

S2.D.2. Stability

In contrast to the stability analysis in §2.H that based on S being a maximal at equilibrium, the discussion here is based on G being a minimum there. With G given by (2.236) of §S2.D.1, this means

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P}^0 = \mathcal{A}^0 = 0 \quad (2.246)$$

and

$$\left(\frac{\partial^2 G}{\partial \xi^2}\right)_{T,P}^0 = \left(\frac{\partial \mathcal{A}}{\partial \xi}\right)_{T,P}^0 > 0 \quad (2.247)$$

Putting

$$H = G + TS$$

into (2.246) gives

$$\begin{aligned} \left(\frac{\partial H}{\partial \xi}\right)_{T,P}^0 &= T \left(\frac{\partial S}{\partial \xi}\right)_{T,P}^0 \\ &= \text{heat of reaction} \\ &= \text{heat absorbed by each reaction} \end{aligned} \quad (2.248)$$

Thus,

$$\begin{aligned} \left(\frac{\partial H}{\partial \xi}\right)_{T,P}^0 > 0 & \quad \text{for endothermic (heat absorbing) reactions.} \\ \left(\frac{\partial H}{\partial \xi}\right)_{T,P}^0 < 0 & \quad \text{for exothermic (heat releasing) reactions.} \end{aligned} \quad (2.248a)$$

Obviously, if the forward reaction is endothermic, the backward reaction must be exothermic, and vice versa.

Using,

$$S = -\left(\frac{\partial G}{\partial T}\right)_{P,\xi} \quad [\text{See (2.236).}]$$

(2.248) can be written as

$$\begin{aligned} \left(\frac{\partial H}{\partial \xi}\right)_{T,P}^0 &= -T \left[\frac{\partial}{\partial \xi} \left(\frac{\partial G}{\partial T} \right)_{P,\xi} \right]_{T,P}^0 \\ &= -T \left[\frac{\partial}{\partial T} \left(\frac{\partial G}{\partial \xi} \right)_{P,T} \right]_{\xi,P}^0 \\ &= -T \left(\frac{\partial \mathcal{A}}{\partial T} \right)_{\xi,P}^0 \quad [\text{See (2.236).}] \end{aligned} \quad (2.249)$$

Using the ideal gas result [see (2.244) of S2.D.1], this becomes

$$\begin{aligned} \left(\frac{\partial H}{\partial \xi}\right)_{T,P}^0 &= -T \left\{ \sum_{j=A,B,C,D} \nu_j \left\{ -R \ln \left[\frac{P_0}{P} \left(\frac{T}{T_0} \right)^{5/2} \right] - \frac{5}{2} R \right\} + R \ln \left(\frac{x_C^{\nu_C} x_D^{\nu_D}}{x_A^{|\nu_A|} x_B^{|\nu_B|}} \right) \right\} \\ &= \nu_t R T \left\{ \ln \left[\frac{P_0}{P} \left(\frac{T}{T_0} \right)^{5/2} \right] + \frac{5}{2} \right\} - R T \ln \left(\frac{x_C^{\nu_C} x_D^{\nu_D}}{x_A^{|\nu_A|} x_B^{|\nu_B|}} \right) \end{aligned} \quad (2.250)$$

where

$$v_t = \sum_{j=A,B,C,D} v_j \quad (2.250a)$$

= increase (decrease) of the total number of molecules in a forward (backward) reaction.

Using (2) of Ex.2.3 in §2.E, we can write (2.250) as

$$\left(\frac{\partial H}{\partial \xi}\right)_{T,P}^0 = v_t \left[-(\mu - \mu_0) + \frac{5}{2} R T \right] + T \Delta S_{\text{mix}} \quad (2.250b)$$

where [see (2.218) of §2.B]

$$\Delta S_{\text{mix}} = R \ln (x_A^{v_A} x_B^{v_B} x_C^{v_C} x_D^{v_D}) \quad (2.250c)$$

is the increase of entropy due to mixing in each forward reaction.

Note that if the total number of molecules is unchanged, i.e., $v_t = 0$, only the entropy mixing term contributes to the heat of reaction.

