ChemE 2200 – Chemical Thermodynamics Lecture 11

Today:

The Thermodynamics of Chemical Equilibrium:

Extent of Reaction, ξ

Reactant Quotient and Equilibrium Constant

Defining Question:

For pure H_2O below its boiling point, $\Delta G_{\text{evaporation}} > 0$,
and there is exactly *zero* H_2O vapor above the H_2O liquid.

For $N_2 + O_2$ at STP, $\Delta G_{\text{rxn}} > 0$, but some NO forms.

Why?

Reading for Today's Lecture:

McQuarrie & Simon, Chapter 26.1-26.7

Reading for Thermodynamics Lecture 12:

McQuarrie & Simon, Chapter 26.7

CornellEngineering
R. F. Smith School of Chemical
and Biomolecular Engineering

ENERGY ENGINEERING SEMINAR SPRING 2025

CHEME 5880, BEE 5469, ECE 5880, MAE 5469

Energy storage economics

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Wood Mackenzie
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12:20 - 1:10 PM
Olin 155

Stationary energy storage has become a critical part of US electrical infrastructure, providing peak shaving, time shifting, resource adequacy, and ancillary services, especially in regions with high variable renewable energy penetration like California and Texas. However, storage technology is still evolving, and grid operators have yet to capture the full value of storage. In this seminar, we will introduce some basic frameworks needed to quantitatively assess the financial attractiveness of energy storage assets operating in wholesale power markets. We will also discuss how energy storage costs and revenues vary with duration, providing some initial views on the economic viability of long-duration storage. More broadly, we will also explore careers in energy research & consulting.

Kasim Khan (CBE ’20) is a Senior Research Analyst at Wood Mackenzie, where he focuses on researching energy storage technologies & operations, vendor & technology competitive assessment, system cost benchmarking, and operational profiles including costs & revenues for markets in the US. Previously, Kasim worked in Woodmac’s Supply Chain Consulting practice, where he created nearly $100M in savings for utilities and oil & gas companies across North America through energy supply chain management & power purchase agreement negotiations. Prior to joining Woodmac, he conducted lithium-metal battery research with Dr. Lynden Archer at Cornell University, resulting in several publications and a U.S. patent. He is currently based in Boston, Massachusetts.

Supported by a gift from Dr. Mary Lou West '63, MS '65 and Dr. Roger K. West '61, PhD '65

Recap: Fundamental Thermodynamics

$$dG(T,P) = -SdT + VdP + \sum \mu_i(T,P)dn_i$$

$\mu_i(T,P)$ is the molar Gibbs energy at a given temperature and pressure.

Use data tables for the standard molar Gibbs energy at 1 bar (= P^0).

$$\mu_i^0(T) = \frac{G^0(T)}{n} = \overline{G}^0(T)$$

How does $\mu_i(T,P)$ vary with pressure?

Define the activity of substance i, a_i, such that

$$a_i = \exp\left(\frac{\mu_i(T,P) - \mu_i^0(T)}{RT}\right)$$

or $\mu_i(T,P) = \mu_i^0(T) + RT\ln a_i$

The Activity of a Substance

$$a_i = \exp\left(\frac{\mu_i(T,P) - \mu_i^0(T)}{RT}\right)$$

$$\text{or} \quad \mu_i(T,P) = \mu_i^0(T) + RT\ln a_i$$

What is the activity of a substance?

"The activity of a substance is whatever is needed
to make (the above equations) correct."

L. M. Raff, *The Principles of Physical Chemistry* (2001)

Approximations for ideal systems:

For a pure liquid or a pure solid, $a_i \approx 1$ Liquids and solids have small molar volumes.

$$\left(\frac{\partial \mu}{\partial P}\right)_T = \left(\frac{\partial \overline{G}}{\partial P}\right)_T = \overline{V} \qquad \overline{V}_{\text{solid}} \text{ is small.}$$

For an ideal gas, $a_i \approx \dfrac{P_i}{P^0}$ such that $P^0 = 1$ bar.

