

A-C. Phases, constraints and inventory

Solutions page 1 | Check only after attempting the corresponding worksheet questions. All numerical cases are synthetic.

A. Describe the physical system first

A1. (i) SLE: pure solid plus liquid solution; (ii) bulk GSE: solid plus vapor; (iii) adsorption: gas exchanges molecules with a surface-associated phase, represented by uptake. None of these descriptions requires a chemical reaction. **A2.** Stable equilibrium minimizes Helmholtz energy at fixed T,V and conserved total amounts. Week 3 used Gibbs energy at fixed T,P. Pressure is an output in the rigid vessel.

A3. For ideal gases at fixed T,V, adding nonreacting, nonsorbing inert gas changes total pressure but not volatile partial pressure or the volatile gas/solid amounts. While solid remains, $P_A = P_{\text{sub}}$. This conclusion need not hold for a pressure-controlled vessel or a nonideal mixture.

B. Saturated liquid composition

$\ln x = -(10000/8.314462618)(1/300 - 1/350) = -0.5727255$; $x = 0.5639862$. This is a saturated liquid mole fraction, not the liquid phase fraction or remaining solid amount. An inventory balance is needed for amounts. With nonideal liquid, solve $x\gamma = x_{\text{ideal}}$ using a stated activity model. The pure solid has unit activity on its own standard state; the subcooled-liquid reference accounts for the fusion free-energy difference.

C1-C2. Independent GSE case

At 300 K and $V=2$ L, $P_{\text{sub}}=8$ kPa gives $n_{\text{cap}}=8 \times 2 / (8.314462618 \times 300) = 0.00641452560$ mol. Adding 0.001 mol inert gas gives $P_{\text{inert}}=1.247169393$ kPa.

nA / mol	ngas / mol	nsolid / mol	PA / kPa	Ptotal with inert / kPa
0.010	0.006414526	0.003585474	8.000000	9.247169
0.004	0.004000000	0	4.988678	6.235847

Both balances recover the supplied volatile inventory. The larger inventory supports solid plus vapor; the smaller gives vapor only. With no inert gas, $P_{\text{total}}=P_A$. Adding inert leaves the four volatile quantities unchanged and adds its partial pressure to P_{total} .

C3. Equality is conditional on phase presence

For the solid-present case, $\ln(P_A/P_{\text{sub}})=0$. For the depleted case, $\ln(4.988677571/8) \approx -0.472271$. Moving a hypothetical infinitesimal amount from solid into the gas would lower free energy, but no solid is available. The nonnegative solid-amount constraint is active, so this inequality is compatible with equilibrium.

At $n_A=n_{\text{cap}}$ exactly, the gas is saturated with zero remaining solid. This is the depletion boundary; an infinitesimal excess inventory creates solid without changing P_A at the specified T,V. Do not claim a positive solid amount from pressure equality alone.

D. Lab 10 evidence and numerical checks

Solutions page 2 | Lab 10 at $T=T_{\text{ref}}=300\text{ K}$, $V=1\text{ L}$ and $P_{\text{ref}}=P_{\text{sub}}=10\text{ kPa}$. $\Delta H_{\text{sub}}=50000\text{ J/mol}$.

The capacity is $n_{\text{cap}}=10/(8.314462618 \times 300)=\mathbf{0.004009078501\text{ mol}}$. The 250-350 K declared correlation range is retained for the plots. These synthetic properties are not assigned to a real substance.

Case	10A	10B	10C
nA / mol	0.010	0.002	0.002
ninert / mol	0	0	0.002
ngas / mol	0.004009079	0.002	0.002
nsolid / mol	0.005990921	0	0
PA / kPa	10.000000	4.988678	4.988678
Ptotal / kPa	10.000000	4.988678	9.977355
Present phases	Solid + vapor	Vapor only	Vapor only

D1-D3. Interpret the controlled changes

From 10A to 10B, the inventory drops below n_{cap} . All 0.002 mol are in the gas, so $P_A=n_A R T/V=\mathbf{4.988677571\text{ kPa}}$, below P_{sub} . From 10B to 10C, the added inert gas contributes another **4.988677571 kPa**. P_A remains unchanged; P_{total} becomes **9.977355142 kPa**.

An independent balance gives $0.004009078501+0.005990921499=0.010$ for 10A, and $0.002+0=0.002$ for 10B/10C. The inert gas belongs in its own balance, not in the volatile gas-plus-solid sum.

The plots vary temperature at fixed specified inventories and free gas volume. While solid remains, actual partial pressure follows $P_{\text{sub}}(T)$. Once the finite inventory is entirely gaseous, P_A follows $n_A R T/V$. The amount plot transfers inventory between gas and solid while preserving their sum. Plot gaps can reflect the pressure guard rather than a physical discontinuity.

D4. What a useful saved record contains

Keep the original prediction, model/property definitions, T, V , inventories, phase label, pressures, amount balance and one annotated plot. A JSON file preserves numerical evidence and controls. Restoring controls does not itself establish a current result: verify inputs and click **Calculate equilibrium** →.

A correct balance and equality while solid is present verify the admitted teaching model. They do not establish real-property accuracy, kinetics, a solid-solution model, adsorption behavior or the absence of liquid formation outside the declared conditions.

E-G. Uptake and closed-vessel balance

Solutions page 3 | $T=300\text{ K}$; $q_s=2\text{ mol/kg}$, $b=0.1\text{ kPa}^{-1}$ and matched Henry $K=0.2\text{ mol kg}^{-1}\text{ kPa}^{-1}$.