Using (2.6) of §2.B, we have, for P fixed,

$$\begin{aligned} \left(\frac{\partial \xi}{\partial T}\right)_{P,\mathcal{A}} &= - \frac{\left(\frac{\partial \mathcal{A}}{\partial T}\right)_{P,\xi}}{\left(\frac{\partial \mathcal{A}}{\partial \xi}\right)_{P,T}} \\ &= \frac{\frac{1}{T} \left(\frac{\partial H}{\partial \xi}\right)_{P,T}}{\left(\frac{\partial \mathcal{A}}{\partial \xi}\right)_{P,T}} \quad [(2.249) \text{ used. }] \end{aligned} \quad (2.251)$$

Setting

$$c = \frac{1}{T \left(\frac{\partial \mathcal{A}}{\partial \xi}\right)_{P,T}^0} > 0 \quad [\text{ See (2.247) }]$$

we have,

$$\Delta \xi \approx c \left(\frac{\partial H}{\partial \xi}\right)_{P,T}^0 \Delta T \quad \text{at equilibrium} \quad (2.251a)$$

Therefore, a small increase in T at equilibrium ($\mathcal{A} = 0$ and no net reactions) will cause ξ to increase for endothermic reactions [$\left(\frac{\partial H}{\partial \xi}\right)_{P,T}^0 > 0$], thus pushing the system off the equilibrium and into the direction of endothermic reactions. This is to be expected since adding heat to the system obviously enables the heat absorbing reactions.

(2.236) implies the Maxwell relation at fixed T ,

$$\left(\frac{\partial \mathcal{A}}{\partial P}\right)_{T,\xi} = \left(\frac{\partial V}{\partial \xi}\right)_{T,P} \quad (2.252)$$

Taking $T \leftrightarrow P$ in (2.251) gives

$$\left(\frac{\partial \xi}{\partial P}\right)_{T,\mathcal{A}} = - \frac{\left(\frac{\partial \mathcal{A}}{\partial P}\right)_{T,\xi}}{\left(\frac{\partial \mathcal{A}}{\partial \xi}\right)_{P,T}}$$

$$= - \frac{\left(\frac{\partial V}{\partial \xi}\right)_{T,P}}{\left(\frac{\partial \mathcal{A}}{\partial \xi}\right)_{P,T}} \quad [(2.252) \text{ used. }] \quad (2.253)$$

Setting

$$c' = \frac{1}{\left(\frac{\partial \mathcal{A}}{\partial \xi}\right)_{P,T}^0} > 0 \quad [\text{ See (2.247) }]$$

we have,

$$\Delta \xi \approx -c' \left(\frac{\partial V}{\partial \xi}\right)_{T,P}^0 \Delta P \quad \text{at equilibrium} \quad (2.251a)$$

Therefore, a small increase in P at equilibrium will cause ξ to increase for reactions that decrease the volume [$\left(\frac{\partial V}{\partial \xi}\right)_{T,P}^0 < 0$], thus pushing the system off the equilibrium and into the direction of the volume decreasing reactions.

Ex. 2.11.

Consider the gaseous reaction



Start with 1 mol of $N_2 O_4$ and no $N O_2$ at temperature T and pressure P . Use the ideal gas values for the chemical potentials.

- Compute and plot $G(T, P, \xi)$ as a function of ξ for
 - $P = 1 \text{ atm}$ and $T = 298 \text{ K}$ (25°C)
 - $P = 1 \text{ atm}$ and $T = 596 \text{ K}$ (323°C)
- Compute and plot $\mathcal{A}(T, P, \xi)$ as a function of ξ for
 - $P = 1 \text{ atm}$ and $T = 298 \text{ K}$ (25°C)
 - $P = 1 \text{ atm}$ and $T = 596 \text{ K}$ (323°C)
- What is ξ at $P = 1 \text{ atm}$ and $T = 298 \text{ K}$?
How many moles of $N_2 O_4$ and $N O_2$ are present at equilibrium?
- If the volume is initially at V_0 , what is the volume at $P = 1 \text{ atm}$ and $T = 298 \text{ K}$?
- What is the heat of reaction $P = 1 \text{ atm}$ and $T = 298 \text{ K}$?

Answer

Using (2.235) on (1a), we have

$$\frac{dn_{N_2 O_4}}{-1} = \frac{dn_{N O_2}}{2} = d\xi$$

$$\rightarrow n_{N_2 O_4} = -\xi + c_1$$

$$n_{N O_2} = 2\xi + c_2 \quad (1b)$$

where c_1 & c_2 are constants. Note that $[\xi] = \text{mole}$.

