

Announcements

To join clicker to class today (Clickers with LCD display joins automatically):

- Turn on the Clicker (the red LED comes on).
- Push “Join” button followed by “20” followed by the “Send” button (switches to flashing green LED if successful).

- Now hiring students to prep for general chemistry next Fall. See Ms. Hauer in HS-449

- Even if the weather is nice do not forget to wear appropriate clothing to lab! Calorimetry lab involves caustics that will eat your skin!
- Exam scores are posted. Let me know about problems by next Tuesday.

Review

- Enthalpies of Solution Contributions:
 - $\Delta H_{\text{ionic}} > 0$, $\Delta H_{\text{H-bonds}} > 0$, $\Delta H_{\text{ion-dipole}} < 0$
 - $\Delta H_{\text{ionic}} + \Delta H_{\text{H-bonds}} + \Delta H_{\text{ion-dipole}} = \Delta H_{\text{soln}}$
 - overall sign depends on balance.
- Entropy (S) quantifies disorder
 - $\Delta S_{\text{univ}} > 0$ for spontaneous processes
 - So even processes where $\Delta H > 0$ can occur if $\Delta S_{\text{univ}} > 0$

Second Law of Thermodynamics

- A process is spontaneous only if the entropy of the universe increases during the process.
- Entropy is times arrow, as time moves forward entropy increases.
- Spontaneous Process: $\Delta S_{\text{univ}} > 0$
- Non-spontaneous Process $\Delta S_{\text{univ}} < 0$
- $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$
- $\Delta S_{\text{sys}} \approx \Delta S^{\circ}_{\text{rxn}} = \sum S^{\circ}_{\text{prod}} - \sum S^{\circ}_{\text{reac}}$
 - $S(\text{perfect crystal at } 0 \text{ K}) = 0$
 - S° is relative to this perfect crystal
 - NOTE: $S^{\circ}(\text{element in standard state}) \neq 0$
- $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \Delta S_{\text{sys}} - \Delta H_{\text{sys}}/T$

ΔG – Free Energy

- $\Delta G_{\text{sys}} = -T\Delta S_{\text{univ}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}}$
- Interpretation of G:
 - $\Delta G < 0$ spontaneous
 - $\Delta G > 0$ nonspontaneous
 - $\Delta G = 0$ equilibrium
- Calculating ΔG
 - From ΔH_f° and S° . $\Delta G = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}}$

Calculating ΔG

- From ΔH_f° and S°

– Calculate ΔH° and ΔS° , then use in $\Delta G = \Delta H - T\Delta S$

– Ex: $\text{NaCl(s)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq}) + \text{H}_2\text{O(l)}$

$S^\circ(\text{J}\cdot\text{mol}^{-1}\text{K}^{-1})$ 72.1 70.0 59.0 56.5 70.0

$\Delta H_f^\circ(\text{kJ}\cdot\text{mol}^{-1})$ -411.2 -285.8 -240.1 -167.2 -285.8

$$\Delta S_{\text{rxn}}^\circ = 43.4 \text{ J/K}$$

$$\Delta H_{\text{rxn}}^\circ = 3.9 \text{ kJ}$$

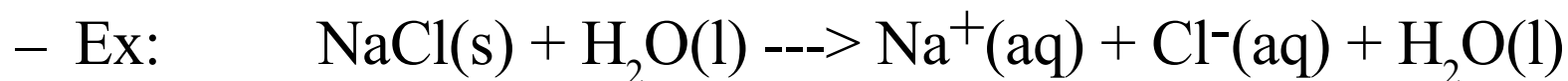
$$\Delta G_{\text{rxn}}^\circ = 3.9 \times 10^3 \text{ J} - (298 \text{ K})(43.4 \text{ J/K}) = -9.0 \times 10^3 \text{ J}$$

Calculating ΔG

- From ΔG_f°

- $\Delta G_{\text{RXN}}^\circ = \sum \Delta G_f^\circ(\text{prod}) - \sum \Delta G_f^\circ(\text{reac})$

- Note: like ΔH_f° , for elements in their standard state $\Delta G_f^\circ = 0$



$$\Delta G_f^\circ (\text{kJ}\cdot\text{mol}^{-1}) \quad -384.2 \quad -237.2 \quad -261.9 \quad -131.2 \quad -237.2$$