Coal to Syngas to Methanol to Dimethylether to Olefins

Consider some industrially important reactions.

coal gasification: $\underbrace{\mathrm{C(graphite)}}_{\text{coal}} + \underbrace{\mathrm{H_2O(g)}}_{\text{steam}} \leftrightarrow \underbrace{\mathrm{CO(g)} + \mathrm{H_2(g)}}_{\text{synthesis gas, aka syngas}}$

The U.S. has coal to last 500 years.

methanol synthesis: $\mathrm{CO(g)} + 2\mathrm{H_2(g)} \leftrightarrow \mathrm{CH_3OH(g)}$

dimethylether synthesis: $2\mathrm{CH_3OH(g)} \leftrightarrow \mathrm{CH_3OCH_3(g)} + \mathrm{H_2O(g)}$

olefin synthesis: $n\mathrm{CH_3OCH_3(g)} \leftrightarrow \mathrm{CH_2{=}(CH_2)_{2(n-1)}{=}CH_2} + n\mathrm{H_2O(g)}$

Plus various side reactions …

Consider equilibrium of the methanol synthesis.

Chemical Equilibrium

methanol synthesis: $CO(g) + 2H_2(g) \leftrightarrow CH_3OH(g)$

Start with CO and $2H_2$. What is dG if an infinitesimal amount of methanol forms?

$$dG = -SdT + VdP + \mu_{CO}dn_{CO} + \mu_{H2}dn_{H2} + \mu_{CH3OH}dn_{CH3OH}$$

Assume T and P are constant.

$$dG = \mu_{CO}dn_{CO} + \mu_{H2}dn_{H2} + \mu_{CH3OH}dn_{CH3OH}$$

Define $\xi \equiv$ extent of reaction = number of moles produced.

ξ [=] moles ξ is pronounced 'kah-sigh'

$$dn_{CH3OH} = +d\xi$$

$$dn_{CO} = -d\xi$$

stoichiometric coefficients

$$dn_{H2} = -2d\xi$$

$$dG = \underbrace{(-\mu_{CO} - 2\mu_{H2} + \mu_{CH3OH})}_{= \Delta\mu}d\xi$$

Chemical Equilibrium

methanol synthesis: $CO(g) + 2H_2(g) \leftrightarrow CH_3OH(g)$

$$dG = (\Delta\mu)d\xi$$

$$\Delta\mu = -\mu_{CO} - 2\mu_{H2} + \mu_{CH3OH} \text{ at } P^0 \text{ and any } T.$$

If $\Delta\mu < 0$, need $d\xi > 0$ for $\Delta G < 0$

If $\Delta\mu < 0$, reaction goes forward.

If $\Delta\mu > 0$, need $d\xi < 0$ for $\Delta G < 0$

If $\Delta\mu > 0$, reaction goes backward.

If $\Delta\mu = 0$, $\Delta G = 0$

If $\Delta\mu = 0$, reaction is at equilibrium.

Chemical Equilibrium

$\Delta\mu \;=\; -\mu_{CO} \;-\; 2\mu_{H2} \;+\; \mu_{CH3OH}$ at P^0 and any T.

Express the chemical potentials in terms of the standard pressure, P^0.

For example, $\mu_{CO}(T,P) \;=\; \mu^0_{CO}(T) \;+\; RT\ln a_{CO} \;\approx\; \mu^0_{CO}(T) \;+\; RT\ln\dfrac{P_{CO}}{P^0}$

$\mu_{CO}(=\ \overline{G}_{CO})$ at P^0 and any T

$$\Delta\mu \;=\; (-\mu^0_{CO} - 2\mu^0_{H_2} + \mu^0_{CH_3OH}) \;+\; RT\left(-\ln\frac{P_{CO}}{P^0} - 2\ln\frac{P_{H_2}}{P^0} + \ln\frac{P_{CH_3OH}}{P^0}\right)$$

$$\Delta\mu \;=\; \Delta\mu^0 \;+\; RT\left(\ln\frac{\dfrac{P_{CH_3OH}}{P^0}}{\dfrac{P_{CO}}{P^0}\left(\dfrac{P_{H_2}}{P^0}\right)^2}\right)$$

$$\Delta\mu \;=\; \Delta\mu^0 \;+\; RT\left(\ln\frac{P_{CH_3OH}(P^0)^2}{P_{CO}P^2_{H_2}}\right)$$