Initially, we have

$$1 = -\xi(0) + c_1$$

$$0 = 2\xi(0) + c_2$$

where $\xi(0)$ is the value of ξ at time $t = 0$. (1b) thus becomes

$$n_{N_2O_4} = -\xi + 1 + \xi(0) = 1 - \xi'$$

$$n_{NO_2} = 2\xi - 2\xi(0) = 2\xi' \quad (1c)$$

where

$$\xi' = \xi - \xi(0) \quad (1d)$$

Thus,

$$n = n_{N_2O_4} + n_{NO_2} = 1 + \xi' \quad (1e)$$

As mentioned before, only the difference $d\xi$ is physically significant. Therefore, without loss of generality, we can set $\xi(0) = 0$ so that $\xi' = \xi$.

The mole fractions are therefore

$$x_{N_2O_4} = \frac{n_{N_2O_4}}{n} = \frac{1 - \xi}{1 + \xi} \quad x_{NO_2} = \frac{n_{NO_2}}{n} = \frac{2\xi}{1 + \xi} \quad (1)$$

Answer (a)

Putting (1) & (1.c-e) into (2.243a) gives

$$\begin{aligned} G(T, P, \xi) &= -nRT \ln \left[\frac{P_0}{P} \left(\frac{T}{T_0} \right)^{5/2} \right] + n_{N_2O_4} \mu_{N_2O_4}^0 + n_{NO_2} \mu_{NO_2}^0 + RT \ln (x_{N_2O_4}^{n_{N_2O_4}} x_{NO_2}^{n_{NO_2}}) \\ &= -(1 + \xi) RT \ln \left[\frac{P_0}{P} \left(\frac{T}{T_0} \right)^{5/2} \right] + (1 - \xi) \mu_{N_2O_4}^0 + 2\xi \mu_{NO_2}^0 + RT \ln \left[\left(\frac{1 - \xi}{1 + \xi} \right)^{1 - \xi} \left(\frac{2\xi}{1 + \xi} \right)^{2\xi} \right] \quad [(1c) \text{ used.}] \\ &= -(1 + \xi) RT \ln \left[\frac{P_0}{P} \left(\frac{T}{T_0} \right)^{5/2} \right] + (1 - \xi) \mu_{N_2O_4}^0 + 2\xi \mu_{NO_2}^0 + RT \ln \left[\frac{(1 - \xi)^{1 - \xi}}{(1 + \xi)^{1 + \xi}} (2\xi)^{2\xi} \right] \quad (2) \end{aligned}$$

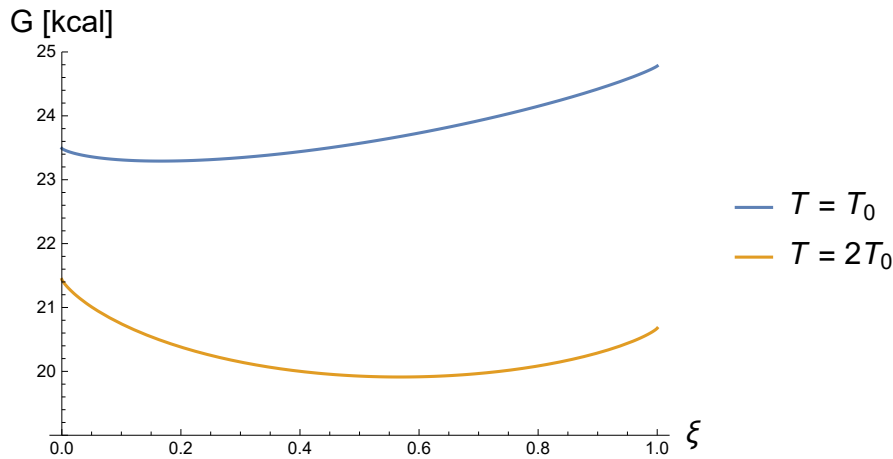
$$\rightarrow G(T_0, P_0, \xi) = (1 - \xi) \mu_{N_2O_4}^0 + 2\xi \mu_{NO_2}^0 + RT_0 \ln \left[\frac{(1 - \xi)^{1 - \xi}}{(1 + \xi)^{1 + \xi}} (2\xi)^{2\xi} \right] \quad (2a)$$

$$\begin{aligned} G(2T_0, P_0, \xi) &= -5(1 + \xi) RT_0 \ln 2 + (1 - \xi) \mu_{N_2O_4}^0 + 2\xi \mu_{NO_2}^0 \\ &\quad + 2RT_0 \ln \left[\frac{(1 - \xi)^{1 - \xi}}{(1 + \xi)^{1 + \xi}} (2\xi)^{2\xi} \right] \quad (2b) \end{aligned}$$

