Chapter 6. Chemical Equilibrium

Summary

- the **First and Second Laws** are combined to predict conditions for spontaneous processes, including chemical reactions
- the **Helmholtz energy** $\boldsymbol{A = U - TS}$ provides $\boldsymbol{\Delta A_{T,V} < 0}$ for spontaneous processes at constant temperature and volume
- the **Gibbs energy** $\boldsymbol{G = U + pV - TS}$ provides $\boldsymbol{\Delta G_{T,p} < 0}$ for spontaneous processes at constant temperature and pressure
- the Gibbs energy is used to derive expressions for the equilibrium constant of chemical reactions

Motivation for Chapter 6

Could do most of thermodynamics with p, V, T, q, w, U, S .

Ok. But sometimes the calculations are ***very inconvenient*!**

Example: Prove that freezing liquid water is spontaneous at –10 °C.

Take the **3-step reversible path** (Why? So ΔS can be calculated.):

$$\begin{tikzcd}
H_2O(l) \arrow[r, "\text{II}", "\text{freeze}"'] & H_2O(s) \arrow[d, "\text{III}", "\text{cool}"'] & 0\ ^{o}\text{C} \\
H_2O(l) \arrow[u, "\text{I}", "\text{heat}"'] & H_2O(s) & -10\ ^{o}\text{C}
\end{tikzcd}$$

$$H_2O(l) \xrightarrow[\Delta H_{\mathrm{m,freeze}} \;=\; -\Delta H_{\mathrm{m,fusion}}]{\textbf{Spontaneous ?}} H_2O(s) \qquad -10\ {}^{\mathrm{o}}\mathrm{C}$$

$$\begin{aligned}\Delta H(-10\ {}^{\mathrm{o}}\mathrm{C}) &= \Delta H_{\mathrm{I}} + \Delta H_{\mathrm{II}} + \Delta H_{\mathrm{III}} \\ &= C_{pm}(l)(273-263)\mathrm{K} - \Delta H_{\mathrm{fus,m}}(273\mathrm{K}) + C_{pm}(\mathrm{s})(263-273)\mathrm{K} \\ &= -\ 5618\ \mathrm{J\ mol^{-1}}\end{aligned}$$

$$\begin{aligned}\Delta S(-10\ {}^{\mathrm{o}}\mathrm{C}) &= \Delta S_{\mathrm{I}} + \Delta S_{\mathrm{II}} + \Delta S_{\mathrm{III}} \quad \text{(all steps reversible)} \\ &= \int_{263\,\mathrm{K}}^{273\,\mathrm{K}} \frac{C_{pm}(l)}{T}\,\mathrm{d}T + \frac{-\Delta H_{\mathrm{fus,m}}}{273\ \mathrm{K}} + \int_{273\,\mathrm{K}}^{263\,\mathrm{K}} \frac{C_{pm}(\mathrm{s})}{T}\,\mathrm{d}T \\ &= -\ 19.20\ \mathrm{J\ K^{-1}\ mol^{-1}}\end{aligned}$$

$\boxed{q/T = 21.36\ \mathrm{J\ K^{-1}} \neq \Delta S\ \ !}$

$$\Delta S_{\mathrm{system}} + \Delta S_{\mathrm{surroundings}} = -19.20\ \mathrm{J} + \frac{5618\ \mathrm{J}}{263\ \mathrm{K}} = +2.15\ \mathrm{J\ K^{-1}}$$

$\boxed{\Delta S > 0 \text{ [isolated (system + surroundings)]} \quad \therefore \textbf{ Spontaneous}}$

What to do?

Legendre Transformations *to the rescue !*

Given the exact differential $\mathrm{d}Y_{\mathrm{I}}$

$$\mathrm{d}Y_{\mathrm{I}} = C_1\mathrm{d}X_1 + C_2\mathrm{d}X_2$$

the function $Y_{\mathrm{I}}(X_1,X_2)$ can be “transformed” into the new functions (*maybe more convenient?*):

$$Y_{\mathrm{II}} = Y_{\mathrm{I}} - C_1X_1$$

$$Y_{\mathrm{III}} = Y_{\mathrm{I}} - C_2X_2$$

$$Y_{\mathrm{IV}} = Y_{\mathrm{I}} - C_1X_1 - C_2X_2$$

Legendre Transformations for Thermodynamics

$$\mathrm{d}U = \mathrm{d}q + \mathrm{d}w \qquad \text{(First Law)}$$

For a reversible path ($\mathrm{d}q = T\mathrm{d}S$ and $\mathrm{d}w = -p\mathrm{d}V$):

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$$

Legendre transforms of $U(S,V)$ are:

$U - TS$ (A = Helmholtz function)

$U + pV$ (H = enthalpy)

$U - TS + pV$ (G = Gibbs function)

Section 6.1 Predicting Spontaneous Processes

a) Using the Internal Energy ($\mathrm{d}U_{S,V} \leq 0$)

$\Delta U_{S,V} < 0$ **spontaneous process**

$\Delta U_{S,V} = 0$ **reversible process**

Where do these rules come from?

First Law: $\mathrm{d}U = \mathrm{d}q + \mathrm{d}w$

For a reversible path: $\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$ (I)

($\mathrm{d}q = T\mathrm{d}S$ and $\mathrm{d}w = -p\mathrm{d}V$)

For a spontaneous path: $\mathrm{d}U = \mathrm{d}q - p_{\text{ext}}\mathrm{d}V$ (II)

Eq. I minus Eq. II: $0 = T\mathrm{d}S - \mathrm{d}q - (p_{\text{ext}} - p)\mathrm{d}V$

same as: $\mathrm{d}q = T\mathrm{d}S - (p_{\text{ext}} - p)\mathrm{d}V$

Irreversible Expansions $\quad p - p_{\text{ext}} > 0 \quad \mathrm{d}V > 0$

Irreversible Compressions $\quad p - p_{\text{ext}} < 0 \quad \mathrm{d}V < 0$

notice: $\boldsymbol{(p - p_{\text{ext}})\mathrm{d}V \geq 0}$

always ≥ 0

from previous slide: $\quad \mathrm{d}q = T\mathrm{d}S - \boxed{(p_{\text{ext}} - p)\mathrm{d}V}$

Important Result: $\boxed{\boldsymbol{\mathrm{d}q \leq T\mathrm{d}S}}$

Why important? First Law: $\quad \mathrm{d}U = \mathrm{d}q + \mathrm{d}w = \mathrm{d}q - p_{\text{ext}}\mathrm{d}V$

(assuming only p-V work)

using $\mathrm{d}q \leq T\mathrm{d}S$ gives $\quad \mathrm{d}U \leq T\mathrm{d}S - p_{\text{ext}}\mathrm{d}V$

at constant S, V this means $\quad \mathrm{d}U_{S,V} \leq 0$

($\mathrm{d}S = 0$, $\mathrm{d}V = 0$)

$\boldsymbol{\mathrm{d}U_{S,V} < 0}$	**spontaneous**
$\boldsymbol{\mathrm{d}U_{S,V} = 0}$	**reversible**

$\Delta U_{S,V} \leq 0$ is a useful result, but **experimentally inconvenient**.
How do you keep the entropy constant? Try the enthalpy?

b) Predicting Spontaneous Processes using the Enthalpy

$$\boldsymbol{H \equiv U + pV}$$

$$\boxed{\begin{array}{ll} \Delta H_{S,p} < 0 & \textbf{spontaneous process} \\ \Delta H_{S,p} = 0 & \textbf{reversible process} \end{array}}$$

$$\begin{aligned} \mathrm{d}H &= \mathrm{d}(U + pV) \\ &= \mathrm{d}U + \mathrm{d}(pV) \\ &= \mathrm{d}U + p\mathrm{d}V + V\mathrm{d}p \\ &= \mathrm{d}q - p_{\mathrm{ext}}\mathrm{d}V + p\mathrm{d}V + V\mathrm{d}p \end{aligned}$$

At constant pressure ($p_{\mathrm{ext}} = p$):

$$\mathrm{d}H_p = \mathrm{d}q \cancel{- p_{\mathrm{ext}}\mathrm{d}V} \cancel{+ p\mathrm{d}V} \cancel{+ V\mathrm{d}p} = \mathrm{d}q \leq T\mathrm{d}S$$

At constant S,p: $\boxed{\mathrm{d}H_{S,p} \leq 0}$

Still inconvenient.
How is S held constant?

c) Predicting Spontaneity using the Helmholtz Energy *A*

$$A \equiv U - TS$$

$$\boxed{\begin{array}{ll} \Delta A_{T,V} < 0 & \textbf{spontaneous process} \\ \Delta A_{T,V} = 0 & \textbf{reversible process} \end{array}}$$

The Helmholtz energy, like the enthalpy, is an "auxiliary" thermodynamic state function. Useful property:

$$\begin{aligned} dA &= d(U - TS) \\ &= dU - d(TS) \\ &= dU - TdS - SdT \\ &= dq + dw - TdS - SdT \\ &= dq - p_{ext}dV - TdS - SdT \end{aligned}$$

$$dA \le -p_{ext}dV - SdT \qquad (\text{using } dq - TdS \le 0)$$

At constant temperature and volume (can be arranged):

$$\boxed{dA_{T,V} \le 0}$$

constant T,V conditions are ***experimentally convenient***

$A = U - TS$ is sometimes called the **Helmholtz <u>Free</u> Energy**

Why? From the previous slide:

$$\begin{aligned} \mathrm{d}A &= \mathrm{d}(U - TS) \\ &= \mathrm{d}U - \mathrm{d}(TS) \\ &= \mathrm{d}U - T\mathrm{d}S - S\mathrm{d}T \\ &= \mathrm{d}q + \mathrm{d}w - T\mathrm{d}S - S\mathrm{d}T \end{aligned}$$

Use $\mathrm{d}q \leq T\mathrm{d}S$ to get

$$\mathrm{d}A_T \leq \mathrm{d}w_T$$

$$-\,\mathrm{d}w_T \leq -\,\mathrm{d}A_T$$

$$\boxed{-\,w_T \leq -\Delta A_T}$$

In an isothermal process, the maximum work free to be done on the surroundings equals the decrease in the Helmholtz Energy.

d) Predicting Spontaneity using the Gibbs Energy *G*

$$G \equiv U - TS + pV$$
$$= H - TS$$

$\Delta G_{T,p} < 0$ **spontaneous process**

$\Delta G_{T,p} = 0$ **reversible process**

The Gibbs Energy is another "auxiliary" thermodynamic state function. Useful property:

$$\begin{aligned} dG &= d(U - TS + pV) \\ &= dU - d(TS) + d(pV) \\ &= dU - TdS - SdT + pdV + Vdp \\ &= dq + dw - TdS - SdT + pdV + Vdp \end{aligned}$$

At fixed *T*,*p*, assuming only *p*-*V* work:

$$dG_{T,p} = dq - \cancel{p_{ext}dV} - TdS - \cancel{SdT} + \cancel{pdV} + \cancel{Vdp} = dq - TdS$$

$$\boxed{dG_{T,p} \leq 0}$$

constant T,p conditions are experimentally convenient

$G = U - TS + pV$ is sometimes called the **Gibbs Free Energy**

Why? From the previous slide:

$$\begin{aligned}
\mathrm{d}G &= \mathrm{d}(U - TS + pV) \\
&= \mathrm{d}U - \mathrm{d}(TS) + \mathrm{d}(pV) \\
&= \mathrm{d}U - T\mathrm{d}S - S\mathrm{d}T + p\mathrm{d}V + V\mathrm{d}p \\
&= \mathrm{d}q + \mathrm{d}w - T\mathrm{d}S - S\mathrm{d}T + p\mathrm{d}V + V\mathrm{d}p \\
&= \mathrm{d}q - p_{\mathrm{ext}}\mathrm{d}V + \mathrm{d}w' - T\mathrm{d}S - S\mathrm{d}T + p\mathrm{d}V + V\mathrm{d}p
\end{aligned}$$

w' is work other than p-V work (such as electrical work)

At fixed T,p ($\mathrm{d}T = 0$ and $p_{\mathrm{ext}} = p$):

$$\mathrm{d}G_{T,p} = \mathrm{d}q + \mathrm{d}w' - T\mathrm{d}S$$

$$\mathrm{d}G_{T,p} \leq \mathrm{d}w' \qquad (\text{ using } \mathrm{d}q \leq T\mathrm{d}S\ )$$

$$-\mathrm{d}w' \leq -\mathrm{d}G_{T,p}$$

$$\boxed{-w' \leq -\Delta G_{T,p}}$$

At fixed T,p the maximum non-p-V work free to be done on the surroundings equals the decrease in the Gibbs Energy.