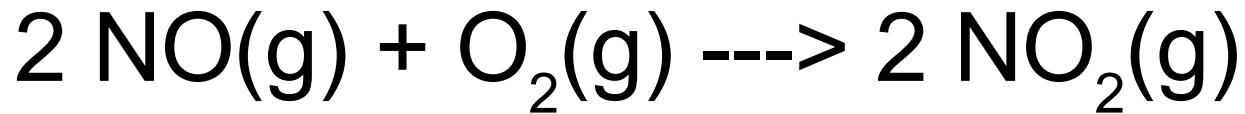
$$\Delta G_{\text{RXN}}^\circ = (1\text{mol Cl}^-)(-131.2 \text{ kJ/mol}) + (1\text{mol Na}^+)(-261.9 \text{ kJ/mol}) \\ - (1\text{mol NaCl})(-384.2 \text{ kJ/mol}) = -8.9 \text{ kJ}$$

Kinetics

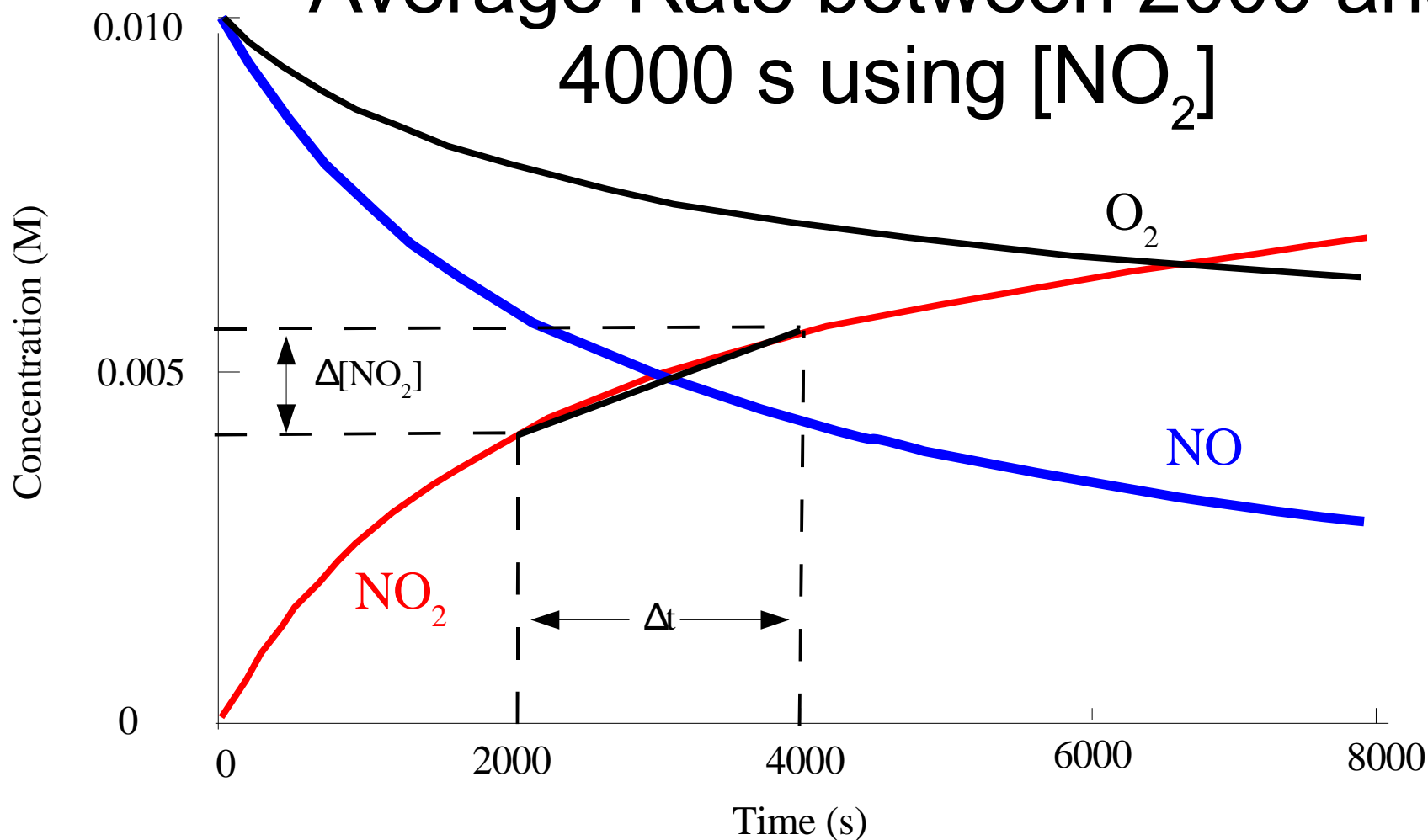
- Reaction Rates
- Concentration effects
 - reaction order
 - rate constant
 - rate laws
- Determining rate laws (initial rate method)
- Temperature effects
 - activation energy
 - transition state
 - Arrhenius equation
- Catalysis
 - Homogeneous
 - heterogeneous

