ChemE 2200 – Chemical Thermodynamics Lecture 12

Today:

The Thermodynamics of Chemical Equilibrium:

The Temperature Dependence of ΔG

Coupling Reactions to Lower Spontaneity Temperature

Defining Question:

What is an Ellingham Diagram?

Reading for Today's Lecture:

McQuarrie & Simon, Chapter 26.7

Reading for Lecture 1 of Chemical Kinetics:

McQuarrie & Simon, Chapter 28.1

Karina Chakov	I have a pet bearded dragon named Mango.
Isabelle Qiu	I was hit in the face by a sign board last Slope Day
Alyssa Peeters	I'm a dual citizen. (Belgium and United States)
Carter Knight	I had 12 dogs at one point
Demir Muhtaroglu	I once gave a power point presentation on donkeys.
Lulu Wang	I have two titanium bars in my chest.
Noyonima Masud	I did Synchronized Swimming for 4 years
Stephanie Fingerman	I am a black belt in karate
Daniel Fransen	I share a birthday with ChatGPT.
Maria Gravini	I speak Spanish at home
Sabequn Hossain	I shaved my own head when I was 16, going from shoulder-length hair to completely bald.
Megan Cheng	I know every single Taylor Swift song by heart
Anjali Asthagiri	During COVID, I did jigsaw puzzles, totaling ~13,000 pieces.
Thomas Cherry	I am a beekeeper
Ian Vann	I have permanent burns on my hands from falling in a fireplace.
Winifred Matanmi	I was born in Ireland & have triple citizenship
Joseph (Joe) Wang	I've flown a drone into myself on accident
Shani Abeyakoon	I'm from Las Vegas!
Michael Puscaso	I own several patents
Kylie Kaneshige	I have collected all 56 U.S. state and territories quarters.
Eryk Nguyen	I once broke into my own house with paperclips
Julia Vizza	I inoculated a cow when I was five years old.
Michelle Nguyen	I collect thimbles but I don't know how to sew
Kiefer Kleist	I have a goose.
Christina Boehm	I got a Post AP French 6 Award without ever taking French.
Charlotte Larson	I have a twin brother
Anthony Brooks	I am an officer of the Cornell Brazilian Jiu Jitsu Club.
Emily Perry	My left ear can fold into itself
Kiera Joyce	I started dancing when I was 4 years old.
Loobna Shego	I studied abroad in Italy for a semester.
Gee Tam	I've taken a different PE every semester: fencing, ballroom dancing, ADK canoe camping, and aerials.
Olivia Askowitz	In my spare time I do large-scale Minecraft Architecture.
Sophia Wu	I was fully awake while having my wisdom teeth removed.
Neha Chopade	My twin and I swam with sharks
Anirudh Tenneti	I have modded at least 6 web/mobile games
Bhavya Anoop	I went to 5 different elementary schools.
Mahika Arora	In 2022, I was in the top 6% of Chipotle customers :)
Lizzy Frazier	I’ve dyed my hair pink
Nathan Smith	I play steel pan

GUEST SPEAKER EVENT

Harnessing Ocean Power

Dr. Maha Haji leads the SEA Lab, driving innovation in sustainable technology. Come to explore her groundbreaking research and discover the impactful work of her team!

FEATURING

Dr. Maha Haji

Monday, March 24

4:30 - 5:30 PM

ROCKEFELLER 132

SALT

SEA Lab
Symbiotic Engineering and Analysis Lab

Recap: The Equations of Thermodynamics

energy	definition	natural variables	fundamental equation	Maxwell relation	practical equation
internal	$U = q + w$	S and V	$dU = TdS - PdV$	$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$	$dU = C_V dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right]dV$
Helmholtz	$A = U - TS$	T and V	$dA = -SdT - PdV$	$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$	$dS = \frac{C_V}{T}dT + \left(\frac{\partial P}{\partial T}\right)_V dV$
enthalpy	$H = U + PV$	S and P	$dH = TdS + VdP$	$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$	$dH = C_P dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right]dP$
Gibbs	$G = H - TS$	T and P	$dG = -SdT + VdP$	$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$	$dS = \frac{C_P}{T}dT - \left(\frac{\partial V}{\partial T}\right)_P dP$

need C_P or C_V and an equation of state.

Properties of matter

$\left(\frac{\partial U}{\partial T}\right)_V$	$= C_V$	heat capacity at constant volume
$\left(\frac{\partial H}{\partial T}\right)_P$	$= C_P$	heat capacity at constant pressure
$\left(\frac{\partial T}{\partial P}\right)_H$	$= \mu$	Joule-Thomson coefficient
$\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$	$= \alpha$	coefficient of thermal expansion
$-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$	$= \kappa_T$	isothermal compressibility
$-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S$	$= \kappa_S$	adiabatic compressibility

Some Useful Relations

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}$$

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

$$\left(\frac{\partial A}{\partial T}\right)_V = -S$$

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

$$\left(\frac{\partial A}{\partial V}\right)_T = -P$$

$$\overline{C}_P = \overline{C}_V + T\left(\frac{\partial P}{\partial T}\right)_{\overline{V}}\left(\frac{\partial \overline{V}}{\partial T}\right)_P$$

example: provides C_V dependence on V.

$$\boxed{\left(\frac{\partial C_V}{\partial V}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V}$$

$$\left(\frac{\partial C_P}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P$$

$$\left(\frac{\partial T}{\partial P}\right)_H = -\frac{1}{C_P}\left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right]$$

$$\left(\frac{\partial H}{\partial V}\right)_T = \left[T - V\left(\frac{\partial T}{\partial V}\right)_P\right]\left(\frac{\partial P}{\partial T}\right)_V$$

Recap: Chemical Equilibrium

$$dG = (\Delta\mu)d\xi \quad \Rightarrow \quad dG = (\Delta\mu^0 + RT\ln Q)d\xi$$

$$dG = \Delta\mu^0 d\xi + (RT\ln Q)d\xi$$

note: $dG^0 = (\Delta\mu^0)d\xi \quad \Rightarrow \quad dG = dG^0 + (RT\ln Q)d\xi$ integrate from $\xi = 0$ to $\xi = 1$:

$$\int dG^0 = \Delta G^0_{\text{rxn}}(T)$$

Standard Gibbs energy of reaction at temperature *T*.