Summary of Criteria Used for the Prediction of Reversible and Spontaneous Processes

$$\Delta U_{S,V} \leq 0$$

$$\Delta H_{S,p} \leq 0$$

$$\Delta A_{T,V} \leq 0$$

$$\Delta G_{T,p} \leq 0$$

$= 0$ **reversible**

< 0 **spontaneous**

U is the **Internal Energy**

$H = U + pV$ is the **Enthalpy**

$A = U - TS$ is the **Helmholtz Energy**

$G = U - TS + pV$ is the **Gibbs Energy**

Section 6.2 and 6.3 Differential Forms of *U*, *H*, *A* and *G*

(the mathematical formulation of thermodynamics)

a) The Internal Energy

The First Law $\Delta U = q + w$

In differential form (**infinitesimally small changes in *U***):

$$\mathrm{d}U = \mathrm{d}q + \mathrm{d}w$$

The internal energy is a state function. Any path, reversible or ireversible, can be used to calculate d*U*.

For convenience, take a reversible path ($\mathrm{d}q = T\mathrm{d}S$ and $\mathrm{d}w = -p\mathrm{d}V$):

$$\boxed{\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V}$$

Applications?

Differentials of State Functions (from Chapter 2)

Recall that the differential equation

$$\mathrm{d}f = g(x,y)\mathrm{d}x + h(x,y)\mathrm{d}y$$

for state function $f(x,y)$ of variables x an y is equivalent to

$$\mathrm{d}f = \left(\frac{\partial f}{\partial x}\right)_y \mathrm{d}x + \left(\frac{\partial f}{\partial y}\right)_x \mathrm{d}y$$

Comparing the two equations for df shows

$$g(x,y) = \left(\frac{\partial f}{\partial x}\right)_y \qquad h(x,y) = \left(\frac{\partial f}{\partial y}\right)_x$$

Reversing the order of differentiation gives

$$\left[\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_y\right]_x = \left(\frac{\partial g}{\partial y}\right)_x = \left[\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)_x\right]_y = \left(\frac{\partial h}{\partial x}\right)_y$$

(∂x first then ∂y) **(∂y first then ∂x)**

Differential of the Internal Energy

The differential of $U(T,V)$

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$$

is equivalent to

$$\mathrm{d}U = \left(\frac{\partial U}{\partial S}\right)_V \mathrm{d}S + \left(\frac{\partial U}{\partial V}\right)_S \mathrm{d}V$$

which shows

$$\left(\frac{\partial U}{\partial S}\right)_V = T \qquad \text{and} \qquad \left(\frac{\partial U}{\partial V}\right)_S = -p$$

(*new ways of understanding the temperature and pressure*)

Reversing the order of second differentiation gives

$$\left[\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right)_V\right]_T = \left(\frac{\partial T}{\partial V}\right)_S = \left[\frac{\partial}{\partial S}\left(\frac{\partial U}{\partial V}\right)_S\right]_V = -\left(\frac{\partial p}{\partial S}\right)_V$$

(∂S first then ∂V) **(∂V first then ∂S)**

Differential of the Enthalpy

The differential of $H(T,p)$

$$\mathrm{d}H = \mathrm{d}(U + pV) = \mathrm{d}U + \mathrm{d}(pV) = \mathrm{d}U + p\mathrm{d}V + V\mathrm{d}p$$

$$\mathrm{d}H = T\mathrm{d}S - \cancel{p\mathrm{d}V} + \cancel{p\mathrm{d}V} + V\mathrm{d}p$$

$$\boxed{\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}p}$$

is equivalent to

$$\mathrm{d}H = \left(\frac{\partial H}{\partial S}\right)_p \mathrm{d}S + \left(\frac{\partial H}{\partial p}\right)_S \mathrm{d}p$$

which shows

$$\left(\frac{\partial H}{\partial S}\right)_p = T \qquad \text{and} \qquad \left(\frac{\partial H}{\partial p}\right)_S = V$$

Reversing the order of second differentiation gives

$$\left[\frac{\partial}{\partial p}\left(\frac{\partial H}{\partial S}\right)_p\right]_S = \left(\frac{\partial T}{\partial p}\right)_S = \left[\frac{\partial}{\partial S}\left(\frac{\partial H}{\partial p}\right)_S\right]_p = \left(\frac{\partial V}{\partial S}\right)_p$$

Differential of the Helmholtz Energy

The differential of $A(T,V)$

$$\mathrm{d}A = \mathrm{d}(U - TS) = \mathrm{d}U - \mathrm{d}(TS) = \mathrm{d}U - T\mathrm{d}S - S\mathrm{d}T$$

$$\mathrm{d}A = \cancel{T\mathrm{d}S} - p\mathrm{d}V - \cancel{T\mathrm{d}S} - S\mathrm{d}T$$

$$\boxed{\mathrm{d}A = -S\mathrm{d}T - p\mathrm{d}V}$$

is equivalent to

$$\mathrm{d}A = \left(\frac{\partial A}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial A}{\partial V}\right)_T \mathrm{d}V$$

which shows

$$\left(\frac{\partial A}{\partial T}\right)_V = -S \qquad \text{and} \qquad \left(\frac{\partial A}{\partial V}\right)_T = -p$$

Reversing the order of second differentiation gives

$$\left[\frac{\partial}{\partial V}\left(\frac{\partial A}{\partial T}\right)_V\right]_T = -\left(\frac{\partial S}{\partial V}\right)_T = \left[\frac{\partial}{\partial T}\left(\frac{\partial A}{\partial V}\right)_T\right]_V = -\left(\frac{\partial p}{\partial T}\right)_V$$

<u>conveniently</u>
in terms of
p*, *V*, *T

Differential of the Gibbs Energy

The differential of $G(T,p)$

$$\mathrm{d}G = \mathrm{d}(U - TS + pV) = \mathrm{d}U - \mathrm{d}(TS) + \mathrm{d}(pV)$$

$$\mathrm{d}G = \cancel{T\mathrm{d}S} - \cancel{p\mathrm{d}V} - \cancel{T\mathrm{d}S} - S\mathrm{d}T + \cancel{p\mathrm{d}V} + V\mathrm{d}p$$

$$\boxed{\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p}$$

is equivalent to

$$\mathrm{d}G = \left(\frac{\partial G}{\partial T}\right)_p \mathrm{d}T + \left(\frac{\partial G}{\partial p}\right)_T \mathrm{d}p$$

which shows

$$\left(\frac{\partial G}{\partial T}\right)_p = -S \qquad \text{and} \qquad \left(\frac{\partial G}{\partial p}\right)_T = V$$

Reversing the order of second differentiation gives

$$\left[\frac{\partial}{\partial p}\left(\frac{\partial G}{\partial T}\right)_p\right]_T = -\left(\frac{\partial S}{\partial p}\right)_T = \left[\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial p}\right)_T\right]_p = \left(\frac{\partial V}{\partial T}\right)_p$$

<u>conveniently</u>
in terms of
p, V, T

Section 6.2 Summary

$$\begin{aligned} dU &= TdS - pdV & \qquad dH &= TdS + Vdp \\ dA &= -SdT - pdV & \qquad dG &= -SdT + Vdp \end{aligned}$$

memorize ?

From the **first derivatives** of *U*, *H*, *A*, and *G*:

$$\left(\frac{\partial U}{\partial S}\right)_V = T \qquad \left(\frac{\partial U}{\partial V}\right)_S = -p \qquad \left(\frac{\partial H}{\partial S}\right)_p = T \qquad \left(\frac{\partial H}{\partial p}\right)_S = V$$

$$\left(\frac{\partial A}{\partial T}\right)_V = -S \qquad \left(\frac{\partial A}{\partial V}\right)_T = -p \qquad \left(\frac{\partial G}{\partial T}\right)_p = -S \qquad \left(\frac{\partial G}{\partial p}\right)_T = V$$

From the **second derivatives** of *U*, *H*, *A*, and *G* **(Maxwell relations)** :

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V \qquad \left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \qquad -\left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial V}{\partial T}\right)_p$$

Example: Derive an expression for $(\partial U/\partial V)_T$ to calculate changes in the internal energy with volume at constant temperature.

Suggestion: start with the differential equation for dU

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$$ then divide by dV at constant temperature.

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p\cancelto{1}{\left(\frac{\partial V}{\partial V}\right)_T}$$

But what is $(\partial S/\partial V)_T$?

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$

Use the Maxwell relation for A.

$$\boxed{\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p}$$

Significance: This result gives $(\partial U/\partial V)_T$ in terms of quantities conveniently measured in terms of p, V, and T.

Exercises:

a) Show

$$Cp = \left(\frac{\partial H}{\partial T}\right)_p = T\left(\frac{\partial S}{\partial T}\right)_p$$

b) Use the Maxwell relation for dG to show

$$\left(\frac{\partial H}{\partial p}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_T + V$$

c) The temperature of a substance increases when it is compressed adiabatically. For a reversible adiabatic compression (constant S), use a Maxwell relation to show

$$\left(\frac{\partial T}{\partial p}\right)_S = \frac{T}{C_p}\left(\frac{\partial V}{\partial T}\right)_p$$

Example: Derive an expression for the **Gibbs energy of an ideal gas** as a function of pressure. (***Why do this?*** A useful result for understanding equilibrium of reacting gases).

$$G(T,p) = G^{o}(T,p^{o}) + \int_{p^{o}}^{p} \left(\frac{\partial G}{\partial p}\right)_T \mathrm{d}p$$

But what is $(\partial G/\partial p)_T$?

Independent variables T and p suggests looking at

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p$$

which shows

$$\left(\frac{\partial G}{\partial p}\right)_T = V = \frac{nRT}{p}$$

Find

$$G(T,p) = G^{o}(T,p^{o}) + \int_{p^{o}}^{p} \frac{nRT}{p}\mathrm{d}p = G^{o}(T,p^{o}) + nRT\int_{p^{o}}^{p} \frac{1}{p}\mathrm{d}p$$

$$\boxed{G(T,p) = G^{o}(T,p^{o}) + nRT\ln(p/p^{o})}$$

$$\boxed{G_{\mathrm{m}}(T,p) = G_{\mathrm{m}}^{o}(T,p^{o}) + RT\ln(p/p^{o})}$$

$G_{\mathrm{m}} = G/n$ is the Gibbs energy per mole of gas

Example: Derive an expression for the temperature dependence of G/T. (***Why do this?*** The logarithm of the equilibrium constant for a chemical reaction is proportional to G/T.)

$$\left(\frac{\partial(G/T)}{\partial T}\right)_p = \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_p + G\left(\frac{\partial(1/T)}{\partial T}\right)_p$$

But what is $(\partial G/\partial T)_p$?

Independent variables T and p suggests looking at $\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p$ which shows $(\partial G/\partial T)_p = -S$.