Define the Reaction Quotient $\equiv\ Q \;=\; \dfrac{P_{CH_3OH}(P^0)^2}{P_{CO}P^2_{H_2}} \qquad \Rightarrow \qquad \Delta\mu \;=\; \Delta\mu^0 \;+\; RT\ln Q$

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.

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

Set $\Delta\overline{G} = 0$ (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 $K_P(T) = \left(\dfrac{P_{CH_3OH}(P^0)^2}{P_{CO}P_{H_2}^2}\right)_{\text{equilibrium}}$

$K_P(T)$ is the equilibrium 'constant'

$K_P(T)$ is constant with respect to pressure.

$K_P(T)$ varies with temperature.

$K_P(T)$ varies with reaction.

Chemical Equilibrium of Methanol Synthesis Reaction

methanol synthesis: $CO(g) + 2H_2(g) \leftrightarrow CH_3OH(g)$

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

$$\left.\begin{aligned} \mu^0_{CO} &= -137.163\ \text{kJ/mol} \\ \mu^0_{H_2} &= 0 \\ \mu^0_{CH_3OH} &= -161.96\ \text{kJ/mol} \end{aligned}\right\}\ \text{from Table 26.1, p. 1057}$$

$$\Delta\overline{G}^0_{\text{rxn}} = -\mu^0_{CO} - 2\mu^0_{H_2} + \mu^0_{CH_3OH} = -24.80\ \text{kJ/mol}$$

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

$$K_P(T) = \exp\left[\frac{-\Delta\overline{G}^0_{\text{rxn}}(T)}{RT}\right] = \exp\left[\frac{-24{,}800\ \text{J/mol}}{(8.314\ \text{J/(K}\cdot\text{mol)})\times 298\ \text{K}}\right] = e^{+10.01} = 2.2\times 10^4$$

How to interpret?

High conversion?

Low conversion?

Chemical Equilibrium of Methanol Synthesis Reaction

methanol synthesis: $CO(g) + 2H_2(g) \leftrightarrow CH_3OH(g)$

$\Delta \overline{G}^0_{\mathrm{rxn}} = -24.80$ kJ/mol $\qquad K_P = 2.2 \times 10^4$

Assume a stoichiometric mixture initially:

			partial pressures	
	initial	later	initial	later
CO	1 mol	$1-\xi$	$\frac{1}{3}P$	$\frac{1-\xi}{3-2\xi}P$
H_2	2	$2-2\xi$	$\frac{2}{3}P$	$\frac{2(1-\xi)}{3-2\xi}P$
CH_3OH	0	ξ	0	$\frac{\xi}{3-2\xi}P$
total:	3 mol	$3-2\xi$	P	P

$$K_P(T) = \frac{P_{CH_3OH}(P^0)^2}{P_{CO}P_{H_2}^2} = \frac{\frac{\xi}{3-2\xi}P}{\frac{1-\xi}{3-2\xi}P\left(\frac{2(1-\xi)}{3-2\xi}\right)^2 P^2} = \frac{(3-2\xi)^2\xi}{4(1-\xi)^3}\frac{1}{P^2} = 2.2 \times 10^4$$

Chemical Equilibrium of Methanol Synthesis Reaction

methanol synthesis: $CO(g) + 2H_2(g) \leftrightarrow CH_3OH(g)$

$$\Delta\overline{G}^0_{\mathrm{rxn}} = -24.80\ \mathrm{kJ/mol} \qquad K_P = 2.2\times10^4$$

$$K_P(T) = \frac{(3-2\xi)^2\xi}{4(1-\xi)^3}\frac{1}{P^2} = 2.2\times10^4$$

Because $\Delta\overline{G}^0_{\mathrm{rxn}}$ is large and negative, the conversion will be high. $\xi \approx 1$

