

February 8, 2002

• Exam #1

- Wednesday, 2/13, 7 pm
- *Conflict? Email me today!*

• Exam Review Session

- Sunday, 4:30-6:00 pm, B203 Angell
- *Quiz Today!*
- No Office Hour today

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Balancing ΔH and ΔS

Remember: $DG = DH - TDS$

Two considerations:

- | | | |
|--|---|--|
| 1. Reactions seek a <i>minimum</i> in Enthalpy (ΔH) | - | + <i>spontaneous</i> |
| 2. Reactions seek a <i>maximum</i> in Entropy (ΔS) | + | - <i>nonspontaneous</i> |
| | - | - <i>spontaneous at low temps</i> |
| | + | + <i>spontaneous at high temps²</i> |

Calculating ΔG for a reaction

ΔG is a *state function*

- Treat like we do ΔH :

$$\Delta G^\circ = \sum \Delta G^\circ_f (\text{products}) - \sum \Delta G^\circ_f (\text{reactants})$$

At 1 atm
and 25°C

Standard Molar Free Energy of Formation:
for 1 mol of compound formed from elemental
constituents in their standard states

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The 3rd Law of Thermodynamics

We can obtain *absolute* values for Entropy because we have a set reference point:

- If $W = 1$ (only 1 microstate possible), then $S = 0$
- So, the 3rd Law says:

"At the *absolute zero of temperature*, the entropy of a perfect crystalline solid is **zero**."

So, we can tabulate **S°** (standard molar entropy) values (NOT ΔS°) - unlike H and E and G

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Calculating ΔS for a reaction

Entropy is *also* a state function:

$$\Delta S^\circ = \sum S^\circ (\text{products}) - \sum S^\circ (\text{reactants})$$

NOTE:

- There are no ΔS°_f values
- $S^\circ = 0$ for pure elements in their standard states

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Let's Get Quantitative!

Consider the following process:



We know:

$$\Delta H^\circ_{\text{vap}} = 38.00 \text{ kJ/mol}$$

$$\Delta S^\circ_{\text{vap}} = 112.9 \text{ J/K}$$

For most liquids:

$$\Delta S^\circ_{\text{vap}} \approx 88 \text{ J/K}$$

(Trouten's Rule)

At what temperature does methanol boil?

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The BP of Methanol

$$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ}$$

➤ At its BP (T_b), system is at *equilibrium* so $\Delta G^{\circ}=0$, and we can write:

$$0 = \Delta H_{\text{vap}}^{\circ} - T_b \Delta S_{\text{vap}}^{\circ}$$

Rearranging:

$$T_b = \Delta H_{\text{vap}}^{\circ} / \Delta S_{\text{vap}}^{\circ}$$

Substituting:

$$T_b = \frac{38.00 \times 10^3 \text{ J}}{112.9 \text{ J/K}} = 336.58 \text{ K} = \boxed{63.4 \text{ }^{\circ}\text{C}}$$

Actual BP of Methanol is . . . 64.96 °C