exp\left(-\frac{\overline{\mu}_{6000,O}^o}{\overline{RT}}\right), \quad (11)$$

$$\frac{n_{O_2}}{n_O + n_{O_2} + n_{O_3}} = \left(\exp\left(\frac{\lambda}{\overline{RT}}\right)\right)^2 \exp\left(-\frac{\overline{\mu}_{6000,O_2}^o}{\overline{RT}}\right), \quad (12)$$

$$\frac{n_{O_3}}{n_O + n_{O_2} + n_{O_3}} = \left(\exp\left(\frac{\lambda}{\overline{RT}}\right)\right)^3 \exp\left(-\frac{\overline{\mu}_{6000,O_3}^o}{\overline{RT}}\right), \quad (13)$$

$$n_O + 2n_{O_2} + 3n_{O_3} = 1000. \quad (14)$$

First get the chemical potentials at the reference pressure for each species:

$$\overline{\mu}_{6000,O} = \overline{h}_O - T\overline{s}_O^o = -9.74 \times 10^{12} \frac{erg}{mole}, \quad (15)$$

$$\overline{\mu}_{6000,O_2} = \overline{h}_{O_2} - T\overline{s}_{O_2}^o = -1.654 \times 10^{13} \frac{erg}{mole}, \quad (16)$$

$$\overline{\mu}_{6000,O_3} = \overline{h}_{O_3} - T\overline{s}_{O_3}^o = -1.935 \times 10^{13} \frac{erg}{mole}. \quad (17)$$

Now scale the chemical potentials at the reference pressure for each species

$$\frac{\overline{\mu}_{6000,O}}{\overline{RT}} = \frac{\overline{h}_O - T\overline{s}_O^o}{\overline{RT}} = -19.5253, \quad (18)$$

$$\frac{\overline{\mu}_{6000,O_2}}{\overline{RT}} = \frac{\overline{h}_{O_2} - T\overline{s}_{O_2}^o}{\overline{RT}} = -33.1569, \quad (19)$$

$$\frac{\overline{\mu}_{6000,O_3}}{\overline{RT}} = \frac{\overline{h}_{O_3} - T\overline{s}_{O_3}^o}{\overline{RT}} = -38.79. \quad (20)$$

So the equations reduce to

$$\frac{n_O}{n_O + n_{O_2} + n_{O_3}} = \exp\left(\frac{\lambda}{\overline{RT}}\right) \exp(19.5253), \quad (21)$$

$$\frac{n_{O_2}}{n_O + n_{O_2} + n_{O_3}} = \left(\exp\left(\frac{\lambda}{\overline{RT}}\right)\right)^2 \exp(33.1569), \quad (22)$$

$$\frac{n_{O_3}}{n_O + n_{O_2} + n_{O_3}} = \left(\exp\left(\frac{\lambda}{\overline{RT}}\right)\right)^3 \exp(38.79), \quad (23)$$

$$n_O + 2n_{O_2} + 3n_{O_3} = 1000. \quad (24)$$

There are three roots to these equations. The first is physical:

$$n_O = 994.532 \text{ mole}, \quad (25)$$

$$n_{O_2} = 2.73424 \text{ mole}, \quad (26)$$

$$n_{O_3} = 2.52537 \times 10^{-6} \text{ mole}, \quad (27)$$

$$\exp\left(\frac{\lambda}{\overline{RT}}\right) = 3.30429 \times 10^{-9} \quad (28)$$

The other two are non-physical because they have negative numbers of moles for some species:

$$n_O = -994.868 \text{ mole}, \quad (29)$$

$$n_{O_2} = 997.938 \text{ mole}, \quad (30)$$

$$n_{O_3} = -0.336289 \text{ mole}, \quad (31)$$

$$\exp\left(\frac{\lambda}{\overline{RT}}\right) = -1.20559 \times 10^{-6} \quad (32)$$

$$n_O = 0.336286 \text{ mole}, \quad (33)$$

$$n_{O_2} = -1000.67 \text{ mole}, \quad (34)$$

$$n_{O_3} = 1000.34 \times 10^{-6} \text{ mole}, \quad (35)$$

$$\exp\left(\frac{\lambda}{RT}\right) = -0.00357638 \quad (36)$$

Now get the molar concentrations at equilibrium. The ideal gas law has

$$PV = (n_O + n_{O_2} + n_{O_3})RT.$$

So at equilibrium the volume is

$$V = \frac{(n_O + n_{O_2} + n_{O_3})RT}{P}.$$

Therefore, we have

$$V = \frac{(994.532 + 2.73424 + 2.52537 \times 10^{-9})(8.314 \times 10^7)(6000)}{1.01 \times 10^6}.$$