Find

$$\left(\frac{\partial(G/T)}{\partial T}\right)_p = \frac{1}{T}(-S) + G\left(\frac{-1}{T^2}\right) = -\frac{S}{T} - \frac{G}{T^2} = -\frac{TS+G}{T^2}$$

$$\boxed{\left(\frac{\partial(G/T)}{\partial T}\right)_p = -\frac{H}{T^2}}$$

($G = H - TS$, so $TS + G = H$)

Sections 6.4 and 6.5 Gibbs Energy of Gas Mixtures

- systems of fixed composition have been considered so far
- chemical reactions consume reactants and form products, causing changes in compositions
- ***no problem*** – just include composition variables
- many chemical reactions occur at fixed temperature and pressure
- $\Delta G_{T,p} \leq 0$ is used to predict equilibrium under these conditions,

Pure Substances or Systems of Fixed Composition

Gibbs energy is a function of temperature and pressure

$$\mathrm{d}G = \left(\frac{\partial G}{\partial T}\right)_p \mathrm{d}T + \left(\frac{\partial G}{\partial p}\right)_T \mathrm{d}p$$

Mixtures of Variable Composition

Gibbs energy is a function *T*, *p* and the number of moles n_1, n_2, n_3, … of each substance in the mixture

$$\mathrm{d}G = \left(\frac{\partial G}{\partial T}\right)_{p,n_1,n_2,n_3,\ldots} \mathrm{d}T + \left(\frac{\partial G}{\partial p}\right)_{T,n_1,n_2,n_3,\ldots} \mathrm{d}p + \left(\frac{\partial G}{\partial n_1}\right)_{T,p,,n_2,n_3,\ldots} \mathrm{d}n_1 + \left(\frac{\partial G}{\partial n_2}\right)_{T,p,n_1,n_3,\ldots} \mathrm{d}n_2 + \left(\frac{\partial G}{\partial n_3}\right)_{T,p,n_1,n_2,\ldots} \mathrm{d}n_3 + \cdots$$

Chemical Potential μ_i of Substance *i* in a Mixture

defined as $\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_{k\neq i}} = G_{\mathrm{m},i}$

Gibbs energy per mole of substance *i*

gives $$\mathrm{d}G = \left(\frac{\partial G}{\partial T}\right)_{p,n_1,n_2,n_3,\ldots}\mathrm{d}T + \left(\frac{\partial G}{\partial p}\right)_{T,n_1,n_2,n_3,\ldots}\mathrm{d}p + \mu_1\,\mathrm{d}n_1 + \mu_2\,\mathrm{d}n_2 + \mu_3\,\mathrm{d}n_3 + \cdots$$

Application of Chemical Potentials

The Gibbs energy of a mixture of different substances is

$$G = n_1\mu_1 + n_2\mu_2 = n_3\mu_3 + \ldots$$

Significance of Chemical Potentials (*Huge !*)

- positive electric charge flows to regions of lower electric potential
- "north" magnetic poles are drawn to "south" magnetic poles
- objects roll downhill to reach lower gravitational potential energy

Useful analogy:

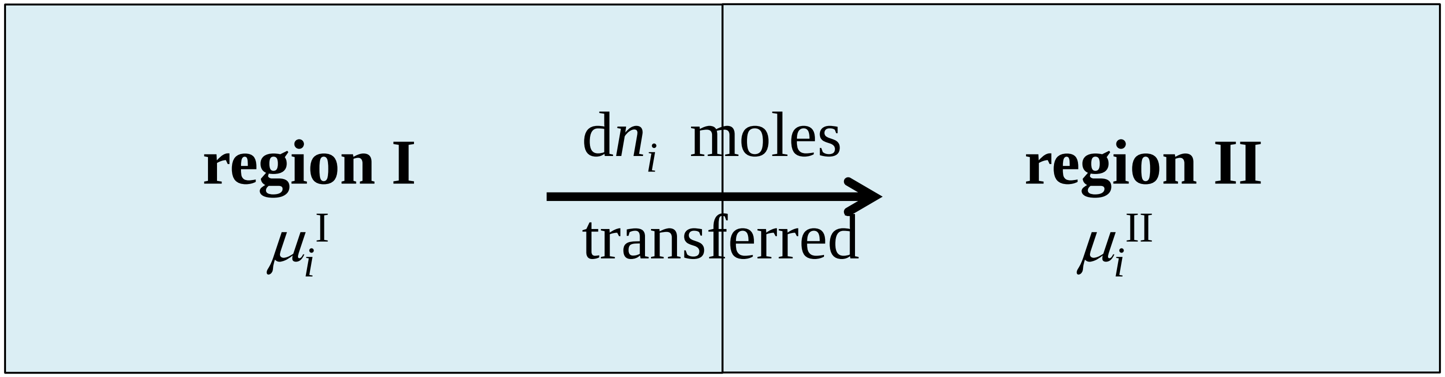
chemical substances:

expand, compress, warm, cool, vaporize, condense,
freeze, melt, sublime, diffuse, mix, crystallize, react, …

to reach lower chemical potential and chemical equilibrium

Example. A system is divided into region I and region II.

$\mathrm{d}n_i$ moles of substance i are transferred from region I to II.



region I

μ_i^{I}

$\mathrm{d}n_i$ moles

transferred

region II

μ_i^{II}

$$\mathrm{d}G_{T,p} = \mu_i^{\mathrm{I}}\mathrm{d}n_i^{\mathrm{I}} + \mu_i^{\mathrm{II}}\mathrm{d}n_i^{\mathrm{II}} = \mu_i^{\mathrm{I}}(-\mathrm{d}n_i) + \mu_i^{\mathrm{II}}(+\mathrm{d}n_i)$$

$$\boxed{\mathrm{d}G_{T,p} = (\mu_i^{\mathrm{II}} - \mu_i^{\mathrm{I}})\,\mathrm{d}n_i}$$

$\mu_i^{\mathrm{II}} < \mu_i^{\mathrm{I}}$	$\mathrm{d}n_i > 0$	transfer **I → II**	$\mathrm{d}G_{T,p} < 0$
$\mu_i^{\mathrm{II}} > \mu_i^{\mathrm{I}}$	$\mathrm{d}n_i < 0$	transfer **I ← II**	$\mathrm{d}G_{T,p} < 0$
$\mu_i^{\mathrm{II}} = \mu_i^{\mathrm{I}}$	$\mathrm{d}n_i > 0$ $\mathrm{d}n_i < 0$	transfer **I ↔ II** (reversible)	$\mathrm{d}G_{T,p} = 0$ (equilibrium)

Chemical Equilibrium

The chemical potential (Gibbs energy per mole) of each substance is constant throughout the system.

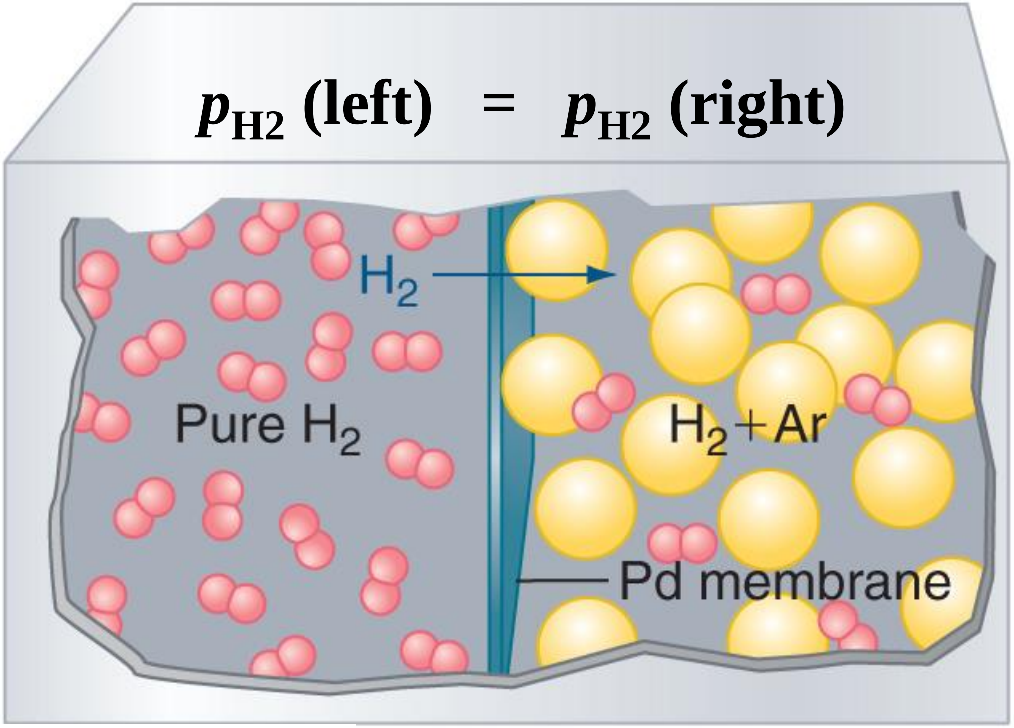
Thermal Equilibrium

The temperature is constant throughout the system.

Mechanical Equilibrium

The pressure is constant throughout the system.

Section 6.6 Gibbs Energy of Mixing



Semipermeable Barrier

H_2 (but not other gases) can pass through palladium metal films. (*Why* ?)

At equilibrium, the pressure of pure H_2 and the partial pressure of H_2 in the mixture are equal.

Important Conclusion: the **chemical potential** (Gibbs energy per mole) of H_2, or **any ideal gas**, mixed or pure, is

$$\boxed{\mu(T, p_i) = G_{mi}(T, p_i) = G_{mi}^{o}(T, p^{o}) + RT \ln(p_i / p^{o})}$$

Gibbs Energy of Mixing of Ideal Gases

Example: Mix n_{H2} moles pure H_2 and n_{Ar} moles pure Ar at constant temperature and pressure.

n_{H2} mol	n_{Ar} mol		n_{H2} mol H_2 + n_{Ar} mol Ar
pure H_2	**pure** Ar	→	**mixed** at T, p
T, p	T, p		total pressure $p = p_{H2} + p_{Ar}$

$$\Delta G_{mix} = G_f - G_i$$

$$= n_{H2}[G_{mH2}{}^{o}(T,p^{o}) + RT\ln(p_{H2}/p^{o})] + n_{Ar}[G_{mAr}{}^{o}(T,p^{o}) + RT\ln(p_{Ar}/p^{o})]$$

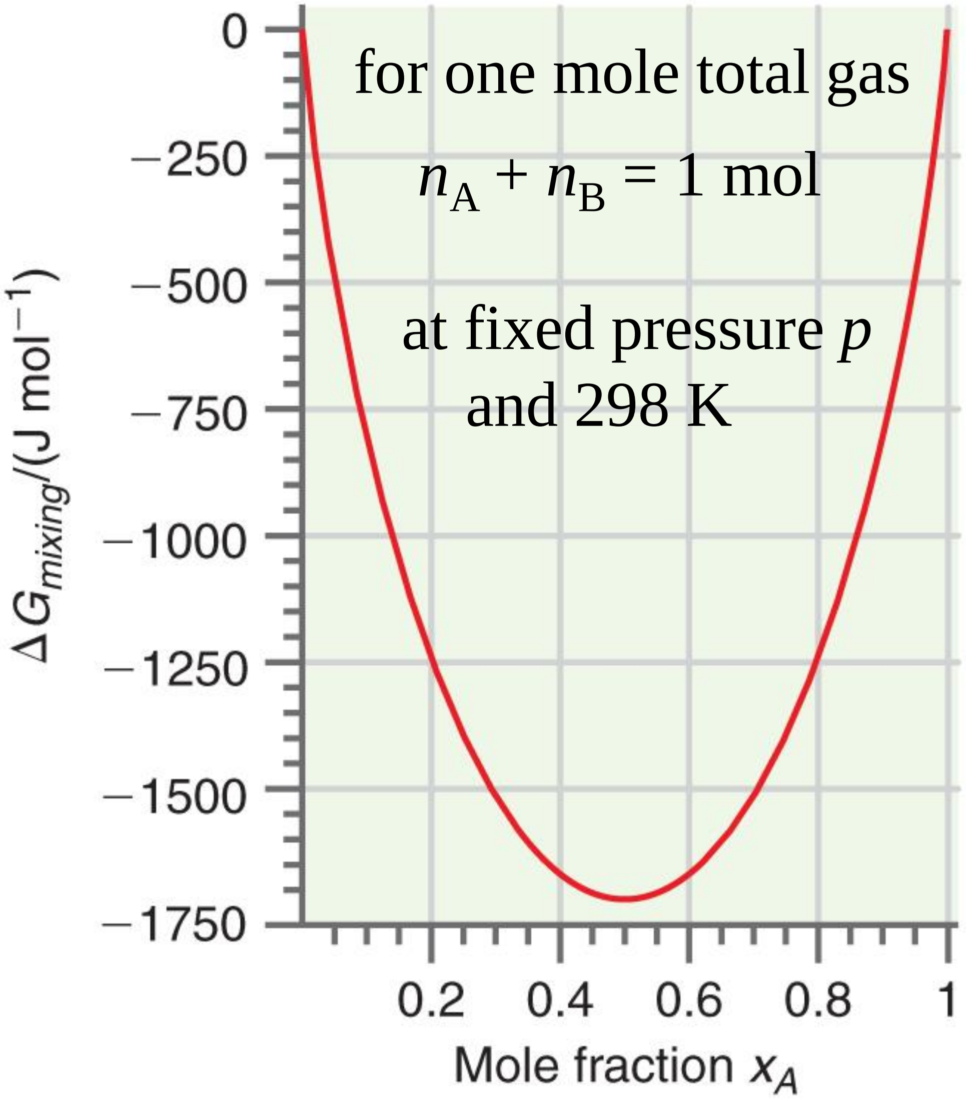
$$- \; n_{H2}[G_{mH2}{}^{o}(T,p^{o}) + RT\ln(p/p^{o})] + n_{Ar}[G_{mAr}{}^{o}(T,p^{o}) + RT\ln(p/p^{o})]$$

$$= n_{H2}RT\ln(p_{H2}/p) + n_{Ar}RT\ln(p_{Ar}/p)$$

$$\boxed{\Delta G_{mix} = n_{H2}RT\ln x_{H2} + n_{Ar}RT\ln x_{Ar}} \qquad \text{(constant } T, p\text{)}$$