Reaction Rates

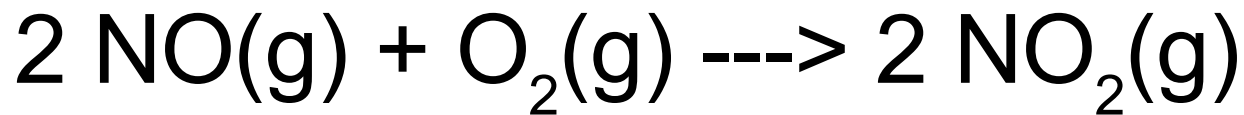
- Reaction Rates. Example: $2 \text{NO} + \text{O}_2 \longrightarrow 2 \text{NO}_2$
 - Rates of change for each species:
 - $\Delta[\text{NO}]/\Delta t$ • $\Delta[\text{O}_2]/\Delta t$ • $\Delta[\text{NO}_2]/\Delta t$
 - Note: $(1/2)\Delta[\text{NO}]/\Delta t = \Delta[\text{O}_2]/\Delta t = (-1/2)\Delta[\text{NO}_2]/\Delta t$
 - Formal rate of reaction:
 - $R = |(1/\text{stoichometric coefficient})\Delta[X]/\Delta t|$, $X =$ any species in the reaction.
 - Example: $R = -(1/2)\Delta[\text{NO}]/\Delta t = -\Delta[\text{O}_2]/\Delta t = (1/2)\Delta[\text{NO}_2]/\Delta t$



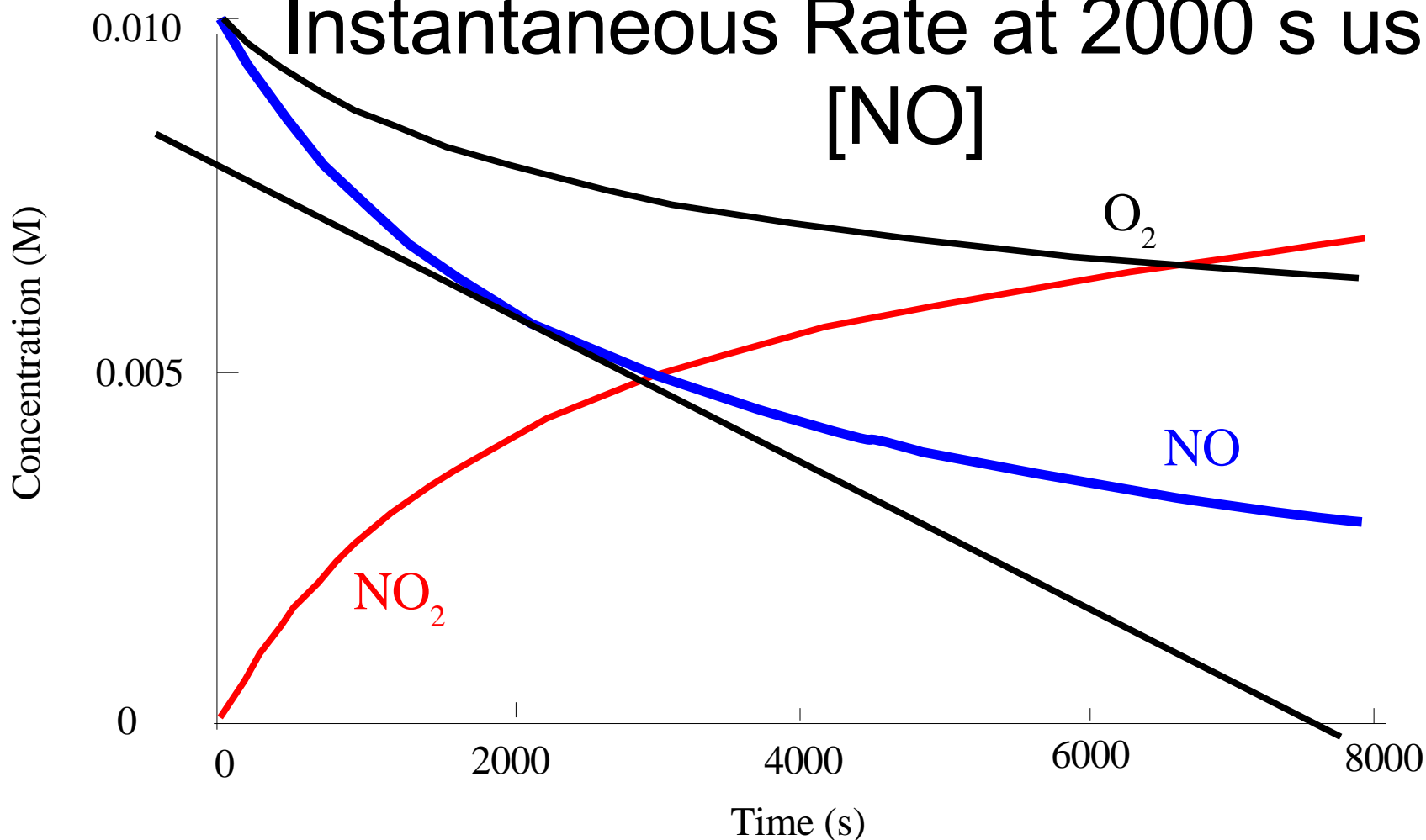
Average Rate between 2000 and 4000 s using $[\text{NO}_2]$