Complete conversion of unmixed reactants → unmixed products.

$$\Delta\overline{G}_{\text{rxn}} = \Delta\overline{G}^0_{\text{rxn}}(T) + RT\ln Q$$

Set $\Delta\overline{G}_{\text{rxn}} = 0$ (reaction at equilibrium)

$$0 = \Delta\overline{G}^0_{\text{rxn}}(T) + RT\ln K_P(T)$$

$$\Delta\overline{G}^0_{\text{rxn}}(T) = -RT\ln K_P(T)$$

where $K_P(T) = \left(\dfrac{P_{\text{CH}_3\text{OH}}(P^0)^2}{P_{\text{CO}}P^2_{\text{H}_2}}\right)_{\text{equilibrium}}$

$K_{\text{P}}(T)$ is the equilibrium ‘constant’

$K_{\text{P}}(T)$ is constant with respect to pressure.

$K_{\text{P}}(T)$ varies with temperature.

$K_{\text{P}}(T)$ varies with reaction.

Recap: Equilibrium in 2-butene ↔ 1-butene

2-butene 1-butene

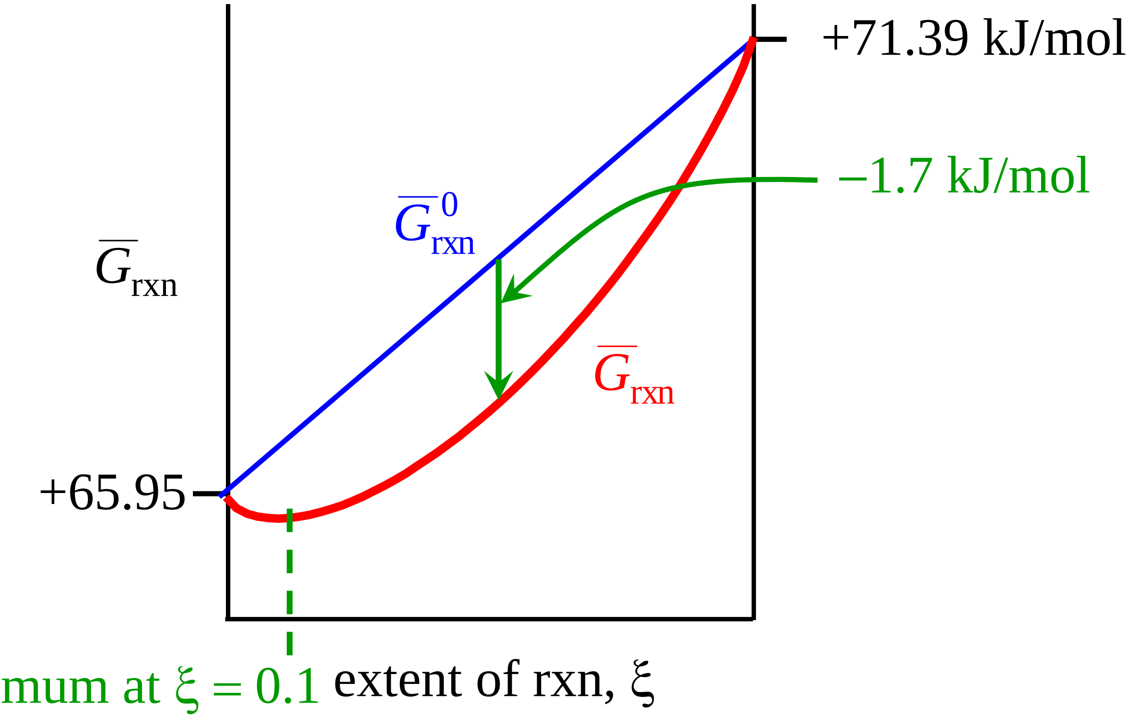
$$CH_3{-}CH{=}CH{-}CH_3 \leftrightarrow CH_2{=}CH{-}CH_2{-}CH_3 \qquad \Delta\overline{G}^0_{\text{rxn}} = +5.44\ \text{kJ/mol}$$

$$\Delta\overline{G}^0_{\text{formation}}: \qquad +65.95\ \text{kJ/mol} \qquad\qquad +71.39\ \text{kJ/mol}$$

$$K_P(T) = \exp\left[\frac{-\Delta\overline{G}^0_{\text{rxn}}(T)}{RT}\right] = \exp\left[\frac{-5{,}440\ \text{J/mol}}{(8.314\ \text{J/(K}\cdot\text{mol)}\times 298\ \text{K}}\right] = e^{-2.2} = 0.11$$

$$K_P(T) = \frac{P_{1\text{–butene}}}{P_{2\text{–butene}}}$$

At $P_{\text{total}} = 1$ atm, $P_{\text{1-butene}} = 0.1$ atm and $P_{\text{2-butene}} = 0.9$ atm



Recap: Pressure Dependence of Chemical Reaction Equilibrium

How does ΔG_{rxn} depend on P?