Gibbs Energy of Mixing

$$\boxed{\Delta G_{\text{mix}} = n_A RT \ln x_A + n_B RT \ln x_B}$$



for one mole total gas

$n_A + n_B = 1$ mol

at fixed pressure p
and 298 K

$$\boxed{\Delta G_{\text{mix}} < 0}$$

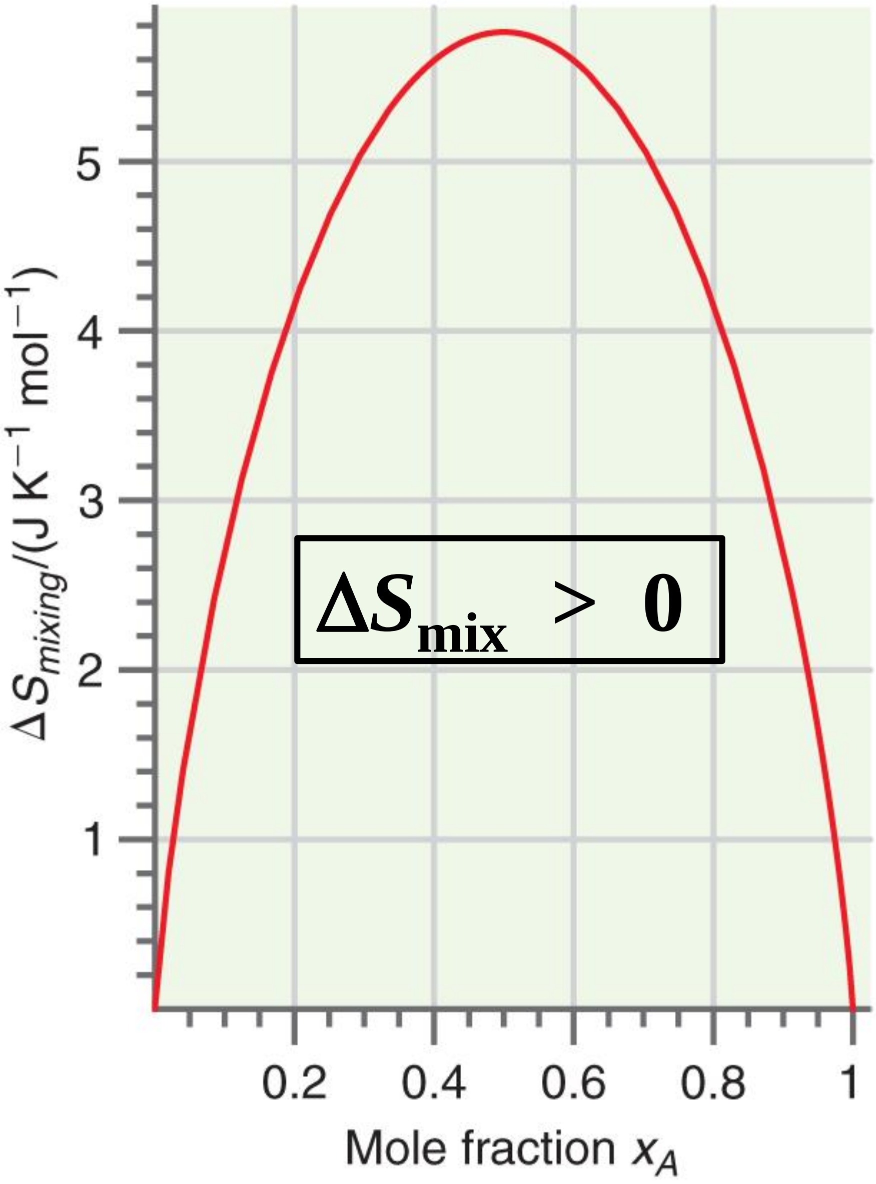
mix

n_A moles of pure gas A
+
n_B moles pure gas B

$$x_A = \frac{n_A}{n_A + n_B} = \frac{p_A}{p}$$

Entropy of Mixing

$$\boxed{\Delta S_{\mathrm{mix}} = -n_A R \ln x_A - n_B R \ln x_B}$$



$$\boxed{\Delta S_{\mathrm{mix}} > 0}$$

mix

n_A moles of pure gas A

+

n_B moles pure gas B

at fixed pressure p

one mole total gas:

$n_A + n_B = 1$ mol

$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$

$$\boxed{\left(\frac{\partial \Delta G_{\mathrm{mix}}}{\partial T}\right)_p = -\Delta S_{\mathrm{mix}}}$$

Section 6.7 Standard Gibbs Energy Change ΔG_R^o for Chemical Reactions

Example: Calculate ΔG_R^o for the following reaction at 298.15 K (25 °C).

stoichiometric coefficients:

$\nu_{NO2} = -2$

$\nu_{N2O4} = +1$

$$2\ \mathrm{NO_2(g)} \rightarrow \mathrm{N_2O_4(g)}$$

$$\begin{aligned}\Delta G_R^o &= \Delta G_f^o(\text{products}) - \Delta G_f^o(\text{reactants}) \\ &= \Delta G_{fm}^o(N_2O_4, g) - 2\Delta G_{fm}^o(NO_2, g) \\ &= 99.8\ \text{kJ mol}^{-1} - (2)\,(51.3\ \text{kJ mol}^{-1}) \qquad \text{(Table 4.1)} \\ &= -2.80\ \text{kJ mol}^{-1}\end{aligned}$$

for any reaction:

$$\Delta G_R^o = \sum_i \nu_i\, \Delta G_{fm}^o(i)$$

Important: $\mathbf{\Delta G_R^o}$ is the change in Gibbs energy for the conversion of **pure reactants to pure products at standard pressure** (p^o = 1 bar)

Section 6.8 Equilibrium Constant *K* for Chemical Reactions in Mixtures of Ideal Gases

Actual reactions occur for

- **mixed gases** (not pure)
- **usually at non-standard pressures**

Example: $2\ NO_2(g) \rightarrow N_2O_4(g)$

Mystery

$$\boxed{\frac{p_{N2O4}}{(p_{NO2})^2} = \text{constant}}$$

at equilibrium and a given temperature

- ***why*** is ***this ratio*** of partial pressures constant ***for any initial conditions***, from pure NO_2 to pure N_2O_4?
- ***why*** is the product pressure in the numerator?
- ***why*** is the reactant pressure in the denominator?
- ***why*** is the reactant pressure squared?

Section 6.8 Equilibrium Constant *K* for the Reaction of Mixtures of Ideal Gases

Actual reactions occur for

- mixed (not pure) gases
- usually at non-standard pressures

Example: Calculate ΔG_R for the following reaction at 298.15 K for the mixed gases at partial pressures p_{NO2} and p_{N2O4}.

$$\boxed{\mathbf{2\,NO_2(g) \rightarrow N_2O_4(g)}}$$

$$\Delta G_R = \Delta G_f\,(\text{products}) - \Delta G_f\,(\text{reactants})$$

$$= \Delta G_{fm}(N_2O_4,\ g) - 2\Delta G_{fm}(NO_2,\ g)$$

$$= \Delta G_{fm}{}^{o}(N_2O_4,\ g) + RT\ln(p_{N2O4}/p^{o}) - 2[\Delta G_{fm}{}^{o}(NO_2,\ g) + RT\ln(p_{NO2}/p^{o})]$$

$$= \mathbf{\Delta G_{fm}{}^{o}(N_2O_4,\ g) - 2\Delta G_{fm}{}^{o}(NO_2,\ g)} + RT\ln(p_{N2O4}/p^{o}) - 2RT\ln(p_{NO2}/p^{o})$$

$$\boxed{\mathbf{\Delta G_R = \Delta G_R{}^{o} + RT\ln[\,(p_{N2O4}/p^{o})^{1}\,(p_{NO2}/p^{o})^{-2}\,]}}$$

Non-Standard ΔG_R for the reaction:

no “ o ” superscript

$$2\,NO_2(g) \rightarrow N_2O_4(g)$$

$$\Delta G_R = \Delta G_R^o + RT\ln\left[\frac{p_{N2O4}/p^o}{(p_{NO2}/p^o)^2}\right]$$

Simpler notation

$$\boxed{\Delta G_R = \Delta G_R^o + RT\ln Q}$$

using the **reaction quotient *Q***

$$\boxed{Q = \frac{p_{N2O4}/p^o}{(p_{NO2}/p^o)^2}}$$

$$\boxed{\Delta G_R \;=\; \Delta G_R^o \;+\; RT\ln Q}$$

Case I: $\Delta G_R = 0$ Equilibrium in the Reacting Gas Mixture

$$2\,NO_2(g) \;\leftrightarrow\; N_2O_4(g)$$

$$0 \;=\; \Delta G_R^o \;+\; RT\ln Q_{\mathrm{equil}}$$

$$\ln Q_{\mathrm{equil}} \;=\; -\Delta G_R^o\,/\,RT$$

$$\boxed{\text{equilibrium constant}\quad K \;=\; Q_{\mathrm{equil}} \;=\; \left(\frac{p_{\mathrm{N2O4}}\,/\,p^o}{(p_{\mathrm{NO2}}\,/\,p^o)^2}\right)_{\mathrm{equil}}}$$

$$\boxed{K \;=\; e^{-\Delta G_R{}^o\,/\,RT}}$$

$$\boxed{\Delta G_{\mathrm{R}} = \Delta G_{\mathrm{R}}^{\circ} + RT\ln Q}$$

Case II: $\Delta G_{\mathrm{R}} < 0$ **<u>Forward Reaction</u> in the Gas Mixture**

$$2\,\mathrm{NO_2(g)} \rightarrow \mathrm{N_2O_4(g)}$$

$$\Delta G_{\mathrm{R}} = \Delta G_{\mathrm{R}}^{\circ} + RT\ln Q < 0$$

$$\boxed{Q < K}$$

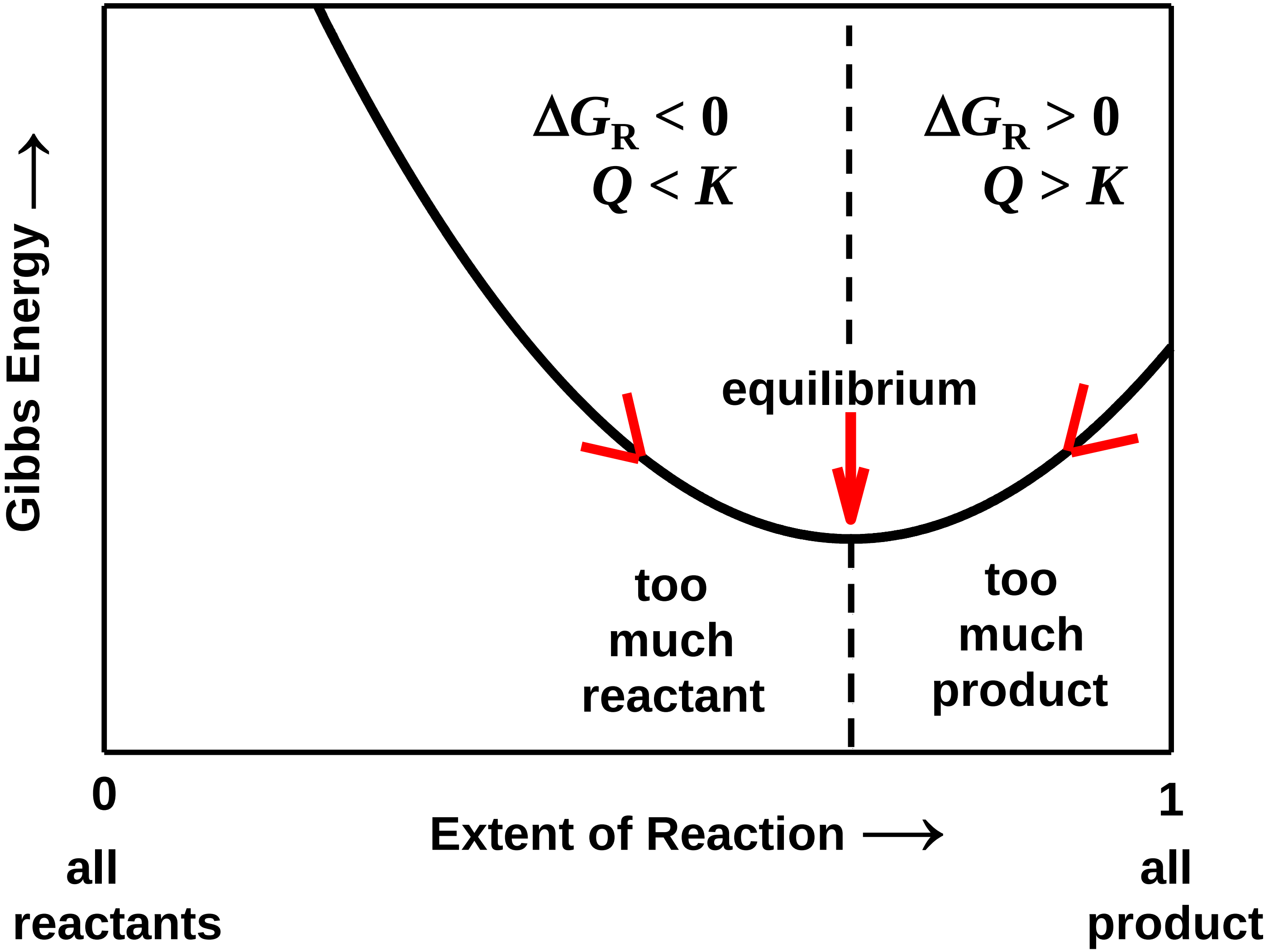
Case III: $\Delta G_{\mathrm{R}} > 0$ **<u>Reverse Reaction</u> in the Gas Mixture**

$$2\,\mathrm{NO_2(g)} \leftarrow \mathrm{N_2O_4(g)}$$

$$\Delta G_{\mathrm{R}} = \Delta G_{\mathrm{R}}^{\circ} + RT\ln Q > 0$$

$$\boxed{Q > K}$$

Spontaneous Chemical Reactions



Example $NO_2(g)$ and $N_2O_4(g)$ are in a reaction vessel at 298 K and partial pressures 0.350 bar and 0.650 bar, respectively.