In the limit $\xi \to 1$

$$\frac{\overset{\approx 1}{(3-2\xi)^2}\,\overset{\approx 1}{\xi}}{4(1-\xi)^3}\frac{1}{P^2} = 2.2\times10^4$$

$$\frac{1}{4\times2.2\times10^4}\frac{1}{P^2} = (1-\xi)^3$$

$$\frac{1.1\times10^{-5}}{P^2} = (1-\xi)^3$$

$$\frac{0.023}{P^{2/3}} = 1-\xi$$

$$\xi = 1-\frac{0.023}{P^{2/3}}$$

pressure	ξ
1 bar	0.977
2 bar	0.986
10 bar	0.995
100 bar	0.999

1 bar = 0.987 atm

Le Châtelier's Principle

methanol synthesis: $CO(g) + 2H_2(g) \leftrightarrow CH_3OH(g)$

Assume reaction is at equilibrium at $P = 1$ atm. $\xi = 0.977$

$$P_{CO} = \frac{1-\xi}{3-2\xi}P = 0.022 \text{ atm}$$

$$P_{H_2} = \frac{2(1-\xi)}{3-2\xi}P = 0.044 \text{ atm}$$

$$P_{CH_3OH} = \frac{\xi}{3-2\xi}P = 0.94 \text{ atm}$$

$$\text{check: } K_P = \frac{P_{CH_3OH}(P^0)^2}{P_{CO}P_{H_2}^2} = \frac{0.94}{0.022 \times 0.044^2} = 2.2 \times 10^4$$

If pressure increases, the reaction is no longer at equilibrium.

The reaction will respond to restore equilibrium by decreasing the number of gas molecules.

The reaction conversion will increase.

Although K_P is independent of pressure, P_{CO}, P_{H2}, and P_{CH3OH} depend on the total pressure.

Pressure Dependence of Chemical Reaction Equilibrium

How does ΔG_{rxn} depend on P?

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

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

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

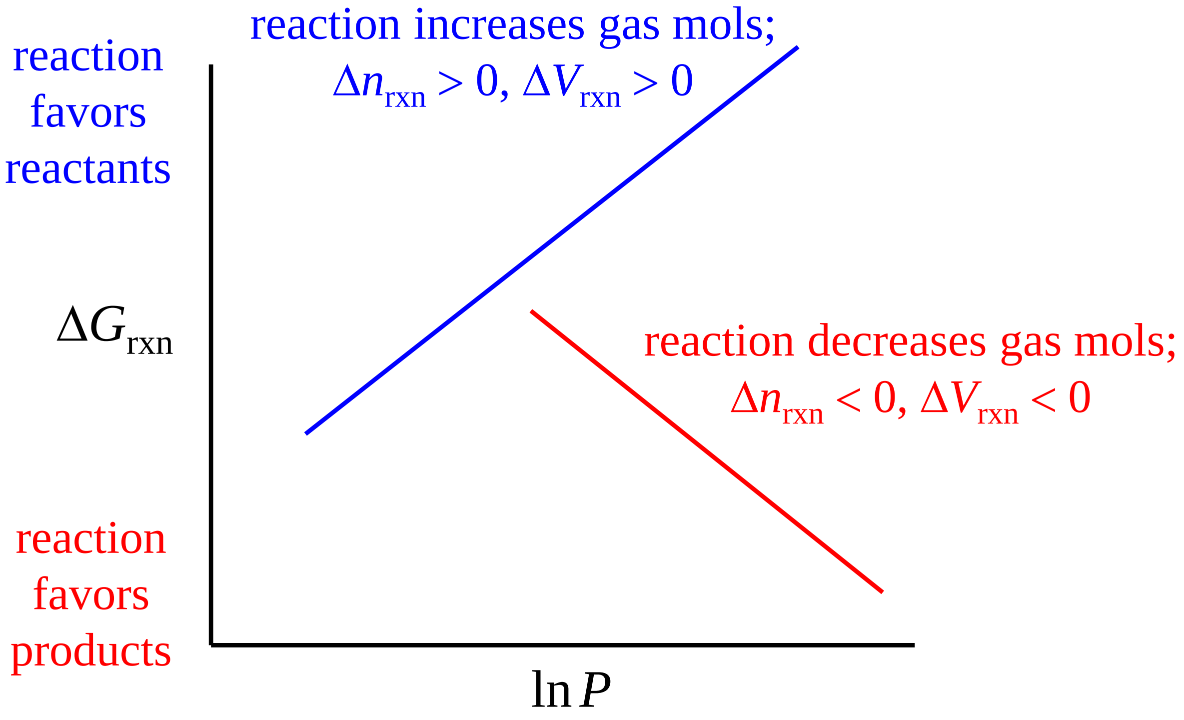
Assume ideal gases: $\Delta V_{\text{rxn}} = \Delta n_{\text{rxn}} \frac{RT}{P}$

