# Which equilibrium model fits the evidence?

Week 7 · After-midterm problem workshop

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# Bring one question from Week 6

Open your Lab 13 notes. Which step would you like to see worked again?

Take one minute to write the step and the value or sign you expected. Compare with a partner, then bring one question to the class discussion.

To get started, consider identical electrodes with unequal ion activities. How could you predict which way the reversible cell would run?

# Plan for the workshop

| Minutes | Work with a partner |
|---|---|
| 0–15 | Resolve a question from Week 6. |
| 15–50 | Calculate two phase fractions and check which phases coexist. |
| 50–80 | Account for the gas inventory in two vessels. |
| 80–90 | Break. |
| 90–135 | Predict the direction of a cell reaction and check its voltage. |
| 135–172 | Change one condition, run a lab, and exchange results. |
| 172–180 | Complete the Week 7 exit ticket (5 min) and the after-midterm feedback survey (3 min). |

# Which fraction of the feed becomes vapor?

At 350 K, an ideal binary mixture has $P_1^{\mathrm{sat}} = 150$ kPa and $P_2^{\mathrm{sat}} = 60$ kPa. The feed contains $z_1 = 0.40$ and the pressure is 90 kPa.

1. Use $P = x_1 P_1^{\mathrm{sat}} + (1 - x_1) P_2^{\mathrm{sat}}$ and $y_1 = x_1 P_1^{\mathrm{sat}} / P$ to find the liquid and vapor compositions.
2. Find the mole fraction of the feed that is vapor, $\beta = (z_1 - x_1)/(y_1 - x_1)$.
3. Open **Teaching binary · synthetic** in Lab 01. Its vapor pressures are supplied by the lab. Select the ideal liquid, set the feed and conditions above, and select **Calculate equilibrium**. Verify the overall composition on paper.

Open Lab 01 · VLE and flash

# What if the compositions came from an experiment?

Suppose the measured values at 350 K are $x_1 = 1/3, y_1 = 5/9$ and $P = 90$ kPa. Assume ideal vapor, negligible Poynting correction, and a pure-liquid standard state.

1. Use $\gamma_1 = y_1 P/(x_1 P_1^{\mathrm{sat}})$. Compare the values inferred using 150 and 120 kPa for $P_1^{\mathrm{sat}}$. Which measured quantity changed?
2. Before choosing an Antoine correlation, identify its log base, temperature and pressure units, and valid temperature range.
3. A model fits these data closely. What additional evidence would you seek across compositions to assess thermodynamic consistency?

# Which fraction forms the second liquid?

Now consider a different binary mixture. The one-parameter Margules model has $A = 3$ and the overall mole fraction is $z_1 = 0.18$.

1. In Lab 04 choose **Margules · 1 parameter**, enter $A = 3$ and $z_1 = 0.18$, then select **Find equilibrium**. Read both liquid compositions from the common tangent.
2. Use the lever rule to calculate the mole fraction of the feed in the liquid richer in component 1. Reconstruct the feed from the two endpoint compositions.
3. Compare the common tangent with the homogeneous curve at $z_1 = 0.18$. Which state has lower Gibbs energy?

Open Lab 04 · Liquid stability

# Check the phases against the feed

| Result | Independent check |
|---|---|
| Flash at 90 kPa. $x_1 = 0.3333, y_1 = 0.5556, \beta = 0.3000$. | $0.70(0.3333) + 0.30(0.5556) \approx 0.4000$. |
| LLE with $A = 3$. The liquids have $x_1 = 0.07072$ and $0.92928$. The fraction in the richer liquid is $0.1273$. | $0.8727(0.07072) + 0.1273(0.92928) \approx 0.1800$. The common tangent lies below the homogeneous liquid at this feed. |

**Week 2–3 data check.** $\gamma_1 = 1.00$ or $1.25$. The measured $x_1, y_1, P, T$ are the same. A small fitting residual measures agreement with the chosen model. Apply a Gibbs–Duhem consistency test appropriate to the experimental path and inspect the local residuals.

# Can the vessel reach 10 kPa?

A closed vessel contains 0.0086712 mol of A at 300 K. The free gas volume is 1.00 L. Treat the gas as ideal and use $R = 8.31446$ L kPa mol$^{-1}$ K$^{-1}$.

**Vessel A.** Pure solid A can sublime. Its sublimation pressure is 10.0 kPa at this temperature. Calculate how many moles are needed in the gas to reach this pressure. How many remain as bulk solid?

**Vessel B.** The inventory of A can occupy the gas or adsorb onto 10.0 g of a separate adsorbent. Use absolute Langmuir uptake $q = q_s b P_A/(1 + bP_A)$, with $q_s = 2.00$ mol kg$^{-1}$ and $b = 0.100$ kPa$^{-1}$. Try $P_A = 5.00$ kPa. Does the inventory close?