Start with the fundamental equation: $dG = -SdT + VdP$

$$d(\Delta G_{\mathrm{rxn}}) = -(\Delta S_{\mathrm{rxn}})dT + (\Delta V_{\mathrm{rxn}})dP$$

At constant T, $\left(\dfrac{\partial(\Delta G_{\mathrm{rxn}})}{\partial P}\right)_T = \Delta V_{\mathrm{rxn}}$

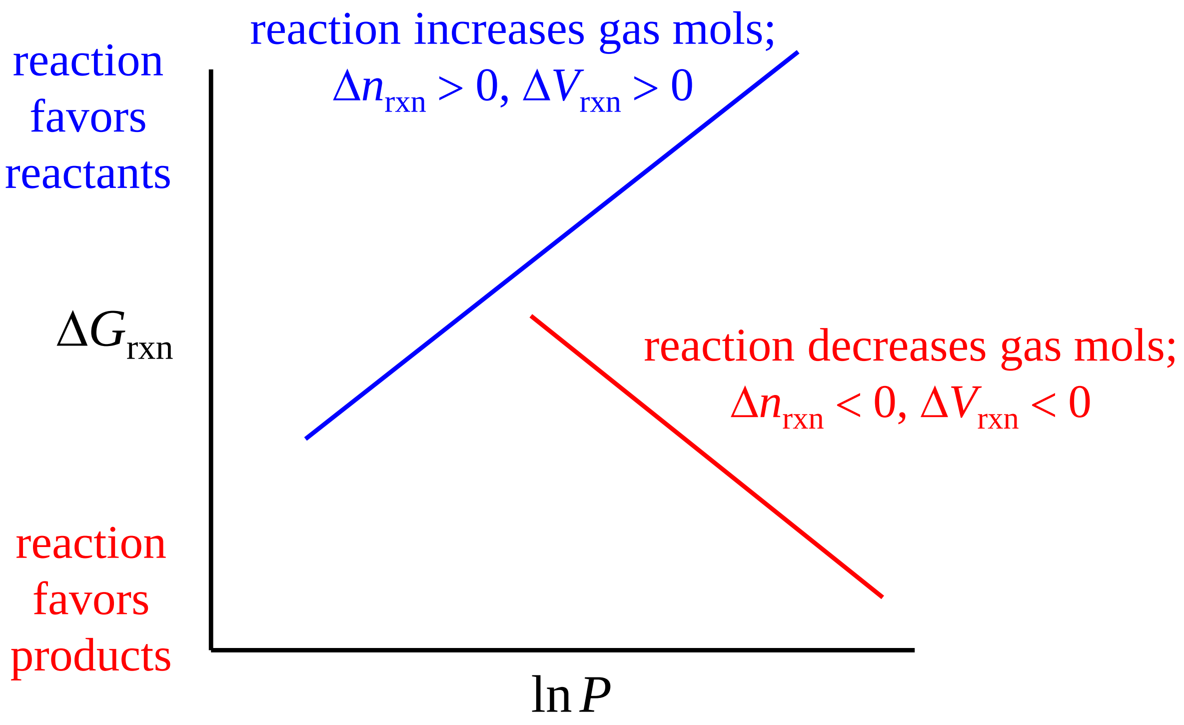
Assume ideal gases: $\Delta V_{\mathrm{rxn}} = \Delta n_{\mathrm{rxn}} \dfrac{RT}{P}$

$$\Rightarrow \left(\frac{\partial(\Delta G_{\mathrm{rxn}})}{\partial P}\right)_T = \Delta n_{\mathrm{rxn}} \frac{RT}{P}$$

$$\int d(\Delta G_{\mathrm{rxn}}) = \int_{P_1}^{P_2} \Delta n_{\mathrm{rxn}} \frac{RT}{P} dP$$

$$\Delta G_{\mathrm{rxn}} = R(\Delta n_{\mathrm{rxn}})(\ln P_2 - \ln P_1)$$

at constant T



Temperature Dependence of Chemical Reaction Equilibrium

How does ΔG_{rxn} depend on T?

Recall from Lecture 13: $$\boxed{\left(\frac{\partial(G/T)}{\partial T}\right)_P = -\frac{H}{T^2}}$$ The Gibbs-Helmholtz Equation

No approximations.

For ΔG of a phase transition or chemical reaction:

$$\boxed{\left(\frac{\partial(\Delta G^0_{\text{rxn}}/T)}{\partial T}\right)_P = -\frac{\Delta H^0_{\text{rxn}}}{T^2}}$$

Also The Gibbs-Helmholtz Equation

Substitute $\Delta G^0_{\text{rxn}} = -RT\ln K_P$

$$-R\left(\frac{\partial \ln K_P}{\partial T}\right)_P = -\frac{\Delta H^0_{\text{rxn}}}{T^2}$$

K_P is independent of P, so we can remove the partial derivative.

$$\boxed{\frac{d\ln K_P}{dT} = \frac{\Delta H^0_{\text{rxn}}}{RT^2}}$$

The van’t Hoff Equation (~1880)