Is this system at equilibrium?

Data: ΔG^o for the reaction **$2\ NO_2(g) \rightarrow N_2O_4(g)$** is -2.80 kJ mol^{-1} at 298 K.

$$K = e^{-\Delta G^o/RT} = e^{-(-2800)/(8.314)(298)} = e^{1.130} = 3.01$$

$$Q = \frac{p_{N2O4}/p^o}{(p_{NO2}/p^o)^2} = \frac{0.650}{(0.350)^2} = 5.31$$

$Q > K$ The gas mixture is not at equilibrium.
Too little NO_2 reactant. Too much N_2O_4 product.

The reverse reaction **$2\ NO_2(g) \leftarrow N_2O_4(g)$** is spontaneous.

Equilibrium Constants K for Ideal-Gas Reactions

$$a\,\mathrm{A(g)} \;+\; b\,\mathrm{B(g)} \;+ \ldots \;\longrightarrow\; c\,\mathrm{C(g)} \;+\; d\,\mathrm{D(g)} \;+ \ldots$$

$$\nu_\mathrm{A} = -a \qquad \nu_\mathrm{B} = -b \qquad \nu_\mathrm{C} = +c \qquad \nu_\mathrm{D} = +d$$

$$K \;=\; \frac{(p_\mathrm{C}/p^\mathrm{o})^c\,(p_\mathrm{D}/p^\mathrm{o})^d\;\cdots}{(p_\mathrm{A}/p^\mathrm{o})^a\,(p_\mathrm{B}/p^\mathrm{o})^b\;\cdots} \;=\; \left(\frac{p_\mathrm{A}}{p^\mathrm{o}}\right)^{\nu\mathrm{A}}\left(\frac{p_\mathrm{B}}{p^\mathrm{o}}\right)^{\nu\mathrm{B}}\left(\frac{p_\mathrm{C}}{p^\mathrm{o}}\right)^{\nu\mathrm{C}}\left(\frac{p_\mathrm{D}}{p^\mathrm{o}}\right)^{\nu\mathrm{D}}\cdots$$

using **<u>equilibrium</u>** partial pressures $p_\mathrm{A},\; p_\mathrm{B},\; p_\mathrm{C},\; p_\mathrm{D},\; \ldots$

$$\boxed{K \;=\; \exp(-\Delta G^\mathrm{o}_\mathrm{R}/RT\,)}$$

$$\Delta G^\mathrm{o} \;=\; c\Delta G_\mathrm{fm}{}^\mathrm{o}(\mathrm{C,\,g}) + d\Delta G_\mathrm{fm}{}^\mathrm{o}(\mathrm{D,\,g}) \;\ldots\; - a\Delta G_\mathrm{fm}{}^\mathrm{o}(\mathrm{C,\,g}) - b\Delta G_\mathrm{fm}{}^\mathrm{o}(\mathrm{D,\,g}) \;\ldots$$

$$\boxed{\Delta G^\mathrm{o}_\mathrm{R} \;=\; \sum_i \nu_i\,\Delta G^\mathrm{o}_\mathrm{fm}(i)}$$

Section 6.9 Calculating Equilibrium Partial Pressures for Mixtures of Reacting Gases

Example NO_2(g) and N_2O_4(g) are in a reaction vessel at 298 K and partial pressures 0.350 bar and 0.650 bar, respectively.

Calculate the gas partial pressures at equilibrium.

Data: at 298 K the equilibrium constant for the reaction

$2NO_2(g) \rightarrow N_2O_4(g)$ is $K = 3.01$

Notice that changes in the number of moles NO_2 and N_2O_4 are linked by **stoichiometry**: $\boldsymbol{\Delta n_{NO2} = -2\Delta n_{N2O4}}$

Also, in a reaction vessel at constant volume, **the partial pressure of each gas is proportional to the number of moles of gas**.

$$p_i = \frac{RT}{V} n_i = \text{constant} \times n_i$$

Example (*cont.*) Let x be the change in the N_2O_4 pressure.

	$2\ NO_2(g)$	**$\rightarrow$**	**$N_2O_4(g)$**
initial pressures:	$p_{NO2(init)}$		$p_{N2O4(init)}$
equilibrium pressures:	$p_{NO2(init)} - 2x$		$p_{N2O4(init)} + x$

$$K = \frac{p_{N2O4} / p^{o}}{(p_{NO2} / p^{o})^{2}} = \frac{(0.650 + x)}{(0.350 - 2x)^{2}} = 3.01$$

Solve for $x = -0.0486$. At equilibrium:

$$p_{NO2} = p_{NO2(init)} - 2x = 0.350 - 2(-0.0486) = 0.447 \text{ bar}$$

$$p_{N2O4} = p_{N2O4(init)} + x = 0.650 + (-0.0486) = 0.601 \text{ bar}$$

check: $0.601/(0.447)^2 = 3.008$

Equilibrium Calculations

A systematic approach frequently works. Suggestions:

1. Write the balanced chemical reaction.
2. Write the equilibrium constant expression.
3. List the available information.
4. Assign a variable (*e.g.*, x) to one of the unknown concentrations
5. Use stoichiometry to relate x to the other unknown concentrations.
6. Use the equilibrium constant expression to calculate x.
7. Calculate the reactant and product concentrations.
8. Check by using the concentrations to calculate K.

Section 6.10 Temperature Dependence of Equilibrium Constants

Helpful result from Section 6.3:
$$\boxed{\left(\frac{\partial (G/T)}{\partial T}\right)_p = -\frac{H}{T^2}}$$

gives
$$\left(\frac{\partial (G_f/T)}{\partial T}\right)_p - \left(\frac{\partial (G_i/T)}{\partial T}\right)_p = -\frac{H_f}{T^2} - \left(-\frac{H_i}{T^2}\right)$$

$$\boxed{\left(\frac{\partial (\Delta G/T)}{\partial T}\right)_p = -\frac{\Delta H}{T^2}}$$

Why helpful? For equilibrium constants $\Delta G_{\mathrm{R}}^{\mathrm{o}} = -RT\ln K$ and

$$\frac{\Delta G_{\mathrm{R}}^{\mathrm{o}}}{T} = -R\ln K$$

Temperature Dependence of Equilibrium Constants

$$\left(\frac{\partial(\Delta G_{\mathrm{R}}^{\mathrm{o}}/T)}{\partial T}\right)_p = \frac{\mathrm{d}}{\mathrm{d}T}\left(\frac{\Delta G_{\mathrm{R}}^{\mathrm{o}}}{T}\right) = \frac{\mathrm{d}}{\mathrm{d}T}\left(-R\ln K\right) = -\frac{\Delta H_{\mathrm{R}}^{\mathrm{o}}}{T^2}$$

Switched from a partial to an ordinary derivative. ***Why?***

gives

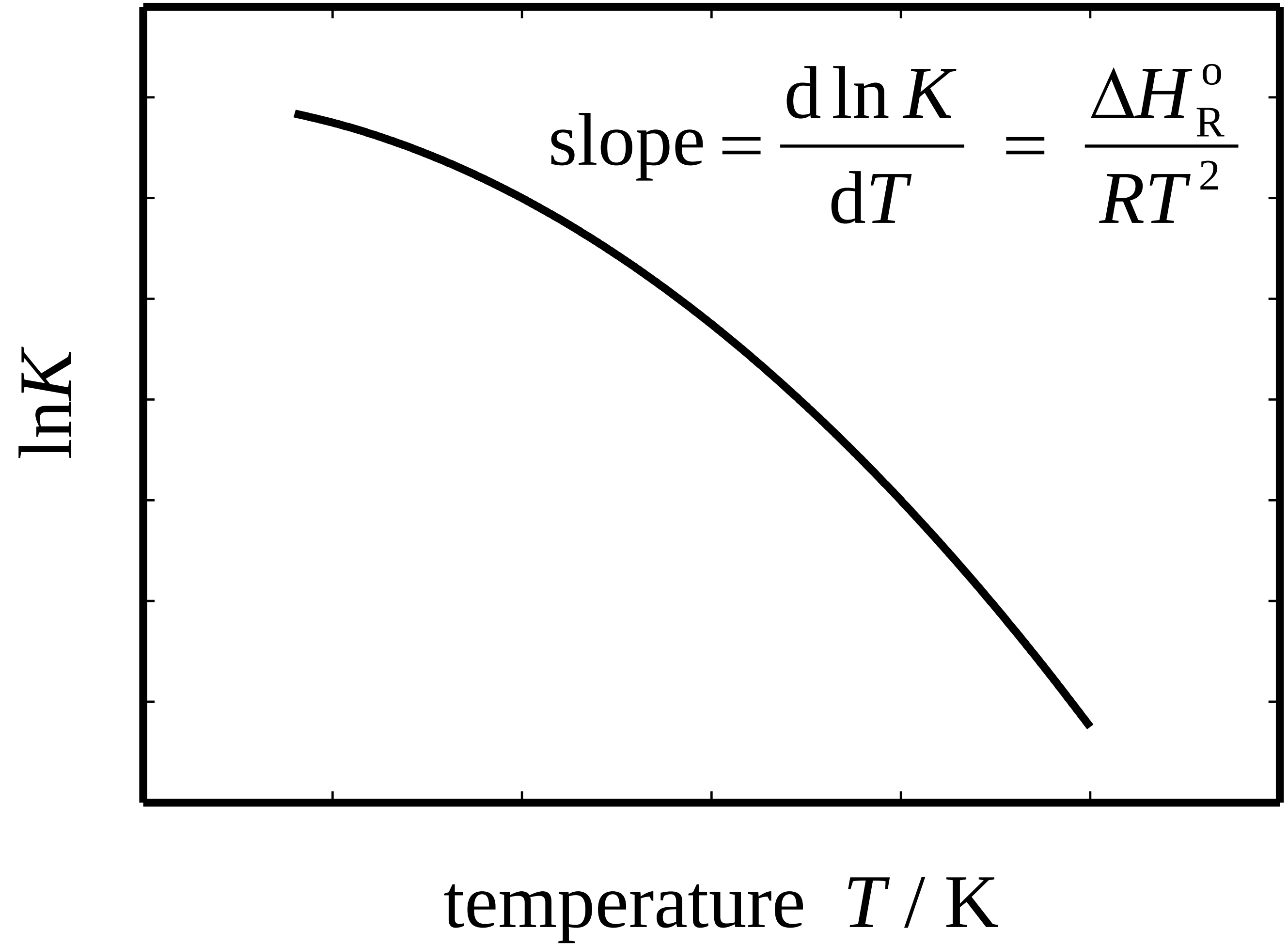
$$\boxed{\frac{\mathrm{d}\ln K}{\mathrm{d}T} = \frac{\Delta H_{\mathrm{R}}^{\mathrm{o}}}{RT^2}}$$

Significance?