# Test what happens when adsorbent mass doubles

In Lab 11, select **Reset synthetic parameters**. Use Langmuir at 300 K, 1 L free gas volume, 10 g adsorbent, 0.0086712 mol total adsorbate, and zero inert gas.

1. Select **Compare & solve vessel** and record $P_A$, the gas moles, and the adsorbed moles.
2. Predict the pressure at 20 g relative to its value at 10 g. Change only the adsorbent mass, recalculate, and check $n_A^g + m_s q$.
3. Compare the roles of the two solids. What sets $P_A$ while bulk solid A remains in vessel A? Which equation sets it in vessel B?

Open Lab 11 · Adsorption

# Follow the material in each vessel

| Vessel | $P_A$ (kPa) | Gas (mol) | Bulk solid or adsorbed A (mol) |
|---|---|---|---|
| A · Pure solid present | 10.00 | 0.0040091 | 0.0046621 in the solid |
| B · 10 g adsorbent | 5.000 | 0.0020045 | 0.0066667 adsorbed |
| B · 20 g adsorbent | 2.389 | 0.0009578 | 0.0077134 adsorbed |

For vessel B at 10 g, $q(5.00) = 0.6667$ mol kg$^{-1}$. Multiplying by 0.0100 kg gives the amount on the surface. Check that each row accounts for 0.0086712 mol of A.

# Which electrode would gain metal?

At 298.15 K, both electrodes use $\mathrm{M^{2+}/M}$. Take oxidation on the left, reduction on the right, and zero junction potential. If the circuit is closed, deposition can occur at the electrode undergoing reduction. Use $a_L = 0.040$ and $a_R = 0.40$.

1. Write the reaction, keeping each species in its own compartment. Which ion activity belongs in the numerator of $Q$?
2. The standard cell potential is zero. What is $K$? Compare $Q$ with $K$ to predict the direction and which electrode gains metal.
3. Calculate $E = E^\circ - (0.05915935\ \mathrm{V}/n)\log_{10} Q$ and $\Delta_r G = -nFE$. Use $n = 2$ and $F = 96485\ \mathrm{C\ mol^{-1}}$.

# Run the three cell conditions

In Lab 13, select **Concentration-cell example**, then **Direct dimensionless activities**. In each $\mathrm{M}^{2+}$ row, edit the **value** column. Keep $\gamma = 1$ and the pure-metal entries at 1.

| Case | Left activity | Right activity | Before selecting **Calculate cell** |
|---|---|---|---|
| Original | 0.040 | 0.40 | Record your predicted sign and voltage. |
| Exchanged | 0.40 | 0.040 | Predict which electrode now gains metal. |
| Equal | 0.40 | 0.40 | Predict $Q$ and $E$. |

Compare the lab's potential with your own $RT\ln(Q/K)$ check on the reaction Gibbs energy.

Open Lab 13 · Electrochemical equilibrium

# Check the direction before rounding

For left oxidation and right reduction, the dissolved ion is produced on the left and consumed on the right, so $Q = a_L/a_R$. Identical electrodes give $E^\circ = 0$ and $K = 1$.

| Case | $Q$ | $E$ (mV) | $\Delta_r G$ (kJ per mol of reaction as written) | Deposition if the cell runs |
|---|---|---|---|---|
| Original | 0.10 | $+29.58$ | $-5.708$ | Right electrode |
| Exchanged | 10 | $-29.58$ | $+5.708$ | Left electrode |
| Equal | 1 | 0 | 0 | No net deposition |

For the original case, $RT\ln(0.10) = -5.708$ kJ mol$^{-1}$. Write one sentence connecting that sign to the observed cell polarity.

# Change one condition and exchange your result

Choose one case and predict the outcome before touching its controls.

| Choose one lab | Change this condition |
|---|---|
| Lab 01 · Flash | Raise $P$ from 90 to 100 kPa at the same $T$ and $z_1$. Which phase or phases remain? |
| Lab 11 · Adsorption | Keep 20 g of adsorbent and double the total inventory. Predict the direction of the pressure change. |
| Lab 13 · Cell | In the original case, double both ion activities. Does the activity ratio change? Predict the voltage. |

Allow 20 minutes to calculate and test. Use 10 minutes to exchange cases with another pair and reproduce their result. In the final 7 minutes, share one result and one check the class can repeat.

# Week 7 exit ticket and after-midterm feedback

**5 min · Exit ticket for today’s workshop**

Choose one case from today. Give a result with its units, or state that it is dimensionless. Explain what it means and name an independent check or a limitation.

**3 min · Feedback on all of Weeks 1–7**

Rate the overall pace after the midterm. Which resource helped you most? Name one thing to keep or change.

Complete both parts in the same form.

Scan to open the Week 7 exit ticket and whole after-midterm feedback survey.

Open the Week 7 form