Temperature Dependence of Chemical Reaction Equilibrium

$$\boxed{\frac{d\ln K_P}{dT} = \frac{\Delta H^0_{\text{rxn}}}{RT^2}}$$

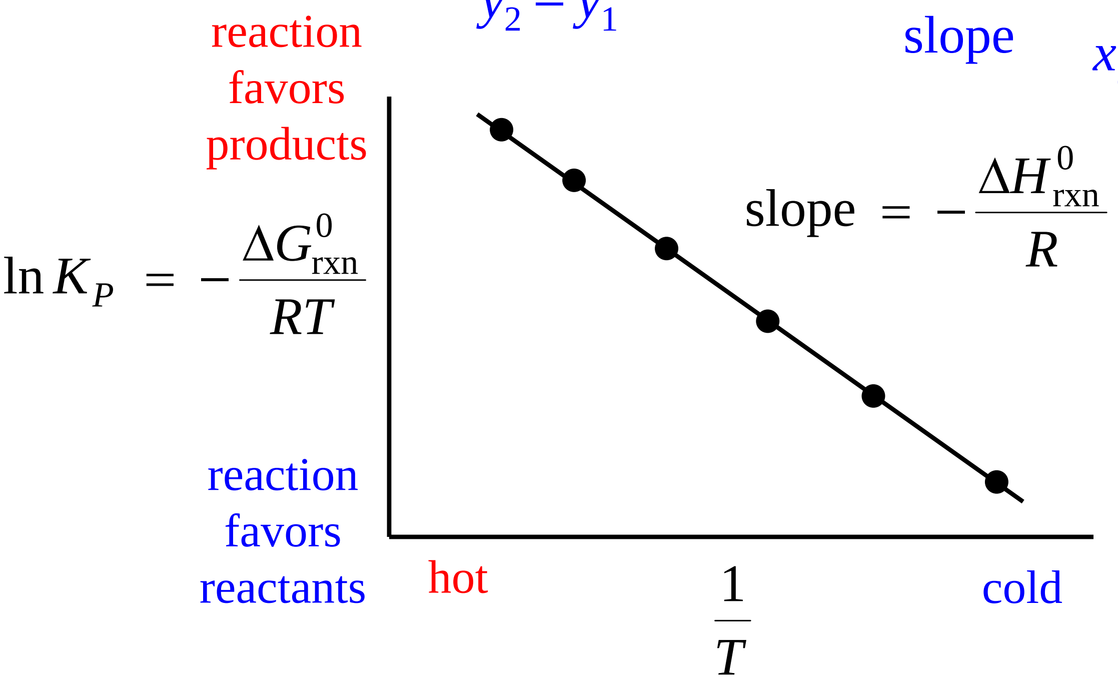
The van’t Hoff Equation (~1880)

Integrate to obtain a useful equation:

$$\int_{\ln K_P(T_1)}^{\ln K_P(T_2)} d\ln K_P = \int_{T_1}^{T_2} \frac{\Delta H^0_{\text{rxn}}}{RT^2}\,dT$$

assume ΔH^0_{rxn} is independent of T

$$\underbrace{\ln K_P(T_2) - \ln K_P(T_1)}_{y_2 - y_1} = -\underbrace{\frac{\Delta H^0_{\text{rxn}}}{R}}_{\text{slope}}\underbrace{\left(\frac{1}{T_2} - \frac{1}{T_1}\right)}_{x_2 - x_1}$$



$$\ln K_P = -\frac{\Delta G^0_{\text{rxn}}}{RT}$$

$$\frac{1}{T}$$

$$\text{slope} = -\frac{\Delta H^0_{\text{rxn}}}{R}$$

straight line if ΔH^0_{rxn}

is independent of T

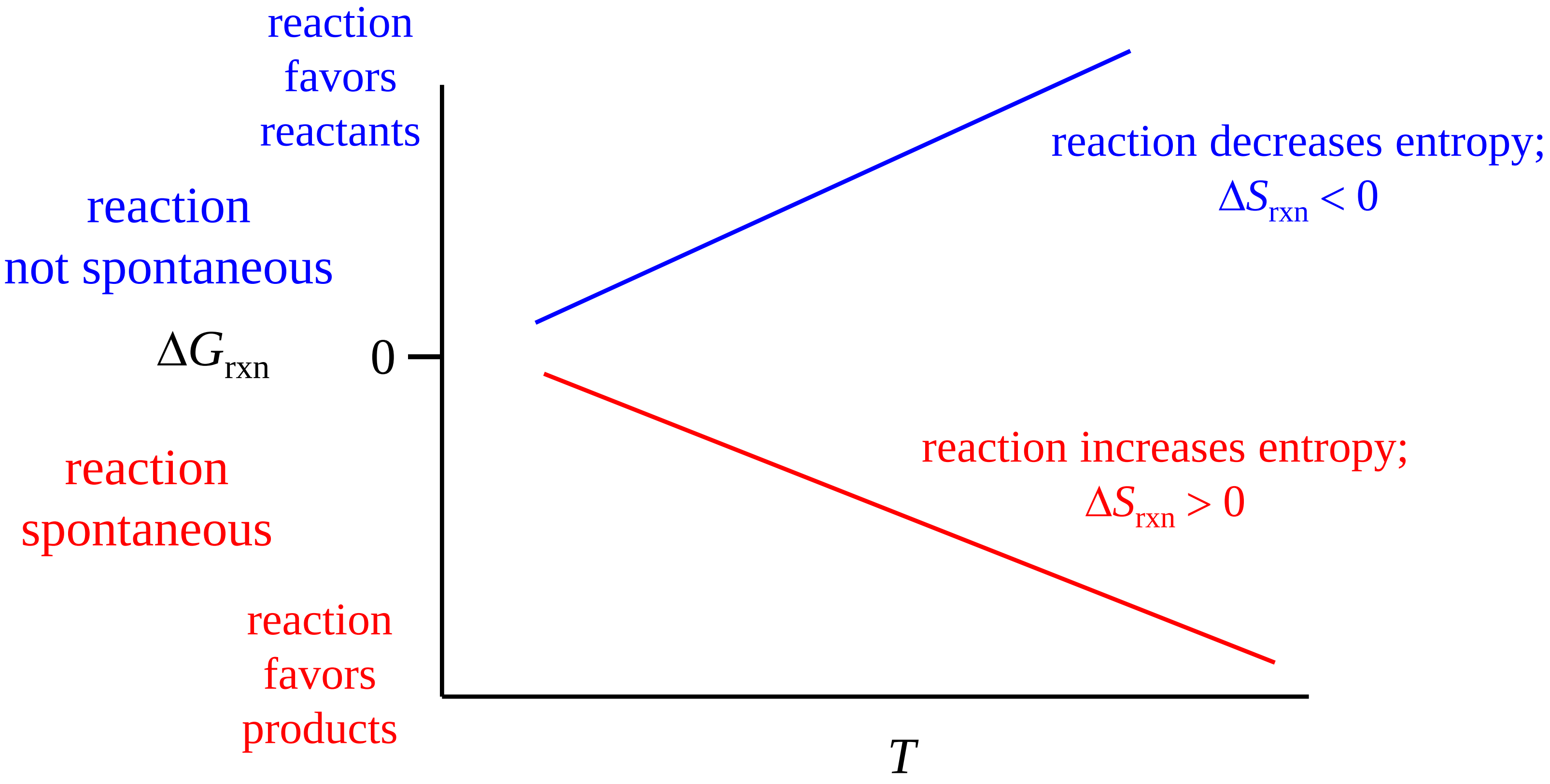
Temperature Dependence of Chemical Reaction Equilibrium