P / kPa	Langmuir q / mol kg ⁻¹	Henry q / mol kg ⁻¹	Langmuir θ
5	0.6666667	1.000000	0.3333333
40	1.600000	8.000000	0.8000000

E2-E3. $bP=0.5$ and 4 , so neither is the asymptotic $bP \ll 1$ limit. $KH=q_s b$ matches the initial slope, not the full curve. Langmuir approaches $q_s=2\text{ mol/kg}$; Henry increases without bound and is a low-pressure approximation. Model agreement with observations alone does not prove a microscopic site mechanism.

F. Known-pressure example and predictions

At $P=10\text{ kPa}$, Langmuir $q=1\text{ mol/kg}$. With $V=1\text{ L}$ and $m_s=0.010\text{ kg}$, $n_{\text{gas}}=\mathbf{0.004009078501\text{ mol}}$ and $n_{\text{ads}}=\mathbf{0.010000\text{ mol}}$, requiring $n_A=\mathbf{0.014009078501\text{ mol}}$. Lab 11 instead uses 0.010 mol total, so F1 predicts $P<10\text{ kPa}$. At positive P the matched Henry model gives more uptake than Langmuir, so F2 predicts a lower closed-vessel pressure. Adding more adsorbent at fixed inventory lowers P in F3.

G1-G2. Actual Lab 11 cases, $n_A=0.010\text{ mol}$

Case	P / kPa	q / mol kg ⁻¹	n_{gas} / mol	n_{ads} / mol
11A: Langmuir / 10 g	6.080248	0.7562381	0.002437619	0.007562381
11B: Henry / 10 g	4.165091	0.8330182	0.001669818	0.008330182
11C: Langmuir / 20 g	2.844978	0.4429713	0.001140574	0.008859426

For 11A: $q=2(0.1 \times 6.080247972)/(1+0.1 \times 6.080247972)=0.7562380857\text{ mol/kg}$.
 $n_{\text{gas}}=6.080247972/(8.314462618 \times 300)=0.002437619143\text{ mol}$; $n_{\text{ads}}=0.010 \times 0.7562380857=0.007562380857\text{ mol}$.
 Their sum is $0.010000000000\text{ mol}$. The same substitutions close 11B/11C; use 0.020 kg in 11C.

G3. Doubling mass lowers pressure and q per kg, but increases total adsorbed moles from 0.00756238 to 0.00885943 mol because there are more kg of adsorbent. The gas amount correspondingly falls. These fixed-T equilibrium models give no uptake rate or thermal transient.

G4. Save each model study and a Lab 11 comparison JSON. After importing and restoring, verify model, parameters, mass, inventory and pressure units, then click **Compare & solve vessel** →. Report unavailable roots as unavailable, not zero; do not extrapolate merely to obtain a numerical answer.

H-I. New cases and supported conclusions

Solutions page 4 | Open only after completing the independent H1-H4 attempt.

H1-H2. A new GSE vessel

At $T=310\text{ K}$, $V=2\text{ L}$ and $P_{\text{sub}}=5\text{ kPa}$, $n_{\text{cap}}=10/(8.314462618 \times 310)=\mathbf{0.003879753388\text{ mol}}$. For 0.001 mol inert gas, $P_{\text{inert}}=\mathbf{1.288741706\text{ kPa}}$.

n_A / mol	$n_{\text{gas}} / \text{mol}$	$n_{\text{solid}} / \text{mol}$	P_A / kPa	$P_{\text{total with inert}} / \text{kPa}$
0.002	0.002000000	0	2.577483	3.866225
0.008	0.003879753	0.004120247	5.000000	6.288742

The first case is vapor only and undersaturated; the second contains solid plus vapor with $P_A=P_{\text{sub}}$. Adding ideal inert gas at fixed free volume changes only total pressure. Equal chemical potentials are required between phases that coexist, while the absent-solid case obeys the appropriate inequality.

H3. A new known-pressure adsorption case

At $P=20\text{ kPa}$, $bP=0.05 \times 20=1$. Thus $q=3 \times 1/(1+1)=\mathbf{1.5\text{ mol/kg}}$. At $T=310\text{ K}$ and $V_g=2\text{ L}$: $n_{\text{gas}}=20 \times 2/(8.314462618 \times 310)=\mathbf{0.015519013554\text{ mol}}$.

With $m_s=5\text{ g}=\mathbf{0.005\text{ kg}}$, $n_{\text{ads}}=0.005 \times 1.5=\mathbf{0.0075\text{ mol}}$. The required total inventory is $n_A=0.015519013554+0.0075=\mathbf{0.023019013554\text{ mol}}$. The matched Henry slope would be $q_s b=0.15\text{ mol kg}^{-1}\text{ kPa}^{-1}$, but the requested calculation uses Langmuir.

H4. Direction without solving a new root

At the old pressure, doubling mass doubles m_{sq} while the gas term stays fixed, exceeding the fixed total inventory. Both gas amount and Langmuir uptake increase monotonically with pressure, so the new equilibrium pressure must be **lower**. A numerical root is not required. Uptake per kg falls, while total adsorbed amount rises as the gas amount decreases.

Both teaching calculations use ideal gas and fixed T /free volume with an inventory balance. Bulk sublimation relates a present pure solid to vapor through P_{sub} ; adsorption uses a surface uptake relation and the mass of adsorbent. Neither model predicts reaction equilibrium or kinetics.

I. Report evidence and actual study time

Use the Session 4 concept question for the finite-inventory/partial-pressure explanation. Include one Lab 10 comparison and one Lab 11 numerical balance in the evidence answer. Add actual minutes, pacing and a remaining question in feedback. Submit once at slide 39 and wait for "Response received"; verify the receipt and save your work at slide 40. The anonymous form does not identify individual attendance.

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