From Table 2.2 in Reichl's text, we have, at $P_0 = 1 \text{ atm}$ and $T_0 = 298 \text{ K}$,

$$\mu_{N_2O_4}^0 = 23.49 \text{ kcal/mol} \quad \mu_{NO_2}^0 = 12.39 \text{ kcal/mol}$$

Plot of $G(T, P, \xi)$ for $P = P_0 = 1 \text{ atm}$ and $T = T_0$ & $2T_0$ is shown in the figure below. Note that $R = 1.987 \times 10^{-3} \text{ kcal/K} \cdot \text{mol}$.



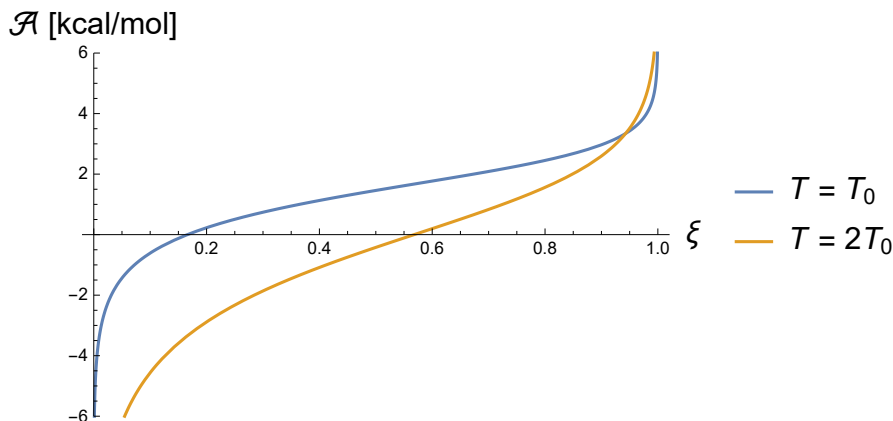
Note: This plot was misplaced in Ex.2.12 in Reichl's text.

Answer (b)

Putting (1) & (1.c-e) into (2.244a) gives

$$\begin{aligned}
 \mathcal{A}(T, P, \xi) &= -(v_{N_2O_4} + v_{NO_2}) RT \ln \left[\frac{P_0}{P} \left(\frac{T}{T_0} \right)^{5/2} \right] + v_{N_2O_4} \mu_{N_2O_4}^0 + v_{NO_2} \mu_{NO_2}^0 + RT \ln (x_{N_2O_4}^{v_{N_2O_4}} x_{NO_2}^{v_{NO_2}}) \\
 &= -RT \ln \left[\frac{P_0}{P} \left(\frac{T}{T_0} \right)^{5/2} \right] - \mu_{N_2O_4}^0 + 2 \mu_{NO_2}^0 + RT \ln \left[\left(\frac{1-\xi}{1+\xi} \right)^{-1} \left(\frac{2\xi}{1+\xi} \right)^2 \right] \\
 &= -RT \ln \left[\frac{P_0}{P} \left(\frac{T}{T_0} \right)^{5/2} \right] - \mu_{N_2O_4}^0 + 2 \mu_{NO_2}^0 + RT \ln \left[\frac{(2\xi)^2}{(1+\xi)(1-\xi)} \right] \quad (3)
 \end{aligned}$$

Plot of $\mathcal{A}(T, P, \xi)$ for $P = P_0 = 1$ atm and $T = T_0$ & $2 T_0$ is shown in the figure below.



Note that as $\xi \rightarrow 1$, the $-RT \ln(1 - \xi)$ term dominates since $\lim_{x \rightarrow 0} \ln x = -\infty$. Hence, the $T = 2 T_0$ curve will rise to about twice the height of the $T = T_0$ one as $\xi \rightarrow 1$, contrary to the graph shown in Reichl's text.