Another perspective on the temperature dependence – start with the fundamental equation.

$$dG = -SdT + VdP$$

$$d(\Delta G_{\text{rxn}}) = -(\Delta S_{\text{rxn}})dT + (\Delta \cancelto{0}{V_{\text{rxn}}})dP \qquad \text{assume constant } P$$

$$\left(\frac{\partial G_{\text{rxn}}}{\partial T}\right)_P = -\Delta S_{\text{rxn}}$$



Example of Temperature Dependence of ΔG_{rxn}

(and how to couple reactions)

Consider the general case of metal oxidation.

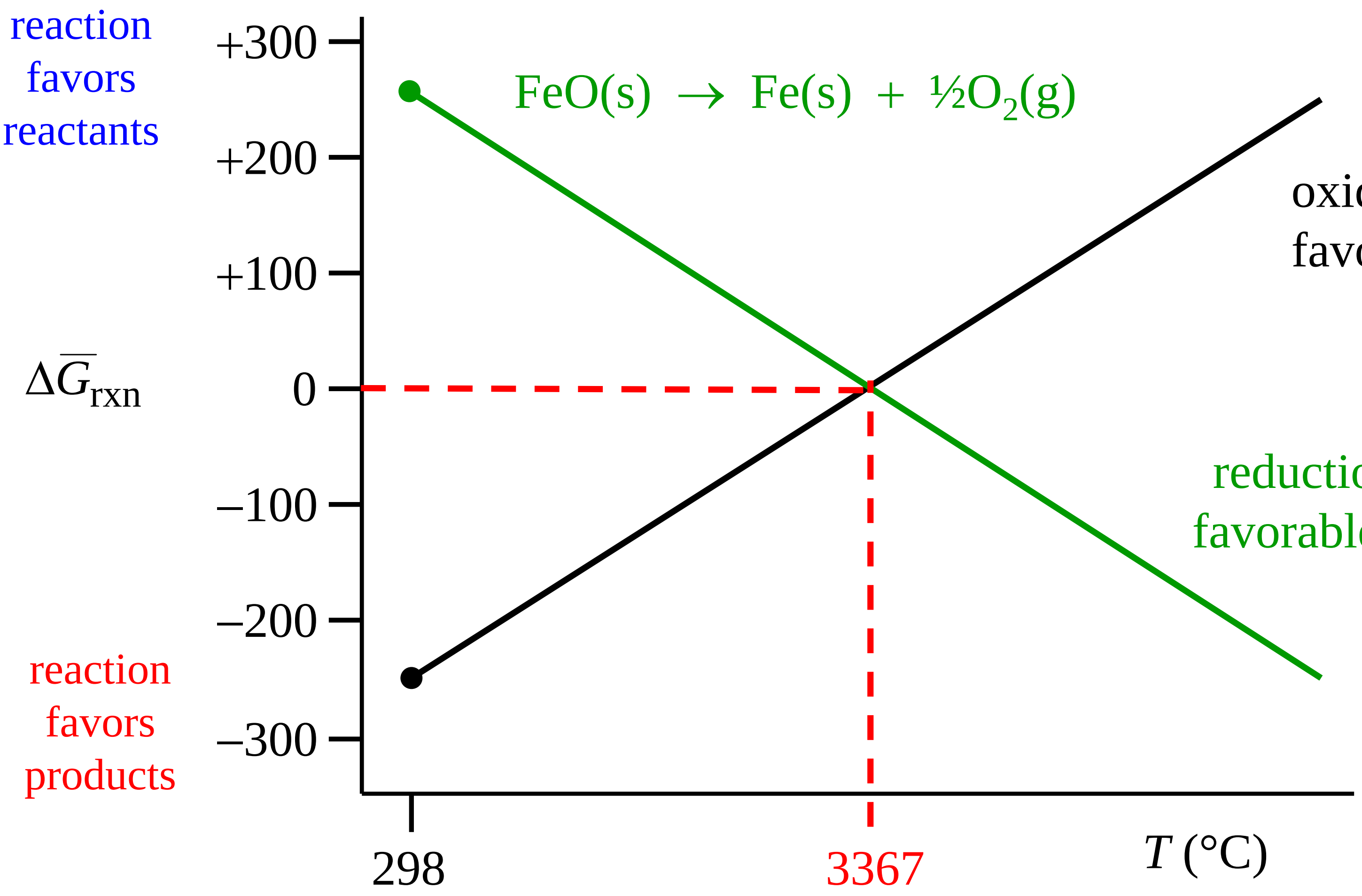
For example, $\quad Fe(s) + \tfrac{1}{2}O_2(g) \rightarrow FeO(s)$