$$V = 4.92551 \times 10^8 \text{ cm}^3.$$

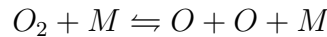
The equilibrium molar concentrations are then

$$\bar{\rho}_O = \frac{994.532}{4.92551 \times 10^8} = 2.01915 \times 10^{-6} \text{ mole/cm}^3, \quad (37)$$

$$\bar{\rho}_{O_2} = \frac{2.73424}{4.92551 \times 10^8} = 5.55118 \times 10^{-9} \text{ mole/cm}^3, \quad (38)$$

$$\bar{\rho}_{O_3} = \frac{2.52537 \times 10^{-6}}{4.92551 \times 10^8} = 5.12713 \times 10^{-15} \text{ mole/cm}^3. \quad (39)$$

(b) Imagine now that the reaction kinetics is governed by the *single reaction*



with collision frequency factor 1.85×10^{11} , temperature exponent $\beta = 0.5$, and activation energy $E = 95560.0 \text{ cal/mole}$. The reaction rate has the typical units of $\text{mole/cm}^3/\text{s}$. Write the appropriate differential-algebraic system that describes the evolution of O , O_2 and O_3 .

Solution

Here, we begin with no O_3 , and there is no mechanism for its creation, so it can safely be ignored for this problem. For this reaction, we have

$$\Delta G^o = \sum_{i=1}^N \bar{\mu}_i \nu_i = 2\bar{\mu}_O - \bar{\mu}_{O_2}, \quad (40)$$

$$= -2.94 \times 10^{12} \frac{\text{erg}}{\text{mole K}}. \quad (41)$$

First, let us calculate the equilibrium constant K_c :

$$K_c = \left(\frac{P_o}{RT} \right)^{\sum_{i=1}^N \nu_i} \exp \left(\frac{-\Delta G^o}{RT} \right) \quad (42)$$

Substituting numbers, we get

$$K_c = \left(\frac{1.01 \times 10^6}{8.314 \times 10^7 6000} \right)^{2-1} \exp \left(\frac{2.94 \times 10^{12}}{8.314 \times 10^7 (6000)} \right) = 0.000734429 \frac{\text{mole}}{\text{cm}^3}. \quad (43)$$

Second, let us calculate the reaction rate r :

$$r = aT^\beta \exp \left(\frac{-\bar{E}}{RT} \right) \bar{p}_{O_2} (\bar{p}_O + \bar{p}_{O_2}) \left(1 - \frac{1}{K_c} \frac{\bar{p}_O^2}{\bar{p}_{O_2}} \right), \quad (44)$$

$$= (1.85 \times 10^{11}) (6000)^{0.5} \exp \frac{95560 \frac{\text{cal}}{\text{mole}}}{1.987 \frac{\text{cal}}{\text{mole K}} (6000 \text{ K})} \quad (45)$$

$$\times \bar{p}_{O_2} (\bar{p}_O + \bar{p}_{O_2}) \left(1 - \frac{1}{0.000734429} \frac{\bar{p}_O^2}{\bar{p}_{O_2}} \right), \quad (46)$$

$$= 4.73357 \times 10^9 \left(1 - \frac{1361.6 \bar{p}_O^2}{\bar{p}_{O_2}} \right) \quad (47)$$

Now for the isobaric reaction, following the in class derivation, we have

$$\frac{d\bar{p}_O}{dt} = r \left(\nu_O - \frac{\bar{p}_O \bar{R}T}{P} (\nu_O + \nu_{O_2}) \right), \quad (48)$$

$$\frac{d\bar{p}_{O_2}}{dt} = r \left(\nu_{O_2} - \frac{\bar{p}_{O_2} \bar{R}T}{P} (\nu_O + \nu_{O_2}) \right). \quad (49)$$

Summing the two kinetics equations, one finds

$$\frac{d}{dt} (\bar{p}_O + \bar{p}_{O_2}) = r (\nu_O + \nu_{O_2}) \left(1 - (\bar{p}_O + \bar{p}_{O_2}) \frac{\bar{R}T}{P} \right), \quad (50)$$

$$= 0. \quad (51)$$

Therefore, as expected for the isothermal, isobaric combustion,

$$\bar{p}_O + \bar{p}_{O_2} = \text{Constant} = \frac{1000}{4.92551 \times 10^8} = 2.03025 \times 10^{-6} \frac{\text{mole}}{\text{cm}^3}. \quad (52)$$

Substituting numbers, one finds

$$\frac{d\bar{p}_O}{dt} = 4.73357 \times 10^9 \left(1 - \frac{1361.6 \bar{p}_O^2}{2.03025 \times 10^{-6} - \bar{p}_O} \right) (2 - 493501 \bar{p}_O). \quad (53)$$

