

Reaction  $\Delta H_{\text{rxn}}^{\circ}$ ,  $\Delta G_{\text{rxn}}^{\circ}$

Key thermodynamic quantities for reactions:  $\Delta H$ ,  $\Delta G$   
Thermochemical tables (such as NIST) list

$\Delta H_{\text{form}}^{\circ}$   $S^{\circ}$  at  $T=298$  for many  
compounds at specified states (gas, liq. etc),  $P=1$  bar.

Formation reaction of  $\text{H}_2\text{O}$ :  $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g})$   
or  $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{l}) \rightarrow \text{H}_2\text{O}(\text{l})$

(g) (l) or (s) specify the "standard states" assumed  
when reporting  $\Delta H_{\text{form}}^{\circ}$ ,  $S^{\circ}$ .

see  
WebBook

For  $\text{H}_2\text{O}(\text{g})$ :  $\Delta H_{\text{form}}^{\circ} = -241.83 \text{ kJ/mol}$   
 $T = 298 \text{ K}$   
 $P = 1 \text{ bar}$   $S^{\circ} = 188.84 \text{ J/(mol K)}$

Note that  $\text{H}_2\text{O}(\text{g})$  at  $T=298 \text{ K}$  and  $P=1 \text{ bar}$   
is a hypothetical, ideal-gas state - real  
water vapor above  $P^{\text{vap}} = 0.032 \text{ bar}$  is metastable

For  $\text{H}_2\text{O}(\text{l})$ :  $\Delta H_{\text{form}}^{\circ} = -285.83 \text{ kJ/mol}$   
 $T = 298 \text{ K}$   
 $P = 1 \text{ bar}$   $S^{\circ} = 69.95 \text{ J/(mol K)}$

To obtain  $\Delta G_{\text{rxn}}^{\circ}$  for the two formation reactions,  
we need the entropies of  $\text{H}_2(\text{g})$ ,  $\text{O}_2(\text{g})$

Since the NIST webbook lists absolute (3rd Law) entropies,  $S^\circ(T=298\text{ K})$  is not zero for the elements.

$$\underline{S}^\circ(\text{H}_2 \text{ gas}, \overset{1\text{ bar}}{298\text{ K}}) = 130.68 \text{ J/mol K}$$

$$\underline{S}^\circ(\text{O}_2 \text{ gas}, \overset{1\text{ bar}}{298\text{ K}}) = 205.15 \text{ J/mol K}$$

$$\begin{aligned} \Delta \underline{G}_{\text{form}}^\circ(\text{H}_2\text{O}(g)) &= \Delta \underline{H}_{\text{f.m}}^\circ - T \Delta \underline{S}_{\text{form}}^\circ = \\ &= \left[ -241.83 - \frac{298}{1000} \cdot \left( 188.84 - \frac{130.68}{1} - \frac{205.15}{2} \right) \right] \frac{\text{kJ}}{\text{mol}} = \\ &\quad \text{to convert J to kJ} \quad = -228.59 \frac{\text{kJ}}{\text{mol}} \end{aligned}$$

$$\Delta \underline{G}_{\text{form}}^\circ(\text{H}_2\text{O}(l)) = -237.14 \frac{\text{kJ}}{\text{mol}}$$

For the "reaction"  $\text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{O}(g)$

$$\Delta \underline{H}_{\text{rxn}}^\circ = -241.83 + 285.83 = \underline{44.00} \frac{\text{kJ}}{\text{mol}}$$

same as  $\Delta \underline{H}_{\text{vap}}^\circ$

$$\Delta \underline{G}_{\text{rxn}}^\circ = -228.59 + 237.14 = 8.55 \frac{\text{kJ}}{\text{mol}}$$

$$\begin{aligned} \text{Equilibrium constant } k(T=298\text{ K}) &= \exp\left(\frac{-8550 \frac{\text{J}}{\text{mol}}}{8314 \cdot 298 \frac{\text{J}}{\text{mol}}}\right) \\ \Rightarrow k(T) = 0.0317 &= \frac{f(\text{H}_2\text{O}(g))}{f(\text{H}_2\text{O}(l))} \end{aligned}$$

But... we expect  $f(\text{liq}) = f(\text{gas})$  at coexistence!