$$\Delta\overline{G}^{0}_{\text{rxn}}(298\text{K}) = -251.5\ \text{kJ/mol}$$

$$\Delta\overline{S}^{0}_{\text{rxn}}(298\text{K}) = -69.1\ \text{J/(K}\cdot\text{mol)}$$

$$\Delta n_{\text{gas}} = -\tfrac{1}{2}\ \text{mol}$$

Temperature dependence?



oxidation is less favorable at high *T*.

reduction is more favorable at high *T*.

How to reduce FeO to Fe at a lower *T*?

Coupling Reduction and Oxidation Reactions

$$\mathrm{FeO(s)} \rightarrow \mathrm{Fe(s)} + \tfrac{1}{2}\mathrm{O_2(g)} \qquad \Delta\overline{G}_{\text{rxn}} = 0 \text{ at } \boxed{3367°\text{C}}$$

Couple an endothermic reduction with an exothermic oxidation.

	$\Delta\overline{G}^{0}_{\text{rxn}}$	$\Delta\overline{S}^{0}_{\text{rxn}}$	Δn_{gas}
$\mathrm{FeO(s)} \rightarrow \mathrm{Fe(s)} + \cancel{\tfrac{1}{2}\mathrm{O_2}}\mathrm{(g)}$	+251.5 kJ/mol	+69.1 J/(K·mol)	+½
$\tfrac{1}{2}\left(\mathrm{C(s)} + \cancel{\mathrm{O_2}}\mathrm{(g)} \rightarrow \mathrm{CO_2(g)}\right)$	–197.2 kJ/mol	–1.4 J/(K·mol)	0
$\mathrm{FeO(s)} + \tfrac{1}{2}\mathrm{C(s)} \rightarrow \mathrm{Fe(s)} + \tfrac{1}{2}\mathrm{CO_2(g)}$	+54.3 kJ/mol	+67.7 J/(K·mol)	+½

$$\text{at } \Delta\overline{G}_{\text{rxn}} = 0, \quad \Delta\overline{G}^{0}_{\text{rxn}} = T\Delta\overline{S}^{0}_{\text{rxn}} \quad \Rightarrow \quad T = \frac{\Delta\overline{G}^{0}_{\text{rxn}}}{\Delta\overline{S}^{0}_{\text{rxn}}} = \frac{54{,}300\ \text{J/mol}}{67.7\ \text{J/(K}\cdot\text{mol)}} = 802\ \text{K} = \boxed{529^{\text{o}}\text{C}}$$

The chief contribution is enthalpy, not entropy.

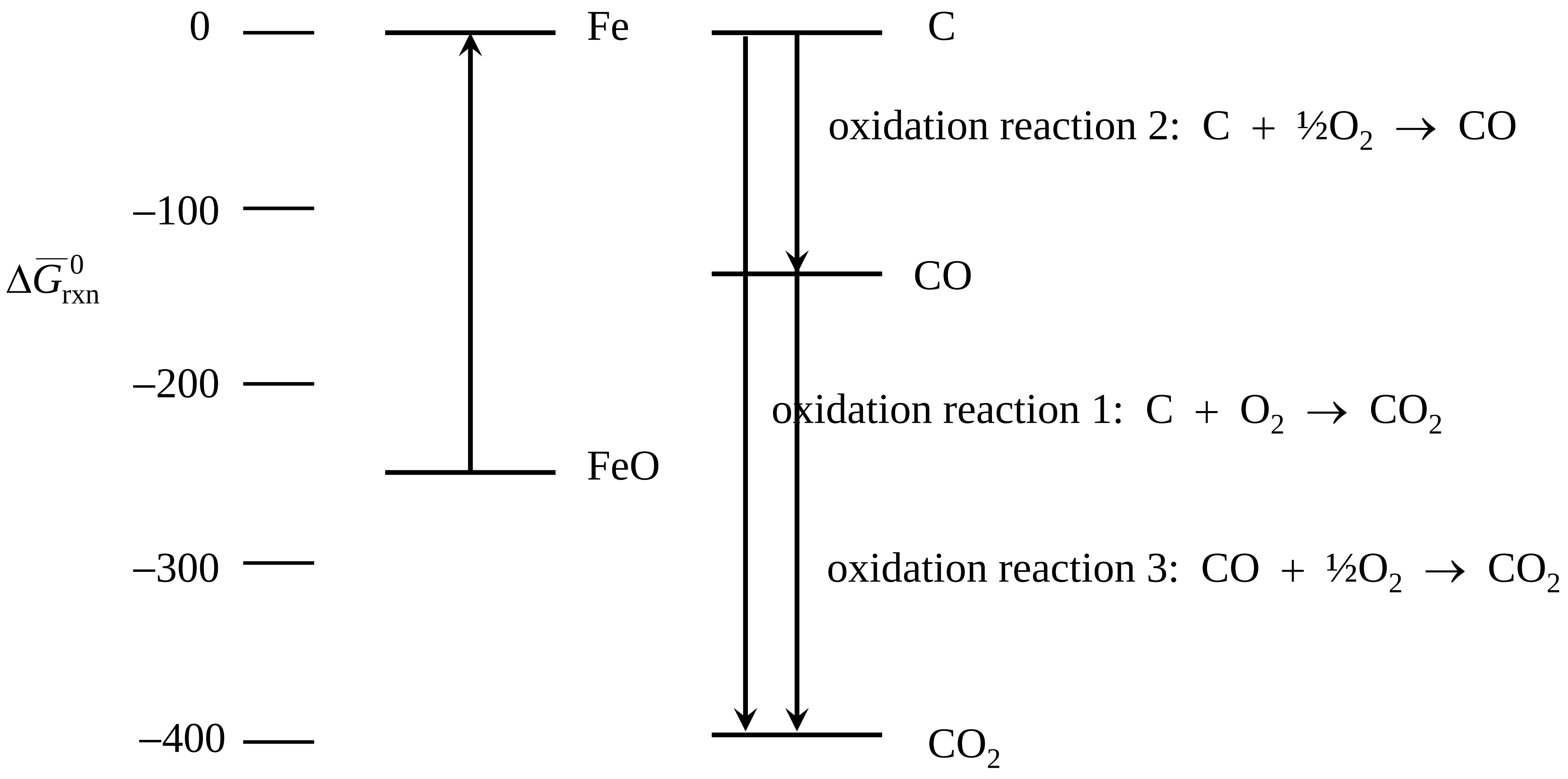
Couple to a different oxidation reaction.