This is one equation in one unknown and forms a complete system. When the right hand side of Eq. (53) is zero, we have equilibrium. Three roots are found, one of which is physical. The physical equilibrium gives

$$\bar{p}_O = 2.02467 \times 10^{-6} \frac{\text{mole}}{\text{cm}^3}, \quad (54)$$

$$\bar{p}_{O_2} = 5.58158 \times 10^{-9} \frac{\text{mole}}{\text{cm}^3}, \quad (55)$$

$$\bar{p}_{O_3} = 0 \frac{\text{mole}}{\text{cm}^3}. \quad (56)$$

Note that because there is no mechanism here to generate O_3 , its value is zero, which perturbs the equilibrium states for O and O_2 slightly from what they were if O_3 were present.

Near equilibrium, the kinetics linearizes as

$$\frac{d\bar{\rho}_O}{dt} = -9663.45(\bar{\rho}_O - 2.02456 \times 10^{-6}). \quad (57)$$

So the time scale of reaction near equilibrium is

$$\tau = \frac{1}{9663.45} = 1.03 \times 10^{-4} \text{ s}. \quad (58)$$

2. Develop an expression for how *element concentration evolves* for an ideal mixture of N ideal gases undergoing J reactions in an *isobaric* environment.

Solution

For an isobaric system, we can repeat the analysis of the course notes to arrive at Eq. (5.355) for a single reaction:

$$\frac{d\bar{\rho}_i}{dt} = r \left(\nu_i - \frac{\bar{\rho}_i \bar{R}T}{P} \sum_{k=1}^N \nu_k \right). \quad (59)$$

Extending this for J reactions, one gets

$$\frac{d\bar{\rho}_i}{dt} = \sum_{j=1}^J r_j \left(\nu_{ij} - \frac{\bar{\rho}_i \bar{R}T}{P} \sum_{k=1}^N \nu_{kj} \right), \quad (60)$$

$$\frac{d\bar{\rho}_i}{dt} = \sum_{j=1}^J \left(\nu_{ij} r_j - \frac{\bar{\rho}_i \bar{R}T}{P} \sum_{k=1}^N \nu_{kj} r_j \right), \quad (61)$$

$$\phi_{li} \frac{d\bar{\rho}_i}{dt} = \sum_{j=1}^J \left(\phi_{li} \nu_{ij} r_j - \phi_{li} \frac{\bar{\rho}_i \bar{R}T}{P} \sum_{k=1}^N \nu_{kj} r_j \right), \quad (62)$$

$$\sum_{i=1}^N \phi_{li} \frac{d\bar{\rho}_i}{dt} = \sum_{i=1}^N \sum_{j=1}^J \left(\phi_{li} \nu_{ij} r_j - \phi_{li} \frac{\bar{\rho}_i \bar{R}T}{P} \sum_{k=1}^N \nu_{kj} r_j \right), \quad (63)$$

$$\frac{d}{dt} \left(\sum_{i=1}^N \phi_{li} \bar{\rho}_i \right) = \sum_{i=1}^N \sum_{j=1}^J \phi_{li} \nu_{ij} r_j - \sum_{i=1}^N \sum_{j=1}^J \phi_{li} \frac{\bar{\rho}_i \bar{R}T}{P} \sum_{k=1}^N \nu_{kj} r_j, \quad (64)$$

$$= \sum_{j=1}^J r_j \underbrace{\sum_{i=1}^N \phi_{li} \nu_{ij}}_{=0} - \frac{\bar{R}T}{P} \sum_{j=1}^J r_j \sum_{i=1}^N \phi_{li} \bar{\rho}_i \sum_{k=1}^N \nu_{kj}, \quad (65)$$

$$= -\frac{\bar{R}T}{P} \sum_{j=1}^J r_j \sum_{k=1}^N \nu_{kj} \sum_{i=1}^N \phi_{li} \bar{\rho}_i, \quad (66)$$

$$\frac{d\bar{\rho}_i^e}{dt} = -\frac{\bar{R}T}{P} \sum_{j=1}^J r_j \sum_{k=1}^N \nu_{kj} \bar{\rho}_i^e, \quad (67)$$

$$= -\frac{\bar{\rho}_i^e \bar{R}T}{P} \sum_{j=1}^J r_j \sum_{k=1}^N \nu_{kj}, \quad (68)$$

$$= -\frac{\bar{\rho}_i^e \bar{R}T}{P} \sum_{j=1}^J r_j \Delta n_j. \quad (69)$$

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