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

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

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

at constant T



Spontaneity in Chemical Reactions

Consider the physical reaction $H_2O(s) \leftrightarrow H_2O(l)$ At 263 K, $\Delta\bar{G}^0_{\text{rxn}} = +0.21$ kJ/mol

$\Delta\bar{G}_{\text{rxn}} > 0$ so the phase change is not spontaneous. Exactly zero liquid forms.

highly toxic

Consider the chemical reaction $N_2(g) + O_2(g) \leftrightarrow 2NO(g)$ At 298 K, $\Delta\bar{G}^0_{\text{rxn}} = +173.1$ kJ/mol

The chemical reaction is not spontaneous, so exactly zero NO forms. Right?

Wrong! Some NO forms!

Key: must consider $\Delta\bar{G}_{\text{rxn}}$ not $\Delta\bar{G}^0_{\text{rxn}}$

If $P_{\text{NO}} = 0$, $\ln 0 = -\infty$

$$\Delta\bar{G}_{\text{rxn}} = \Delta\bar{G}^0_{\text{rxn}} + RT\ln\frac{P^2_{\text{NO}}}{P_{N_2}P_{O_2}}$$

$\Rightarrow \Delta G_{\text{rxn}} = -\infty$

Spontaneous!

$$K_P(T) = \exp\left[\frac{-\Delta\bar{G}^0_{\text{rxn}}(T)}{RT}\right] = \exp\left[\frac{-173{,}100\ \text{J/mol}}{(8.314\ \text{J/(K}\cdot\text{mol)})\times 298\ \text{K}}\right] = e^{-69.9} = 4.5\times 10^{-31}$$

$$K_P(T) = \frac{P^2_{\text{NO}}}{P_{N_2}P_{O_2}} = 4.5\times10^{-31} \Rightarrow P_{\text{NO}} = 3.1\times10^{-16}$$

~1 billion NO molecules in 245 Olin

Aside: Should We Be Concerned About Toxic NO in the Classroom?

Nitric oxide is important for your cardiovascular system. NO is a vasodilator;
NO relaxes the inner muscles of your blood vessels, causing the vessels to widen.
In this way, nitric oxide increases blood flow and lowers blood pressure.
NO also inhibits the aggregation of platelets and prevents thrombotic events.

Nitric oxide is important for your nervous system. NO acts as a neurotransmitter, including in the autonomic nervous system. NO increases cerebral blood flow and oxygenation to the brain.

Nitric oxide is important for your lungs. NO dilates pulmonary vessels.

Nitric oxide is important for your gastrointestinal tract. NO regulates the relaxation of smooth muscles to control peristalsis and the function of the sphincter.

And more!
See "Role of Nitric Oxide in Biology and Physiology." by the National Institutes of Health:
https://pubmed.ncbi.nlm.nih.gov/9622410/

Science magazine pronounced NO as the "Molecule of the Year" in 1992.

Research into the biological functions of NO
awarded the Nobel Prize in Physiology and Medicine in 1998

Why Are Phase Transitions Different From Chemical Transitions?