	$\Delta\overline{G}^{0}_{\text{rxn}}$	$\Delta\overline{S}^{0}_{\text{rxn}}$	Δn_{gas}
$\mathrm{FeO(s)} \rightarrow \mathrm{Fe(s)} + \cancel{\tfrac{1}{2}\mathrm{O_2}}\mathrm{(g)}$	+251.5 kJ/mol	+69.1 J/(K·mol)	+½
$\mathrm{C(s)} + \cancel{\tfrac{1}{2}\mathrm{O_2}}\mathrm{(g)} \rightarrow \mathrm{CO(g)}$	–137.2 kJ/mol	+89.4 J/(K·mol)	+½
$\mathrm{FeO(s)} + \mathrm{C(s)} \rightarrow \mathrm{Fe(s)} + \mathrm{CO(g)}$	+114.3 kJ/mol	+158.5 kJ/mol	+1

$$T = \frac{\Delta\overline{G}^{0}_{\text{rxn}}}{\Delta\overline{S}^{0}_{\text{rxn}}} = \frac{114{,}300\ \text{J/mol}}{158.5\ \text{J/(K}\cdot\text{mol)}} = 721\ \text{K} = \boxed{448^{\text{o}}\text{C}}$$

Coupling Reduction and Oxidation Reactions

Other options for coupled oxidation reactions?



oxidation reaction 2: $C + \frac{1}{2}O_2 \rightarrow CO$

oxidation reaction 1: $C + O_2 \rightarrow CO_2$

oxidation reaction 3: $CO + \frac{1}{2}O_2 \rightarrow CO_2$

Temperature for spontaneous reduction
of FeO with oxidation reaction 3?

Coupling Reduction and Oxidation Reactions

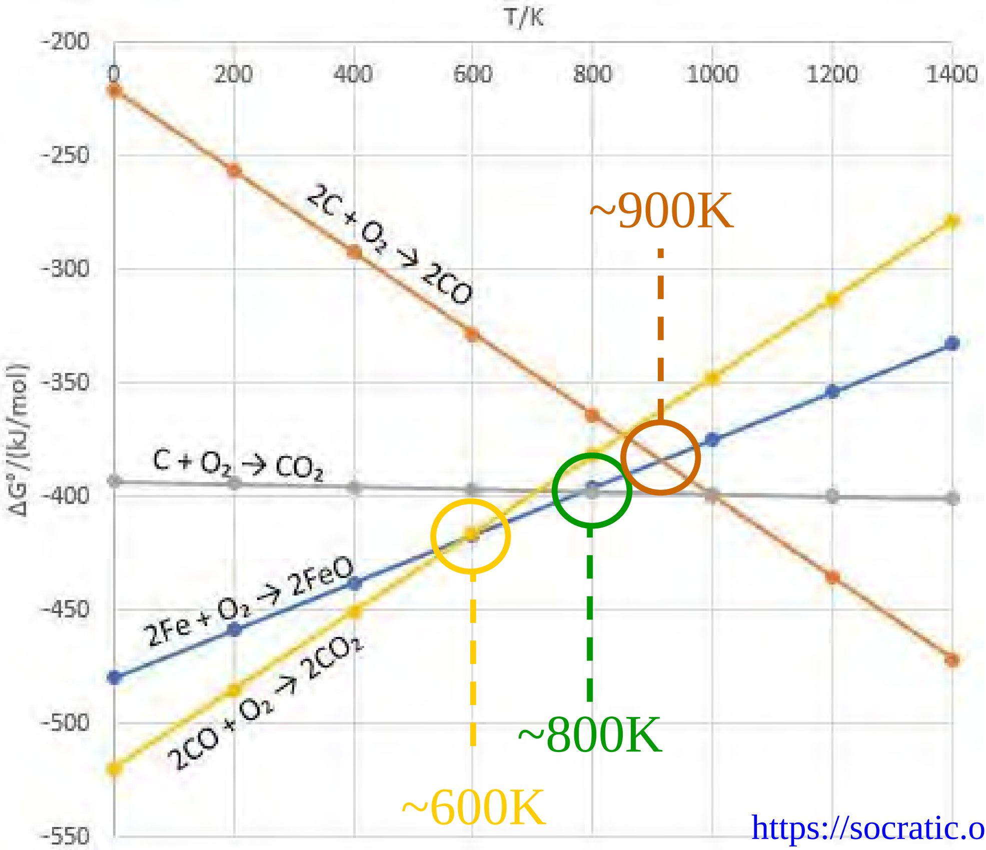
Coupling reduction and oxidation reactions can be analyzed graphically.