Answer (c)

Setting in (3)

$$P = 1 \text{ atm} \quad T = 298 \text{ K}$$

and solve for ξ in

$$\mathcal{A} = 0 \quad [\text{Condition for equilibrium.}]$$

gives

$$\xi_{\text{eq}} = 0.166$$

Incidentally, solving ξ for

$$\left(\frac{\partial G}{\partial \xi} \right)_{T,P} = 0$$

gives the same answer, as expected [§Code].

Putting ξ_{eq} into (1c) then gives, at equilibrium,

$$n_{N_2O_4} = 0.834 \quad n_{NO_2} = 0.332$$

and

$$n = 1.166 \quad (3a)$$

Answer (d)

Since T & P are fixed, the ideal gas law gives

$$\frac{V}{n} = \text{const} \rightarrow \frac{V_0}{1} = \frac{V}{1.166} \quad [(3a) \text{ used.}]$$

$$\therefore V = 1.166 V_0$$

Answer (e)

Setting in (2.250)

$$P = P_0 = 1 \text{ atm} \quad T = T_0 = 298 \text{ K}$$

$$\nu_{N_2O_4} = -1 \quad \nu_{NO_2} = 2 \quad \nu_t = 1$$

gives

$$\begin{aligned} \left(\frac{\partial H}{\partial \xi} \right)_{T,P} &= \frac{5}{2} R T_0 - R T_0 \ln \left(\frac{x_{NO_2}^2}{x_{N_2O_4}} \right) \\ &= \frac{5}{2} R T_0 - R T_0 \ln \left(\frac{(0.332/1.166)^2}{0.834/1.166} \right) \quad [(3a) \text{ used.}] \\ &= 4.677 R T_0 \\ &= 2.770 \text{ kcal/mol} \end{aligned}$$

Code

Note: graphic outputs are all removed to save storage space.

(* [R] = kcal/K·mol *)

R = 1.987 × 10⁻³; T0 = 298;

μ1 = 12.39; μ2 = 23.49;

(* Temperature T is in units of T0=298K *)

$$G[\xi_, T_] := - (1 + \xi) R T T_0 \text{Log}[T^{5/2}] + (1 - \xi) \mu_2 + 2 \xi \mu_1 + R T T_0 \text{Log} \left[\frac{(1 - \xi)^{1 - \xi}}{(1 + \xi)^{1 + \xi}} (2 \xi)^{2 \xi} \right]$$

(* Plot of $G(\xi)$ *)

```
Plot[{G[ξ, 1], G[ξ, 2]}, {ξ, 0, 1},
      PlotRange → {Automatic, {19, 25}},
      AxesLabel → {"ξ", "G [kcal]"},
      PlotLegends → {"T = T0", "T = 2T0"}]
```

$$A[\xi_-, T_-] := -RT T_0 \text{Log}[T^{5/2}] - \mu_2 + 2 \mu_1 + RT T_0 \text{Log}\left[\frac{1}{(1+\xi)(1-\xi)} (2\xi)^2\right]$$

(* Plot of $\mathcal{A}(\xi)$ *)

```
Plot[{A[ξ, 1], A[ξ, 2]}, {ξ, 0, 1},
      PlotRange → {Automatic, 6 {-1, 1}},
      AxesLabel → {"ξ", "A [kcal/mol]"},
      PlotLegends → {"T = T0", "T = 2T0"}]
```

(* ξ_{eq} *)

```
NSolve[A[ξ, 1] == 0, ξ]
```

Solve: Solve was unable to solve the system with inexact coefficients. The answer was obtained by solving a corresponding exact system and numericizing the result.

```
{{ξ → -0.165896}, {ξ → 0.165896}}
```

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = 0$$

```
NSolve[∂ξG[ξ, 1] == 0, ξ, Reals]
```

```
{{ξ → 0.165896}}
```

$$\left(\frac{\partial H}{\partial \xi}\right)_{T,P}$$

$$\frac{5}{2} - \text{Log}\left[\frac{(0.332/1.166)^2}{0.834/1.166}\right]$$

```
4.6773
```

```
% RT0
```

```
2.76955
```