Resolution: For phase equilibrium calculations (Chapters 8-9), we have a common reference state for liquid + gas, namely the gas at  $P=1$  bar gets  $f^\circ=1$  bar

For reactions (Chapter 10) the reference states are different:  $f^\circ=1$  bar for the liquid at 1 bar; different ref. state for gas (the gas at 1 bar)

The fugacity of the liquid at the vapor pressure is:  $f(P^{\text{sat}}) \approx f(P^\circ)$  in both cases

(a) Liquid ref. state  $f_L(P^{\text{sat}}) = f_L(P^\circ) = 1$  bar

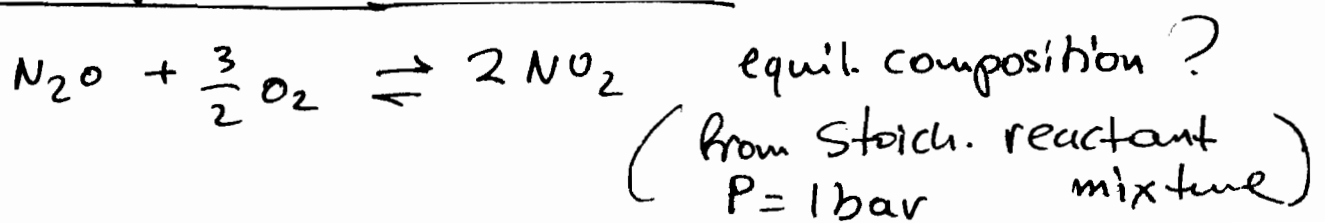
$$\text{So that } \frac{f_G}{f_L} = 0.0317 \Rightarrow f_G = 0.0317 \text{ bar} = P^{\text{sat}}$$

(b) Gas ref. state  $f_L(P^{\text{sat}}) = P^{\text{sat}} = f_G$

In general, at equilibrium for

$$X(l) \rightleftharpoons X(g) \quad P^{\text{sat}} = \exp\left(-\frac{\Delta G_{\text{rxn}}^\circ}{RT}\right)$$

Example 10.1  $\text{N}_2\text{O}$  oxidation



From the EwebBook  $\Delta G_{rxn}^{\circ}(\tau=298K) = -1.66 \frac{kJ}{mol}$

$$K(\tau=298K) = \exp\left[\frac{-\Delta G_{rxn}^{\circ}}{RT}\right] = 1.96$$

"Standard" Table

Species	Amount
$N_2O$	$1-\xi$
$O_2$	$1.5(1-\xi)$
$NO_2$	$2\xi$
<u>Total</u>	<u><math>2.5-0.5\xi</math></u>

$$K = \frac{P_{NO_2}^2}{P_{N_2O} P_{O_2}^{1.5}} = \frac{y_{NO_2}^2}{y_{N_2O} y_{O_2}^{1.5} P^{0.5}}$$

$$\Rightarrow \frac{(2\xi)^2 (2.5-0.5\xi)^{0.5}}{(1-\xi)(1.5-1.5\xi)^{1.5}} = 1.96$$

Non-linear equ., 1 unknown

Excel's goal seek  $\rightarrow \xi = 0.404 \text{ mol}$

Example 10.2 - Approx. Calculations

For NO oxidation  $NO + \frac{1}{2}O_2 \rightleftharpoons NO_2$   $\Delta G_{rxn}^{\circ} = -35.35 \frac{kJ}{mol}$

Equilibrium composition from equimolar NO/O<sub>2</sub> mixture?

$$K(\tau) = \exp\left(-\frac{\Delta G_{rxn}^{\circ}}{RT}\right) = 1.6 \cdot 10^6 \gg 1$$

almost complete conversion  
 $\xi \approx 1$

Species	Amount
NO	$1-\xi \approx 0 \ll 1$
O <sub>2</sub>	$1-0.5\xi \approx 0.5$
NO <sub>2</sub>	<u><math>\xi \approx 1</math></u>
<u>Total</u>	<u><math>2-0.5\xi \approx 1.5</math></u>

$$K = \frac{P_{NO_2}}{P_{NO} P_{O_2}^{0.5}} = \frac{y_{NO_2}}{y_{NO} y_{O_2}^{0.5} P} = \frac{3 \cdot (2-0.5\xi)^{0.5}}{(1-\xi)(1-0.5\xi)^{0.5}} = \frac{1 \cdot \sqrt{1.5}}{\delta \sqrt{0.5}}$$

$$\Rightarrow \delta = 1.1 \cdot 10^{-6}$$