(notice logarithmic relation)

- exothermic reactions ($\Delta H_{\mathrm{R}}^{\mathrm{o}} < 0$) are less favorable as T increases
- endothermic reactions ($\Delta H_{\mathrm{R}}^{\mathrm{o}} > 0$) are more favorable as T increases
- given K values at a single temperature (*e.g.*, 298.15 K), ΔH values from thermochemistry can be used to predict K at other temperatures
- chemical equilibrium constants measured at different temperatures can be used to calculate $\Delta H_{\mathrm{R}}^{\mathrm{o}}$ ***without thermochemistry***

ln*K* Plotted Against the Temperature
(curved)



$$\text{slope} = \frac{\mathrm{d}\ln K}{\mathrm{d}T} = \frac{\Delta H^{\mathrm{o}}_{\mathrm{R}}}{RT^2}$$

Better: For a Linear Plot, Use

$$\frac{\mathrm{d}\frac{1}{T}}{\mathrm{d}T} = -\frac{1}{T^2}$$

and

$$\mathrm{d}\frac{1}{T} = -\frac{\mathrm{d}T}{T^2}$$

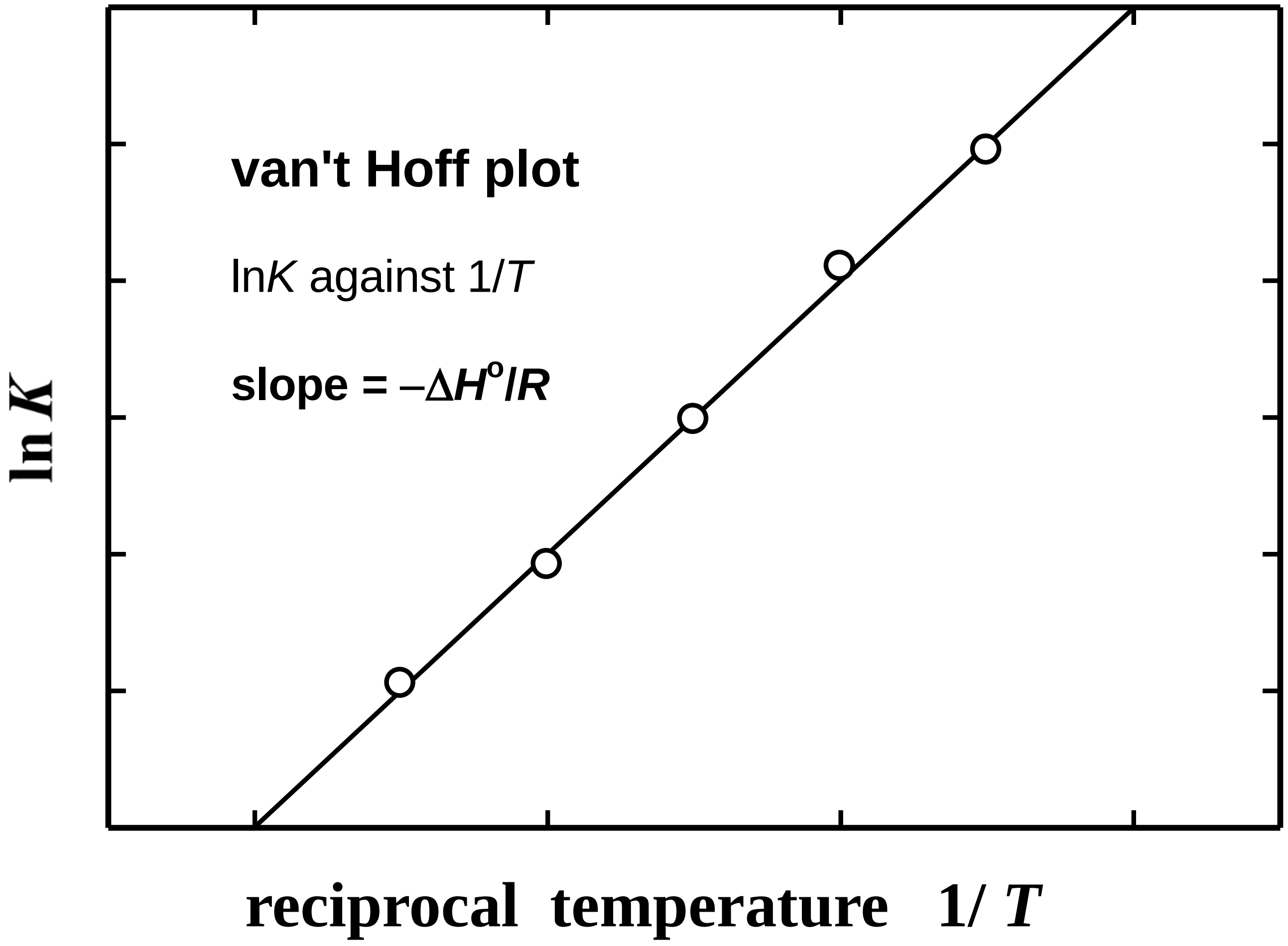
to transform

$$\frac{\mathrm{d}\ln K}{\mathrm{d}T} = \frac{\Delta H_\mathrm{R}^\mathrm{o}}{RT^2}$$

to the van't Hoff equation

$$\boxed{\frac{\mathrm{d}\ln K}{\mathrm{d}\frac{1}{T}} = -\frac{\Delta H_\mathrm{R}^\mathrm{o}}{R}}$$

van’t Hoff Plot. <u>Almost Linear</u> Slope $-\Delta H^o/R$



van't Hoff Calculations: ln*K* as a Function of Temperature

$$\mathrm{d}\ln K = -\frac{\Delta H_{\mathrm{R}}^{\mathrm{o}}}{R}\,\mathrm{d}\left(\frac{1}{T}\right)$$

$$\int_{\ln K(T_1)}^{\ln K(T_2)} \mathrm{d}\ln K = -\int_{1/T_1}^{1/T_2} \frac{\Delta H_{\mathrm{R}}^{\mathrm{o}}}{R}\,\mathrm{d}\left(\frac{1}{T}\right)$$

If $\Delta H_{\mathrm{R}}{}^{\mathrm{o}}$ is constant from T_1 to T_2 :

(a good approximation for small temperature intervals)

$$\boxed{\ln K(T_2) - \ln K(T_1) = -\frac{\Delta H_{\mathrm{R}}^{\mathrm{o}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)}$$

Section 6.11 Chemical Reactions Involving Gases and Pure Solids or Pure Liquids

“Heterogenous” (Multiphase) Equilibria

Equilibrium-constant expressions contain the pressures of reacting gases, but not pressure terms for solids or liquids.

Example: Decomposition of solid calcium carbonate.*

$$\mathbf{CaCO_3(s) \rightarrow CaO(s) + CO_2(g)}$$

$$K = p_{CO2}/p^{o}$$

Are $CaCO_3$(s) and CaO(s) ignored?

*Why is this a “billion-dollar” reaction?

Effect of Pressure on the Gibbs Energy

From $\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p$, get

$$\left(\frac{\partial G}{\partial p}\right)_T = V \qquad \text{(and } V/n = V_\mathrm{m} \text{ per mole)}$$

At 298 K and 1 bar, the molar volume of a gas is about 25 L, but typically less than 0.1 L for solids and liquids.

Useful result:

$$\left(\frac{\partial G_\mathrm{m}}{\partial p}\right)_T$$ is negligibly small for solids and liquids
(but not for gases)

$$\mathbf{CaCO_3(s) \;\rightarrow\; CaO(s) \;+\; CO_2(g)}$$

$$K = p_{\mathrm{CO_2}} / p^{\mathrm{o}}$$

Only CO_2? $CaCO_3$ and CaO are ignored ? *No!*

at equilibrium:

$$G_{\mathrm{m}}(\mathrm{CaCO_3, s}) \;=\; G_{\mathrm{m}}(\mathrm{CaO, s}) \;+\; G_{\mathrm{m}}(\mathrm{CO_2, g})$$

≈ independent of pressure

$$G^{\mathrm{o}}_{\mathrm{m}}(\mathrm{CaCO_3, s}) \;=\; G^{\mathrm{o}}_{\mathrm{m}}(\mathrm{CaO, s}) \;+\; G^{\mathrm{o}}_{\mathrm{m}}(\mathrm{CO_2, g}) + RT\ln(p_{\mathrm{CO2}}/p^{\mathrm{o}})$$

$$\{G^{\mathrm{o}}_{\mathrm{m}}(\mathrm{CaCO_3, s}) - G^{\mathrm{o}}_{\mathrm{m}}(\mathrm{CaO, s}) - G^{\mathrm{o}}_{\mathrm{m}}(\mathrm{CO_2, g})\}/RT \;=\; \ln(p_{\mathrm{CO2}}/p^{\mathrm{o}})$$

$$-\Delta G_{\mathrm{R}}{}^{\mathrm{o}}/RT \;=\; \ln(p_{\mathrm{CO2}}/p^{\mathrm{o}})$$

$$K = \exp(-\Delta G_{\mathrm{R}}{}^{\mathrm{o}}/RT\,) \;=\; (p_{\mathrm{CO2}}/p^{\mathrm{o}})$$

⇒ $CaCO_3$(s) and CaO(s) are included in the standard $\Delta G_{\mathrm{R}}{}^{\mathrm{o}}$ value

Heterogenous Equilibrium

Example Solid ammonium hydrogen sulfide is placed in an evacuated flask at 25 °C. What is the total gas pressure* at equilibrium?

Data: $K = 0.108$ at 25 °C

	$NH_4HS(s)$	$\rightarrow$	$NH_3(g)$	$+$	$H_2S(g)$
initial pressure:			0		0
equilibrium pressure:			p_{NH3}		p_{H2S}

total equilibrium pressure $p = p_{\mathrm{NH3}} + p_{\mathrm{H2S}}$

from stoichiometry $p_{\mathrm{NH3}} = p_{\mathrm{H2S}} = p/2$

$$K_{\mathrm{p}} = (p_{\mathrm{NH3}}/p^{\mathrm{o}})\,(p_{\mathrm{H2S}}/p^{\mathrm{o}}) = (p/2p^{\mathrm{o}})\,(p/2p^{\mathrm{o}}) = 0.108$$

Solve for $p = (4 \times 0.108)^{1/2} =$ **0.657 bar**

*Why might it be important to know the decomposition pressure of NH_4HS?

Section 6.12 Equilibrium Constants in Terms of Molarities or Mole Fractions

Equilibrium Constants K_p for Ideal-Gas Reactions

$$a\,\mathrm{A(g)} \;+\; b\,\mathrm{B(g)} \;+ \ldots \;\longrightarrow\; c\,\mathrm{C(g)} \;+\; d\,\mathrm{D(g)} \;+ \ldots$$

$\nu_\mathrm{A} = -a \qquad \nu_\mathrm{B} = -b \qquad \nu_\mathrm{C} = +c \qquad \nu_\mathrm{D} = +d$

$$K = \frac{(p_\mathrm{C}/p^\circ)^c (p_\mathrm{D}/p^\circ)^d \;\cdots}{(p_\mathrm{A}/p^\circ)^a (p_\mathrm{B}/p^\circ)^b \;\cdots} = \left(\frac{p_\mathrm{A}}{p^\circ}\right)^{\nu\mathrm{A}} \left(\frac{p_\mathrm{B}}{p^\circ}\right)^{\nu\mathrm{B}} \left(\frac{p_\mathrm{C}}{p^\circ}\right)^{\nu\mathrm{C}} \left(\frac{p_\mathrm{D}}{p^\circ}\right)^{\nu\mathrm{D}} \cdots$$

using **equilibrium** partial pressures p_A, p_B, p_C, p_D, …

The terminology K_p (= K) is often used for equilibrium constants defined this way.