Consider the first pair of coupled reduction and oxidation reactions:

$$\begin{array}{ll} \frac{1}{2}(C(s) + \cancel{O_2}(g) \rightarrow CO_2(g)) & \text{C oxidation} \\ -(Fe(s) + \frac{1}{2}\cancel{O_2}(g) \rightarrow FeO(s)) & \text{Fe oxidation} \\ \hline FeO(s) + \frac{1}{2}C(s) \rightarrow Fe(s) + \frac{1}{2}CO_2(g) & \text{coupled} \end{array}$$

$$\Delta\overline{G}_{\text{coupled}} = \Delta\overline{G}_{\text{C oxidation}} - \Delta\overline{G}_{\text{Fe oxidation}}$$

An Ellingham Diagram



How to find $\Delta G_{rxn} = 0$ for two coupled reactions?

Intersection!

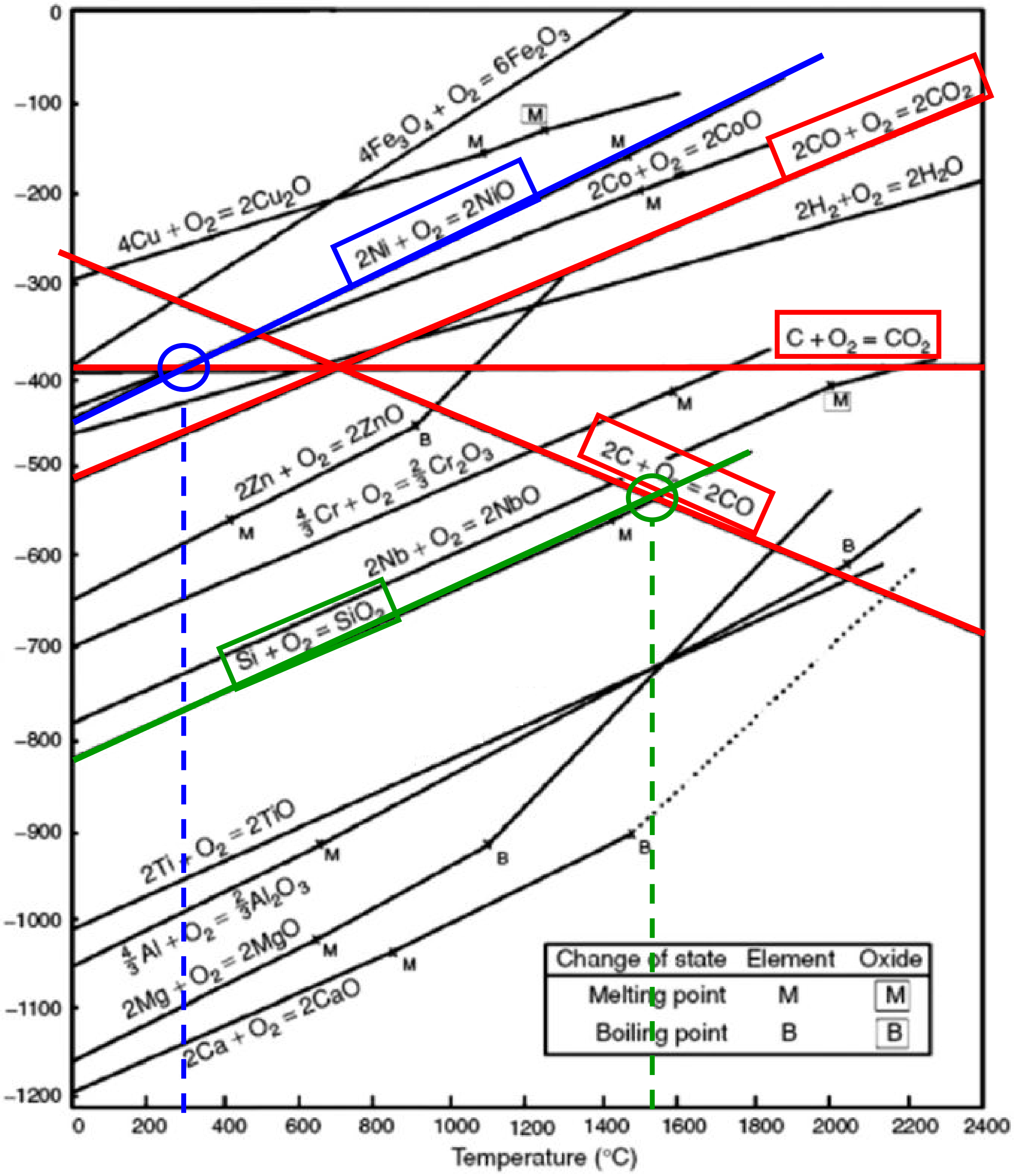
https://socratic.org/questions/using-ellingham-diagram

Ellingham Diagrams

reaction
favors
reactants

$\Delta\overline{G}_{rxn}$

reaction
favors
products



Note: All reactions
with metals are
oxidation reactions.

To subtract
a metal oxidation
reaction from
carbon oxidation
reaction and find
$\Delta G_{rxn} = 0$,
find the intersection.