The entropy of mixing!   Phases do not mix, but reactants and product mix!

Consider an isomerization reaction:

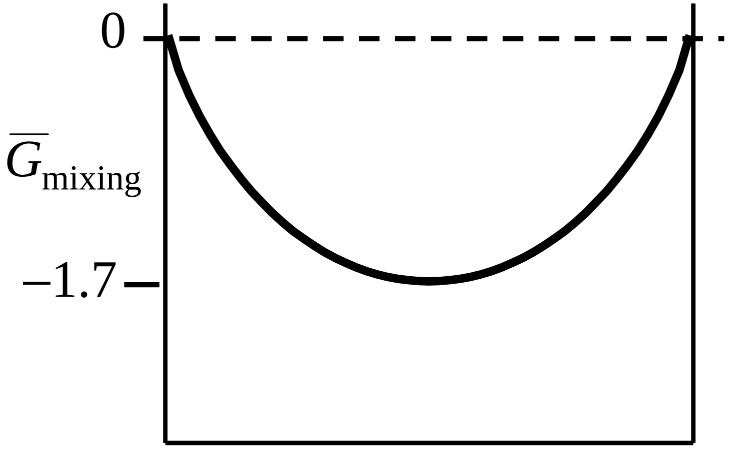
2-butene   1-butene

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

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

$$\text{Recall } \overline{G}_{\text{mixing}} = \frac{RT}{n_A + n_B}(n_A \ln y_A + n_B \ln y_B)$$

$$\text{at } y_A = y_B = 0.5, \ \overline{G}_{\text{mixing}} = -1.7 \text{ kJ/mol at 298K}$$



extent of rxn, ξ

Equilibrium in 2-butene ↔ 1-butene

2-butene 1-butene

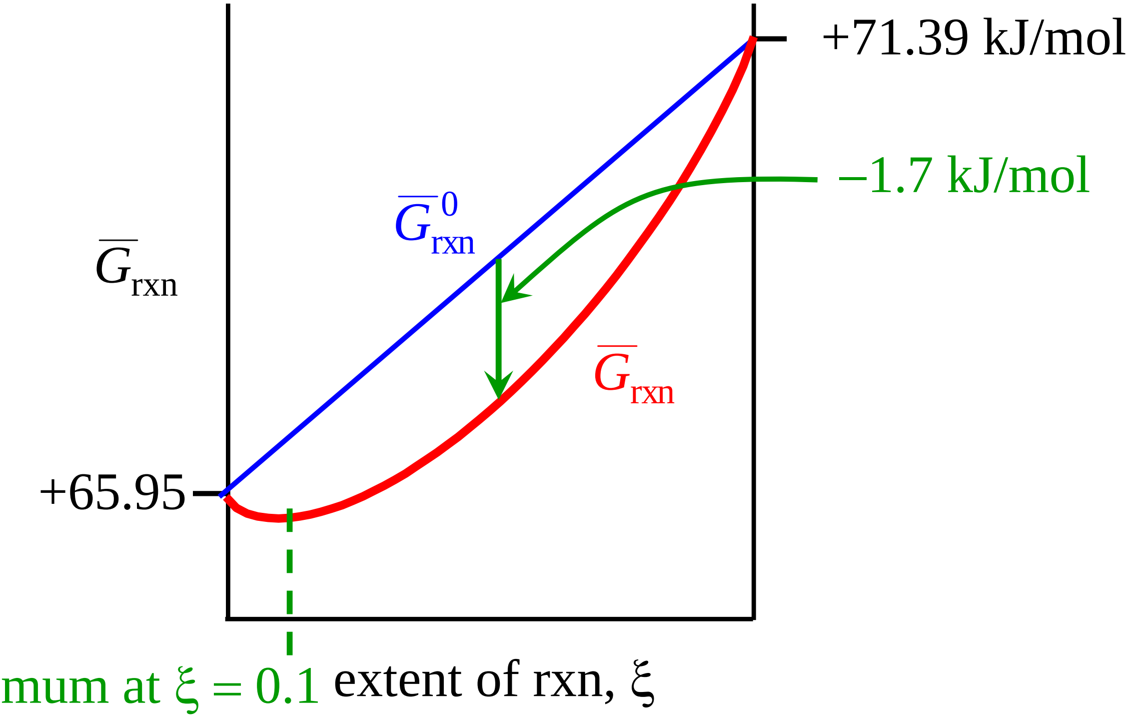
$$CH_3{-}CH{=}CH{-}CH_3 \leftrightarrow CH_2{=}CH{-}CH_2{-}CH_3 \qquad \Delta\overline{G}^0_{rxn} = +5.44 \text{ kJ/mol}$$