Equilibrium Constants K_c for Ideal-Gas Reactions

$$a\,\mathrm{A(g)} + b\,\mathrm{B(g)} + \ldots \longrightarrow c\,\mathrm{C(g)} + d\,\mathrm{D(g)} + \ldots$$

Chemists frequently use equilibrium constants in terms of molarity concentrations, c_i.

$$\begin{aligned}
K_p &= \left(\frac{p_\mathrm{A}}{p^\mathrm{o}}\right)^{\nu\mathrm{A}} \left(\frac{p_\mathrm{B}}{p^\mathrm{o}}\right)^{\nu\mathrm{B}} \left(\frac{p_\mathrm{C}}{p^\mathrm{o}}\right)^{\nu\mathrm{C}} \left(\frac{p_\mathrm{D}}{p^\mathrm{o}}\right)^{\nu\mathrm{D}} \cdots \\
&= \left(\frac{n_\mathrm{A}RT}{p^\mathrm{o}V}\right)^{\nu\mathrm{A}} \left(\frac{n_\mathrm{B}RT}{p^\mathrm{o}V}\right)^{\nu\mathrm{B}} \left(\frac{n_\mathrm{C}RT}{p^\mathrm{o}V}\right)^{\nu\mathrm{C}} \left(\frac{n_\mathrm{D}RT}{p^\mathrm{o}V}\right)^{\nu\mathrm{D}} \cdots \\
&= \left(\frac{n_\mathrm{A}}{Vc^\mathrm{o}}\,\frac{c^\mathrm{o}RT}{p^\mathrm{o}}\right)^{\nu\mathrm{A}} \left(\frac{n_\mathrm{B}}{Vc^\mathrm{o}}\,\frac{c^\mathrm{o}RT}{p^\mathrm{o}}\right)^{\nu\mathrm{B}} \left(\frac{n_\mathrm{C}}{Vc^\mathrm{o}}\,\frac{c^\mathrm{o}RT}{p^\mathrm{o}}\right)^{\nu\mathrm{C}} \left(\frac{n_\mathrm{D}}{Vc^\mathrm{o}}\,\frac{c^\mathrm{o}RT}{p^\mathrm{o}}\right)^{\nu\mathrm{D}} \cdots \\
&= \left(\frac{c_\mathrm{A}}{c^\mathrm{o}}\right)^{\nu\mathrm{A}} \left(\frac{c_\mathrm{B}}{c^\mathrm{o}}\right)^{\nu\mathrm{B}} \left(\frac{c_\mathrm{C}}{c^\mathrm{o}}\right)^{\nu\mathrm{C}} \left(\frac{c_\mathrm{D}}{c^\mathrm{o}}\right)^{\nu\mathrm{D}} \cdots \left(\frac{c^\mathrm{o}RT}{p^\mathrm{o}}\right)^{\nu\mathrm{A}+\nu\mathrm{B}+\nu\mathrm{C}+\nu\mathrm{D}+\,\cdots} \\
&= K_c \left(\frac{c^\mathrm{o}RT}{p^\mathrm{o}}\right)^{\nu\mathrm{A}+\nu\mathrm{B}+\nu\mathrm{C}+\nu\mathrm{D}+\,\cdots}
\end{aligned}$$

Equilibrium Constants K_c for Ideal-Gas Reactions

$$a\,\mathrm{A(g)} + b\,\mathrm{B(g)} + \ldots \longrightarrow c\,\mathrm{C(g)} + d\,\mathrm{D(g)} + \ldots$$

$$\boxed{K_p = K_c \left(\frac{c^{\mathrm{o}}RT}{p^{\mathrm{o}}}\right)^{\Delta n_g}}$$

$$\boxed{K_c = K_p \left(\frac{c^{\mathrm{o}}RT}{p^{\mathrm{o}}}\right)^{-\Delta n_g}}$$

$$\boxed{\Delta n_g = \nu_{\mathrm{A}} + \nu_{\mathrm{B}} + \nu_{\mathrm{C}} + \nu_{\mathrm{D}} + \cdots}$$

Example

$$2\,\mathrm{NO_2(g)} \rightarrow \mathrm{N_2O_4(g)}$$

$$K_c = K_p \left(\frac{c^{\mathrm{o}}RT}{p^{\mathrm{o}}}\right)^{+1} = K_p \frac{c^{\mathrm{o}}RT}{p^{\mathrm{o}}}$$

$$\Delta n_g = -1$$

Equilibrium Constants K_x for Ideal-Gas Reactions

$$a\,\mathrm{A(g)} \;+\; b\,\mathrm{B(g)} \;+ \ldots \;\longrightarrow\; c\,\mathrm{C(g)} \;+\; d\,\mathrm{D(g)} \;+ \ldots$$

Can also use equilibrium constants K_x in of gas mole fractions x_i.

$$\begin{aligned}
K_p &= \left(\frac{p_\mathrm{A}}{p^\mathrm{o}}\right)^{\nu\mathrm{A}} \left(\frac{p_\mathrm{B}}{p^\mathrm{o}}\right)^{\nu\mathrm{B}} \left(\frac{p_\mathrm{C}}{p^\mathrm{o}}\right)^{\nu\mathrm{C}} \left(\frac{p_\mathrm{D}}{p^\mathrm{o}}\right)^{\nu\mathrm{D}} \cdots \\
&= \left(\frac{p_\mathrm{A}}{p}\,\frac{p}{p^\mathrm{o}}\right)^{\nu\mathrm{A}} \left(\frac{p_\mathrm{B}}{p^\mathrm{o}}\,\frac{p}{p^\mathrm{o}}\right)^{\nu\mathrm{B}} \left(\frac{p_\mathrm{C}}{p^\mathrm{o}}\,\frac{p}{p^\mathrm{o}}\right)^{\nu\mathrm{C}} \left(\frac{p_\mathrm{D}}{p^\mathrm{o}}\,\frac{p}{p^\mathrm{o}}\right)^{\nu\mathrm{D}} \cdots \\
&= \left(\frac{p_\mathrm{A}}{p}\right)^{\nu\mathrm{A}} \left(\frac{p_\mathrm{B}}{p^\mathrm{o}}\right)^{\nu\mathrm{B}} \left(\frac{p_\mathrm{C}}{p^\mathrm{o}}\right)^{\nu\mathrm{C}} \left(\frac{p_\mathrm{D}}{p^\mathrm{o}}\right)^{\nu\mathrm{D}} \cdots \left(\frac{p}{p^\mathrm{o}}\right)^{\nu\mathrm{A}+\nu\mathrm{B}+\nu\mathrm{C}+\nu\mathrm{D}+\,\cdots} \\
&= x_\mathrm{A}^{\nu\mathrm{A}}\; x_\mathrm{B}^{\nu\mathrm{B}}\; x_\mathrm{C}^{\nu\mathrm{C}}\; x_\mathrm{D}^{\nu\mathrm{D}} \;\cdots \left(\frac{p}{p^\mathrm{o}}\right)^{\nu\mathrm{A}+\nu\mathrm{B}+\nu\mathrm{C}+\nu\mathrm{D}+\,\cdots} \\
&= K_x \left(\frac{p}{p^\mathrm{o}}\right)^{\nu\mathrm{A}+\nu\mathrm{B}+\nu\mathrm{C}+\nu\mathrm{D}+\,\cdots}
\end{aligned}$$

Section 6.13 Temperature and Pressure Dependence of the Extent of Reaction

See Sections 6.8 to 6.11

Section 6.14 Ammonia Synthesis – a Case Study

Optional reading assignment.

Section 6.15 U, H, C_V, C_p in Terms of Measurable Quantities

Done.

Section 6.16 ΔG for Unfolding RNA Molecules

Optional reading assignment.

Section 6.17 The Role of Mixing in Chemical Reaction Equilibrium

$$\boxed{2\,\mathrm{NO_2(g)} \rightarrow \mathrm{N_2O_4(g)}}$$

Step I. Chemical Reaction (Only)

React 1 mol pure N_2 and 2 mol pure O_2 to form:

$2(1 - \varepsilon)$ mol pure NO_2 + ε mol pure N_2O_4

$$\Delta G_{\mathrm{I(React)}} = 2(1 - \varepsilon)\Delta G_{\mathrm{fm}}{}^{\mathrm{o}}(\mathrm{NO_2, g}) + \varepsilon\,\Delta G_{\mathrm{fm}}{}^{\mathrm{o}}(\mathrm{N_2O_4, g})$$

$$= 2\Delta G_{\mathrm{fm}}{}^{\mathrm{o}}(\mathrm{NO_2, g}) + \varepsilon\,[-2\Delta G_{\mathrm{fm}}{}^{\mathrm{o}}(\mathrm{NO_2, g}) + \Delta G_{\mathrm{fm}}{}^{\mathrm{o}}(\mathrm{N_2O_4, g})]$$

$$\Delta G_{\mathrm{I(React)}} = 2\Delta G_{\mathrm{fm}}{}^{\mathrm{o}}(\mathrm{NO_2, g}) + \varepsilon\,\Delta G_{\mathrm{R}}{}^{\mathrm{o}}$$

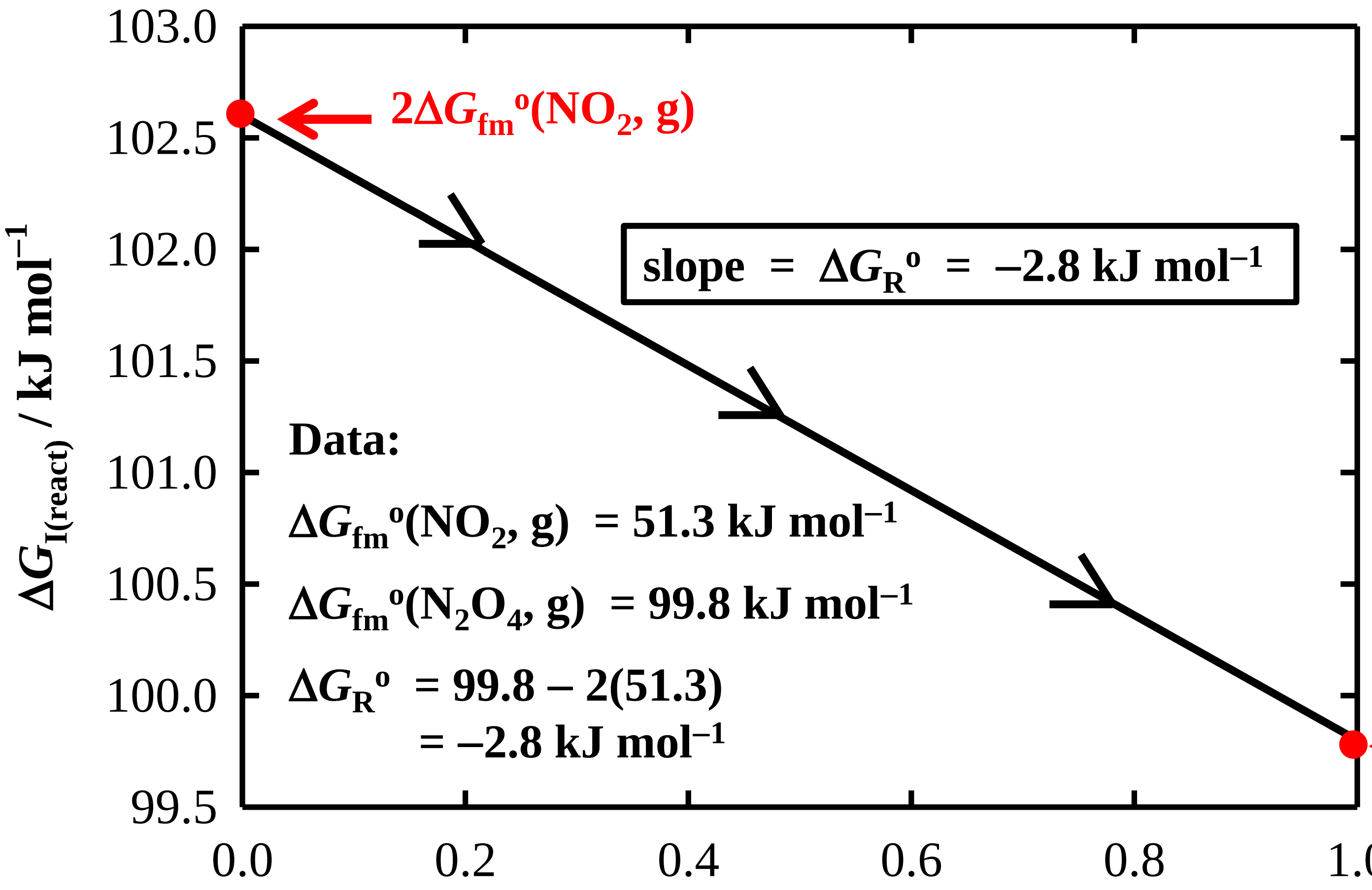
$$\boxed{\Delta G_{\mathrm{I(React)}} = 2\Delta G_{\mathrm{fm}}{}^{\mathrm{o}}(\mathrm{NO_2, g}) + \varepsilon\,\Delta G_{\mathrm{R}}{}^{\mathrm{o}}}$$

ε = extent of reaction

$0 \le \varepsilon \le 1$

$$\boxed{2\,NO_2(g) \rightarrow N_2O_4(g)}$$

Step I. Chemical Reaction (Only)



$2\Delta G_{fm}{}^{o}(NO_2, g)$

$\Delta G_{fm}{}^{o}(N_2O_4, g)$

slope = $\Delta G_R{}^{o}$ = –2.8 kJ mol^{-1}

Data:

$\Delta G_{fm}{}^{o}(NO_2, g)$ = 51.3 kJ mol^{-1}

$\Delta G_{fm}{}^{o}(N_2O_4, g)$ = 99.8 kJ mol^{-1}

$\Delta G_R{}^{o}$ = 99.8 – 2(51.3)
= –2.8 kJ mol^{-1}

pure NO_2

pure N_2O_4

No minimum?

