

February 11, 2002

• Exam #1

• Wednesday, 2/13, 7 pm, B104 Angell

• Problem Session

• Today, 3-4 pm, A531 Cook

• Problem suggestions?

• Quiz *Post Mortem*

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There are many paths to  $\Delta G^{\circ}_{\text{rxn}}$

➤ If  $\Delta G^{\circ}_f$  values are available for products and reactants:

$$\mathbf{DG^{\circ} = \sum DG^{\circ}_f \text{ (products)} - \sum DG^{\circ}_f \text{ (reactants)}}$$

➤ If  $\Delta H^{\circ}_f$  and  $S^{\circ}$  values are available for products and reactants:

• Calculate  $\Delta H^{\circ}_{\text{rxn}}$  and  $\Delta S^{\circ}_{\text{rxn}}$  values

$$\mathbf{DG^{\circ}_{\text{rxn}} = \Delta H^{\circ}_{\text{rxn}} - T \Delta S^{\circ}_{\text{rxn}}}$$

➤ Or, use a combination of both methods!

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## Limits to the utility of $\Delta G^{\circ}_{\text{rxn}}$

- $\Delta G^{\circ}_{\text{rxn}}$  predicts reaction spontaneity only when products and reactants are in their *standard states*
- How does  $\Delta G$  vary with:
  - Pressure (*for gases*)
  - Concentration (*for solutions*)
  - Temperature

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## Effect of Pressure Change

What happens to *free energy* of a **gas** when we change its pressure?

$$\Delta G = \Delta H - T\Delta S$$

$$G - G^{\circ} = 0 - [-nRT \ln(P/P^{\circ})]$$

Independent  
of pressure

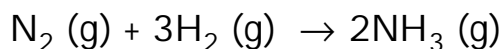
It can be derived!

$$G = G^{\circ} + nRT \ln(P/P^{\circ})$$

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## Now, Apply to a Reaction

Let's make some ammonia:



For 1 mol of each compound, we can write:

$$G_{\text{NH}_3} = G_{\text{NH}_3}^0 + RT \ln(P_{\text{NH}_3}/P^0)$$

$$G_{\text{N}_2} = G_{\text{N}_2}^0 + RT \ln(P_{\text{N}_2}/P^0)$$

$$G_{\text{H}_2} = G_{\text{H}_2}^0 + RT \ln(P_{\text{H}_2}/P^0)$$

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## So, $\Delta G$ for the Reaction

Since we know:

$$\Delta G_{\text{rxn}} = \sum \Delta G_{\text{products}} - \sum \Delta G_{\text{reactants}}$$

Substituting:

$$\Delta G = 2G_{\text{NH}_3} - (G_{\text{N}_2} + 3G_{\text{H}_2})$$

Finally giving:

$$\Delta G = \Delta G^0 + RT \ln \left[ \frac{(P_{\text{NH}_3}/P^0)^2}{(P_{\text{N}_2}/P^0) (P_{\text{H}_2}/P^0)^3} \right]$$

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## Some Tweaking

### ➤ What is $P^0$ ?

- $P^0 = 1 \text{ atm}$  (pressure of a gas in its standard state)

- Numerically:

$$P_{\text{NH}_3} = \frac{P_{\text{NH}_3}}{P^0} \quad \text{Defined as the } \mathbf{ACTIVITY} \quad (= a_{\text{NH}_3})$$

So, now we can write:

$$\Delta G = \Delta G^0 + RT \ln Q$$

Where:

$$Q = \frac{(a_{\text{NH}_3})^2}{(a_{\text{N}_2}) (a_{\text{H}_2})^3}$$

← Reaction Quotient

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## The Reaction Quotient: In General

- For any reaction:



We can write:

$$Q = \frac{(a_C)^c}{(a_A)^a (a_B)^b}$$

Activity (a) is  
UNITLESS!

Where,  $a_x = \text{activity of species X}$

For gases:

$$a_x = \frac{P_x}{P^0} \quad P^0 = 1 \text{ atm}$$

For solutions:

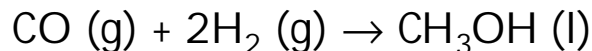
$$a_x = \frac{[X]}{[X]^0} \quad [X]^0 = 1 \text{ mol/L}$$

For *pure* cmpds:  $a_x = 1$

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## An Example

Calculate  $\Delta G$  for the following reaction:



Reaction Conditions:

$$T = 25. \text{ }^\circ\text{C} \quad P_{\text{CO}} = 5.0 \text{ atm} \quad P_{\text{H}_2} = 3.0 \text{ atm}$$

First: Find  $\Delta G^\circ$

$$\Delta G^\circ_{\text{rxn}} = \Delta G^\circ_f (\text{CH}_3\text{OH}) - [\Delta G^\circ_f (\text{CO}) + 2 \Delta G^\circ_f (\text{H}_2)]$$

$$\Delta G^\circ_{\text{rxn}} = (-166.35 \text{ kJ}) - [(-137.15 \text{ kJ}) + 2(0)]$$

$$\Delta G^\circ_{\text{rxn}} = \mathbf{-29.20 \text{ kJ}} \quad (= -2.920 \times 10^4 \text{ J})$$

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## On to $\Delta G$ !

Next: Find  $Q$

$$Q = \frac{a_{\text{CH}_3\text{OH}}}{(a_{\text{CO}}) (a_{\text{H}_2})^2} = \frac{1}{(5.0) (3.0)^2} = \mathbf{2.222 \times 10^{-2}}$$

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