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

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

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

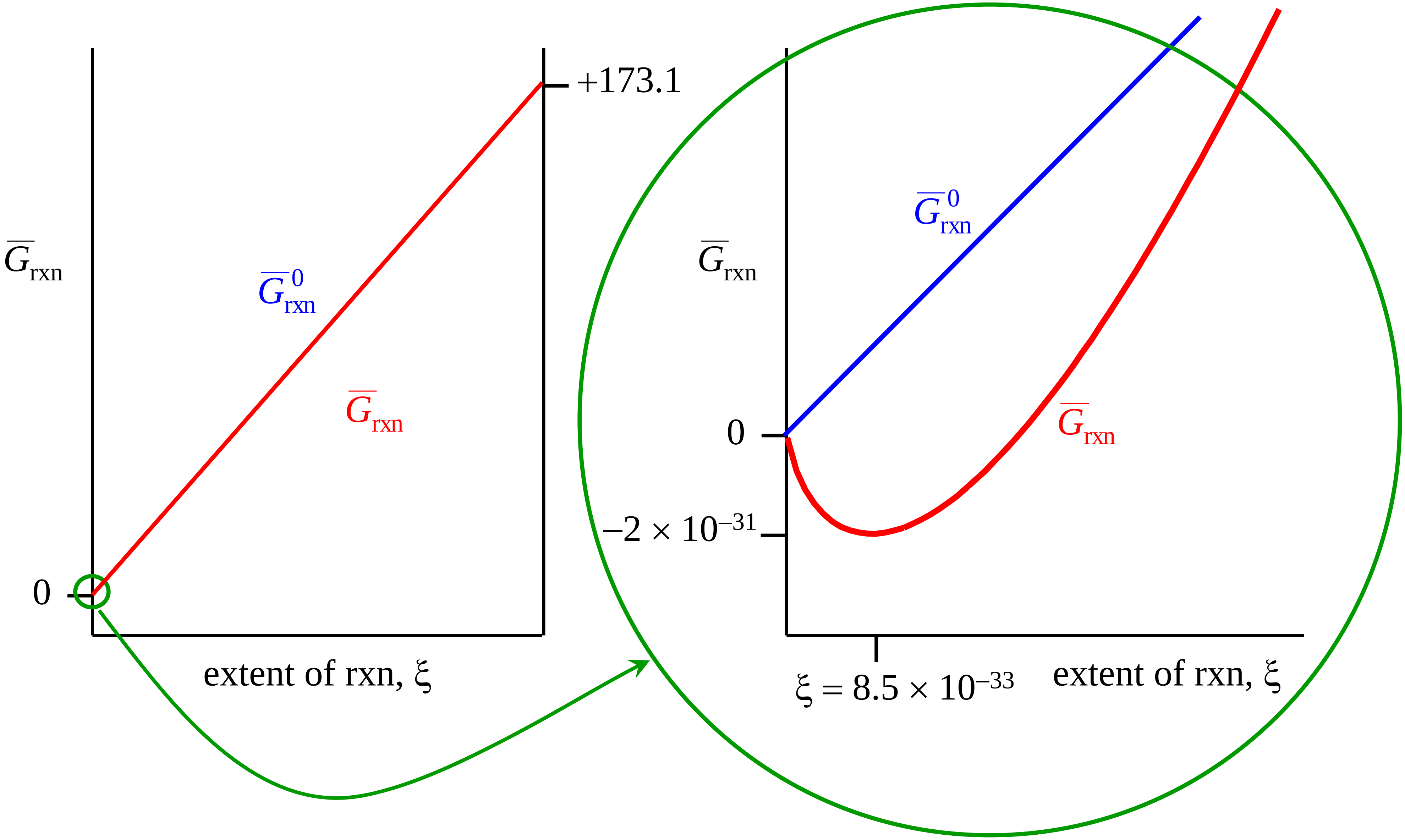
At $P_{total} = 1$ atm, $P_{1\text{-butene}} = 0.1$ atm and $P_{2\text{-butene}} = 0.9$ atm