Reaction goes to 100 % completion (ε = 1)?

$$2\ NO_2(g) \quad \rightarrow \quad N_2O_4(g)$$

Step II. Mixing (Only)

Mix: **$2(1-\varepsilon)$ mol pure NO_2 + ε mol pure N_2O_4**

From Section 6.6:

$$\Delta G_{\text{II(mix)}} = n_{\text{NO2}}RT\ln x_{\text{NO2}} + n_{\text{N2O4}}RT\ln x_{\text{N2O4}}$$

The mole fractions are

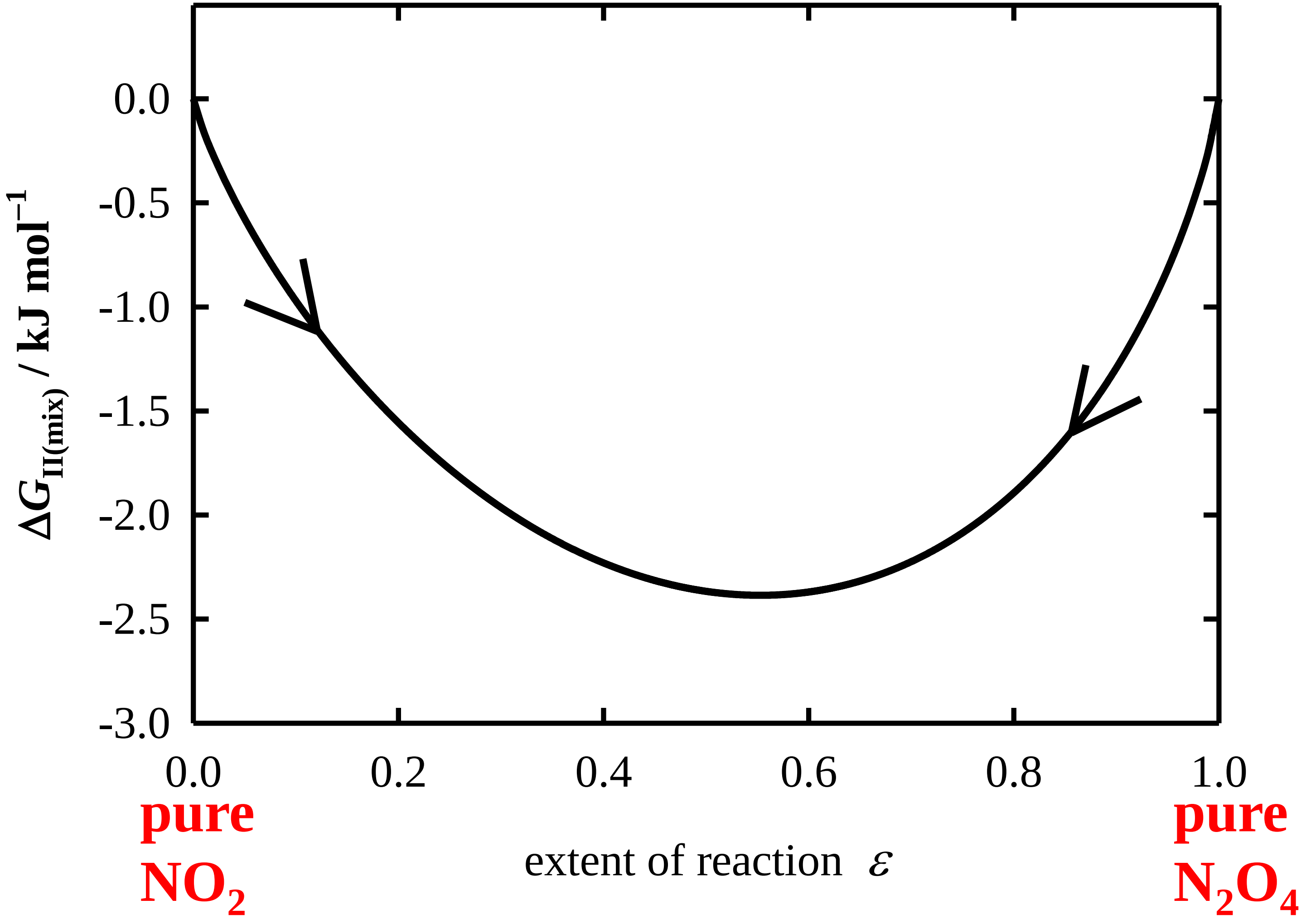
$$x_{\text{NO2}} = \frac{n_{\text{NO2}}}{n_{\text{NO2}}+n_{\text{N2O4}}} = \frac{2(1-\varepsilon)}{2(1-\varepsilon)+\varepsilon} = \frac{2(1-\varepsilon)}{2-\varepsilon}$$

$$x_{\text{N2O4}} = \frac{n_{\text{N2O4}}}{n_{\text{NO2}}+n_{\text{N2O4}}} = \frac{\varepsilon}{2(1-\varepsilon)+\varepsilon} = \frac{\varepsilon}{2-\varepsilon}$$

$$\boxed{\Delta G_{\text{II(mix)}} = 2(1-\varepsilon)RT\ln\left(\frac{2-2\varepsilon}{2-\varepsilon}\right) + \varepsilon RT\ln\left(\frac{\varepsilon}{2-\varepsilon}\right)}$$

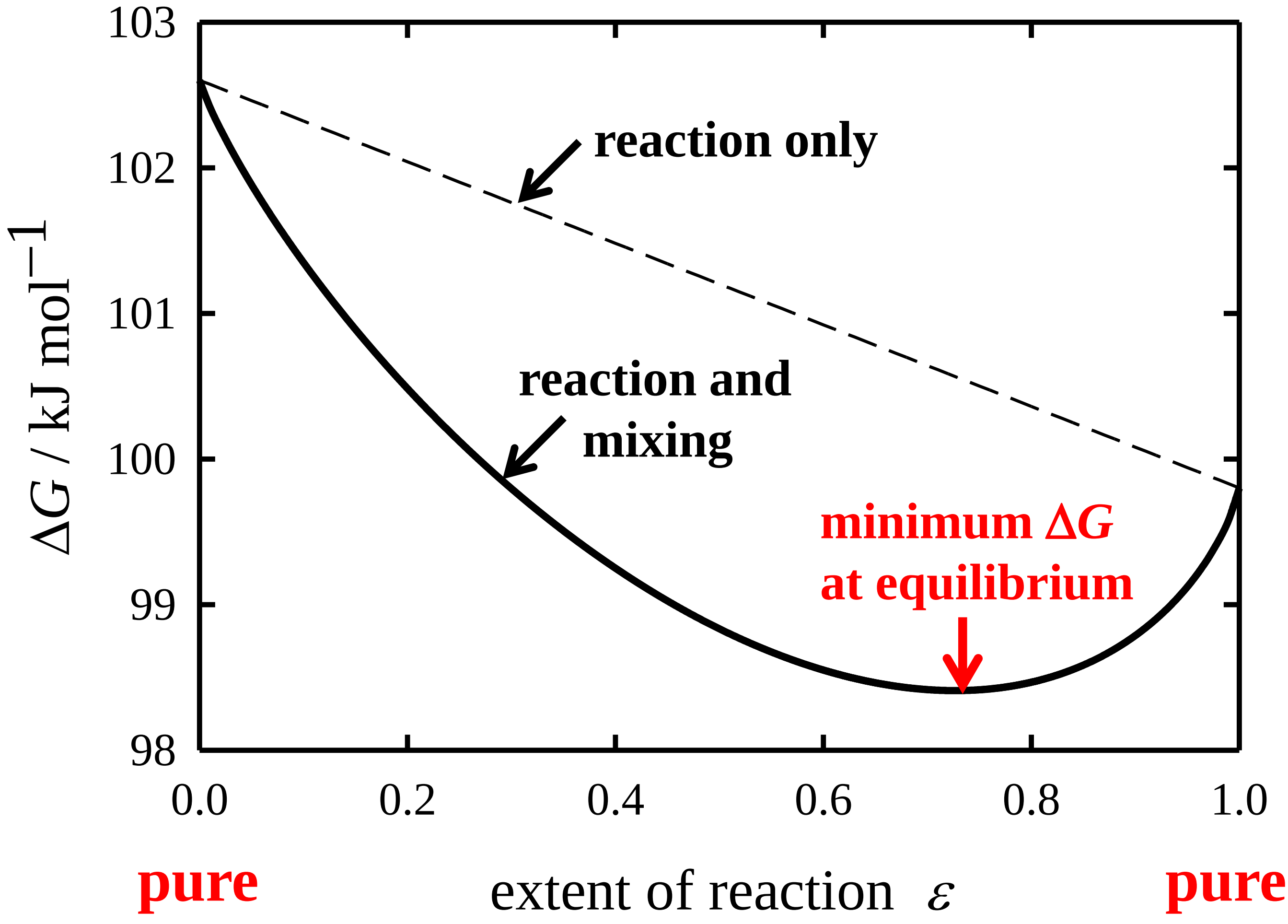
$2\ NO_2(g) \rightarrow N_2O_4(g)$

Step II. Mixing (Only)



$$2\,NO_2(g) \rightarrow N_2O_4(g)$$

Overall: React *and* Mix $\Delta G = \Delta G_{I(react)} + \Delta G_{II(mix)}$



pure NO_2

pure N_2O_4

Significance

(often overlooked)

Physical mixing of reactants and products is required for the equilibrium of chemical reactions.

$$2\,NO_2(g) \rightarrow N_2O_4(g)$$

Summary

React 1 mol pure N_2 and 2 mol pure O_2 to form

$2(1-\varepsilon)$ mol NO_2 mixed with ε mol N_2O_4

$$\begin{aligned}\Delta G &= \Delta G_{\mathrm{I(react)}} + \Delta G_{\mathrm{II(mix)}} \\ &= 2\Delta G_{\mathrm{fm}}{}^{\mathrm{o}}(\mathrm{NO_2}) + \varepsilon\,\Delta G_{\mathrm{R}}{}^{\mathrm{o}} \\ &\qquad + 2(1-\varepsilon)RT\ln\left(\frac{2-2\varepsilon}{2-\varepsilon}\right) + \varepsilon RT\ln\left(\frac{\varepsilon}{2-\varepsilon}\right)\end{aligned}$$

Exercise Show that the minimum in ΔG as a function of ε gives the same equilibrium composition calculated using

$$K = \frac{p_{\mathrm{N2O4}}/p^{\mathrm{o}}}{(p_{\mathrm{NO2}}/p^{\mathrm{o}})^2}$$

Practical Considerations

Thermodynamic equilibrium constants such as

$$K_p = \frac{p_{\mathrm{N2O4}} / p^{\mathrm{o}}}{(p_{\mathrm{NO2}} / p^{\mathrm{o}})^2} \qquad K_c = \frac{c_{\mathrm{N2O4}} / c^{\mathrm{o}}}{(c_{\mathrm{NO2}} / c^{\mathrm{o}})^2}$$

for the reaction **$2\ NO_2(g) \rightarrow N_2O_4(g)$** are dimensionless pure numbers (no units), by definition.

In practice, for convenience, $p^{\mathrm{o}} = 1$ bar and $c^{\mathrm{o}} = 1$ mol L^{-1} are frequently omitted, to give

$$K_p = \frac{p_{\mathrm{N2O4}}}{(p_{\mathrm{NO2}})^2} \qquad K_c = \frac{c_{\mathrm{N2O4}}}{(c_{\mathrm{NO2}})^2}$$

No numerical errors are made, if p^{o} and c^{o} are unity.

!!! Warning !!!

Equilibrium constant expressions such as

$$K_p = \frac{p_{\mathrm{N2O4}} / p^{\mathrm{o}}}{(p_{\mathrm{NO2}} / p^{\mathrm{o}})^2}$$

developed in this Chapter **for ideal gases** are accurate for real gases only in the limit $p \rightarrow 0$.

For **real gases** (the subject of the next Chapter), corrections for nonideal behavior are made using “**fugacity coefficients**”, such as γ_{N2O4} and γ_{NO2}.

$$K_p = \frac{\gamma_{\mathrm{N2O4}} p_{\mathrm{N2O4}} / p^{\mathrm{o}}}{(\gamma_{\mathrm{NO2}} p_{\mathrm{NO2}} / p^{\mathrm{o}})^2}$$