

Announcements – Lecture XXI – Thursday, Apr 19th

1. iClicker:



Pick any letter a-e

2. Quiz 9: Due Tuesday, April 24th.

3. Owl: All remaining Owls for Exam III are now up. The due dates for some are different, based on projected coverage. Just wanted to give you a heads up on the remaining Owls in this course as we quickly approach the end of the semester.



19.2 Calculating Entropy Change

Entropy Change in the Surroundings

$$\Delta S_{\text{UNIV}} = \Delta S_{\text{SYS}} + \Delta S_{\text{SURR}}$$



$$\Delta S_{\text{RXN}}^{\circ} = \sum S^{\circ}(\text{PRODUCTS}) - \sum S^{\circ}(\text{REACTANTS})$$

$$\Delta S_{\text{SURR}} = -\frac{q_{\text{SYS}}}{T}, \text{ @ constant pressure}$$

$$q_{\text{SYS}} = \Delta H_{\text{RXN}}$$

$$\Delta S_{\text{SURR}} = -\frac{\Delta H_{\text{RXN}}}{T}$$

$$\Delta S_{\text{UNIV}}^{\circ} = \Delta S_{\text{RXN}}^{\circ} - \frac{\Delta H_{\text{RXN}}}{T}$$

For a spontaneous process, $\Delta S_{\text{UNIV}} > 0$, and the reaction is thus product favored.

$$\Delta S_{\text{UNIV}} = \Delta S_{\text{RXN}} - \frac{\Delta H_{\text{RXN}}}{T}$$

	\downarrow Entropy	\downarrow Enthalpy
Battle !!	$\begin{cases} \Delta S > 0 \\ \Delta S < 0 \end{cases}$	$\begin{cases} \Delta H > 0 \\ \Delta H < 0 \end{cases}$
		$\begin{cases} \text{Endothermic} \\ \text{Exothermic} \end{cases}$

No Battle	$\begin{cases} 1^* \\ 2^* \end{cases}$	$\begin{cases} \Delta S > 0 \\ \Delta S < 0 \end{cases}$	$\begin{cases} \Delta H < 0 \\ \Delta H > 0 \end{cases}$	$\begin{cases} \text{Exothermic} \\ \text{Endothermic} \end{cases}$
-----------	--	--	--	---

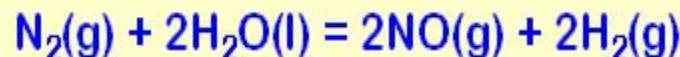
1*: ΔS_{UNIV} always > 0 , product favored.

2*: ΔS_{UNIV} always < 0 , reactant favored

19.2 Calculating Entropy Change

Entropy Change in the Surroundings

Consider the reaction



for which $\Delta H^\circ = 752.2 \text{ kJ}$ and $\Delta S^\circ = 351.6 \text{ J/K}$ at 298.15 K

- At 298.15 K is this reaction product or reactant favored?
- Is the answer to a) entropy or enthalpy driven?

$$\Delta S_{\text{UNIV.}}^\circ = \Delta S_{\text{sys}}^\circ + \Delta S_{\text{surr}}^\circ$$

$$\Delta S_{\text{sys}}^\circ = \Delta S_{\text{RXN}}^\circ = 351.6 \text{ J/K}$$

$$\begin{aligned}\Delta S_{\text{surr}}^\circ &= -\frac{\Delta H_{\text{RXN}}^\circ}{T} \\ &= -\frac{752.200 \text{ J}}{298.15 \text{ K}} = -2522.8 \text{ J/K}\end{aligned}$$

$$\begin{aligned}\Delta S_{\text{UNIV.}}^\circ &= 351.6 - 2522.8 \\ &= -2171.2 \text{ J/K}\end{aligned}$$

a) $\Delta S_{\text{UNIV.}}^\circ < 0$

Nonspontaneous, Reactant favored.

b) $\Delta S_{\text{sys}}^\circ > 0$

$\Delta S_{\text{surr}}^\circ < 0$... determined by ΔH°
Thus $\Delta S_{\text{UNIV.}}^\circ < 0$ is enthalpy driven.

NOTE: To reduce the impact of $\Delta S_{\text{surr}}^\circ$, then move away from standard temperature condition. Substantially increasing T would increase the effect of $\Delta S_{\text{surr}}^\circ$ and one could find a T in which $\Delta S_{\text{surr}}^\circ$ becomes > 0 .
This leads us to Gibbs FREE ENERGY.



19.3 Gibbs Free Energy

Gibbs Free Energy and Spontaneity

$$G = H - TS \quad G = \text{Gibbs Free Energy}$$
$$\Delta G = \Delta H - T\Delta S$$

$$\Delta S_{\text{UNIV}} = \Delta S_{\text{sys}} - \frac{\Delta H_{\text{sys}}}{T} > 0 \quad \text{for a spontaneous reaction.}$$

$$\Delta S_{\text{sys}} - \frac{\Delta H_{\text{sys}}}{T} > 0$$
$$T\Delta S_{\text{sys}} - \Delta H_{\text{sys}} > 0$$
$$-\underbrace{T\Delta S_{\text{sys}} + \Delta H_{\text{sys}}}_{\Delta G_{\text{sys}} < 0} < 0$$

$\Delta G_{\text{sys}} < 0$ for a spontaneous reaction.

$\Delta G < 0$: spontaneous in the forward direction.

$\Delta G > 0$: nonspontaneous in the forward direction ... conversely spontaneous in the reverse direction.

$\Delta G = 0$: at equilibrium

Gibbs Free Energy = the maximum work we can get from a reaction.



19.3 Gibbs Free Energy

Standard Gibbs Free Energy

Two main methods to determine $\Delta G^\circ_{\text{RXN}}$

1. $\Delta G^\circ_{\text{RXN}} = \Delta H^\circ_{\text{RXN}} - T\Delta S^\circ_{\text{RXN}}$

2. $\Delta G^\circ_{\text{RXN}} = \sum \Delta G_f^\circ (\text{products}) - \sum \Delta G_f^\circ (\text{reactants})$

Similar to ΔH_f° are tabulated for a host of molecules.

Just like ΔH_f° for an element in its standard stat,
the ΔG_f° for an element in its standard state is zero.