Equilibrium in $N_2 + O_2 \leftrightarrow 2NO$

$N_2(g) + O_2(g) \leftrightarrow 2NO(g)$ $\Delta\overline{G}^0_{rxn} = +173.1$ kJ/mol

$\Delta\overline{G}^0_{formation}$: 0 0 +173.1



newscripts

CHEMISTRY TATTOOS

Two months ago, on the social media site Reddit, a user called Dolonotikz posted a picture of his **NEW TATTOO,** along with a note rebuffing commenters who said he would regret it.

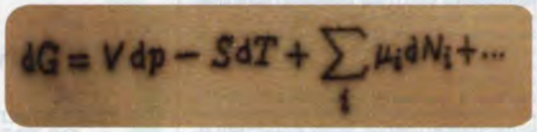
The tattoo is a line structure of MDMA, the active ingredient in the club drug Ecstasy.

Except that it isn't. The structure is wrong, with only two double bonds in what should be the central benzene ring. The photo quickly made its way onto the chemistry section of the site, where the Chemistry Reddit community proceeded to detail and debate the exact route by which the erroneous molecule would break down. Commenters also suggested ways that a skilled tattoo artist could correct the structure.

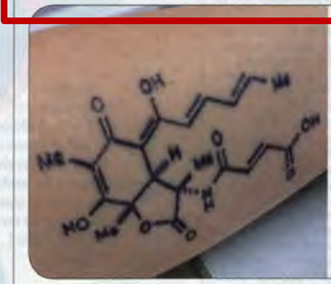
The Newscripts gang knew our readers could do better with structural accuracy, so we asked them to share their own chemical tattoos on Reddit, Twitter, and Facebook. Here are a few of our favorites.

Mirror twins Elliot and Darryl Glotfelty, who both hold degrees in chemistry, have these matching tattoos of D- and L-glucose, respectively. "My twin brother will be joining the Peace Corps in June, and I will be moving to Thailand in April to volunteer with a nongovernmental organization," says Elliot. "The longest we have ever been apart is nine days," he adds, indicating that the tattoos will be a "bond" for the pair while they're on separate continents.

Todd W. Hudnall, an assistant chemistry professor at Texas State University, San Marcos, was a boron chemist in graduate school. During his studies, he carried out nuclear magnetic resonance spectroscopy on boron-11, an isotope he'll never have trouble remembering.



Graduate student Daniel M. Dryden explains the differential thermodynamic equation tattooed on his shoulder thusly: "For anything that has happened on the surface of Earth, from the formation of this ball of rock to the first replication of RNA to me hitting 'save' at the end of this post, the thermodynamic driving force behind it all was a reduction in Gibbs free energy."



Chemistry grad student Kelly Volp published a total synthesis of the marine natural product sorbicillactone A during her third year of graduate school. To celebrate, she got a tattoo of the molecule, which was found to have anti-HIV and antileukemia activity.

CRAIG BETTENHAUSEN *wrote this week's column. Please send comments and suggestions to newscripts@acs.org.*

& PHOTOS ONLINE To see more tattoos, visit http://cenm.ag/tattoo.

REDDIT (MDMA), COURTESY OF ELLIOT GLOTFELTY (GLUCOSE), COURTESY OF TODD HUDNALL (BORON), COURTESY OF DANIEL DRYDEN (GIBBS), COURTESY OF KELLY VOLP (SORBICILLACTONE)