$$\begin{aligned} R &= (1/2)\Delta[\text{NO}_2]/\Delta t = \text{rise/run (2000-4000 s)} \approx (1/2)(0.0054 - 0.0042 \text{ M})/(4000-2000 \text{ s}) \\ &= 3.0 \times 10^{-7} \text{ Ms}^{-1} \end{aligned}$$

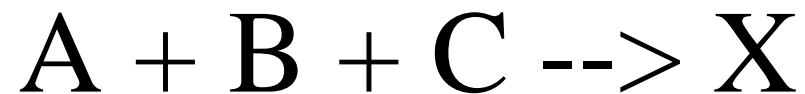


Instantaneous Rate at 2000 s using
[NO]

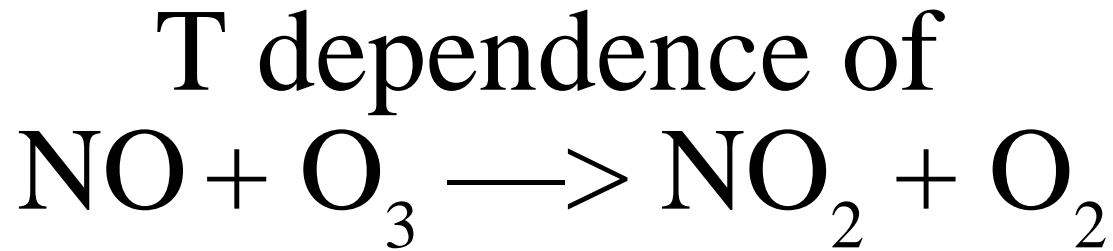


$$\begin{aligned} R &= (-1/2)(\Delta[\text{NO}]/\Delta t)_{2000\text{s}} = (-1/2)(\text{slope of tangent at } 2000 \text{ s}) \\ &= (-1/2)(0.0000 - 0.0078 \text{ M})/(7600 - 0 \text{ s}) = 5.1 \times 10^{-7} \text{ Ms}^{-1} \end{aligned}$$

Initial Rate Data for RXN:



$(\Delta[X]/\Delta t)_0$	$[A]_0$	$[B]_0$	$[C]_0$
1.0 M/s	10.0	10.0	0.01
4.0 M/s	10.0	10.0	0.02
16.0 M/s	10.0	10.0	0.04
2.0 M/s	20.0	10.0	0.01
4.0 M/s	40.0	10.0	0.01
1.0 M/s	10.0	100.0	0.01



T (K)	K ($\text{M}^{-1}\text{s}^{-1}$)	ln k	1/T (K^{-1})
300	1.21E10	23.22	0.00333
325	1.67E10	23.54	0.00308
350	2.20E10	23.81	0.00286
375	2.79E10	24.05	0.00267
400	3.45E10	24.26	0.00250
425	4.15E10	24.45	0.00235

$$\ln(k(T)) = \ln A - (E_a/R) (1/T)$$

