ChemE 2200 – Chemical Thermodynamics Lecture 7

Today:

Analysis with combined 1st and 2nd Laws.
The 3rd Law of Thermodynamics.
Analysis of a Partial Separator

Defining Question:

What criteria must be satisfied for any chemical process?

Reading for Today's Lecture:

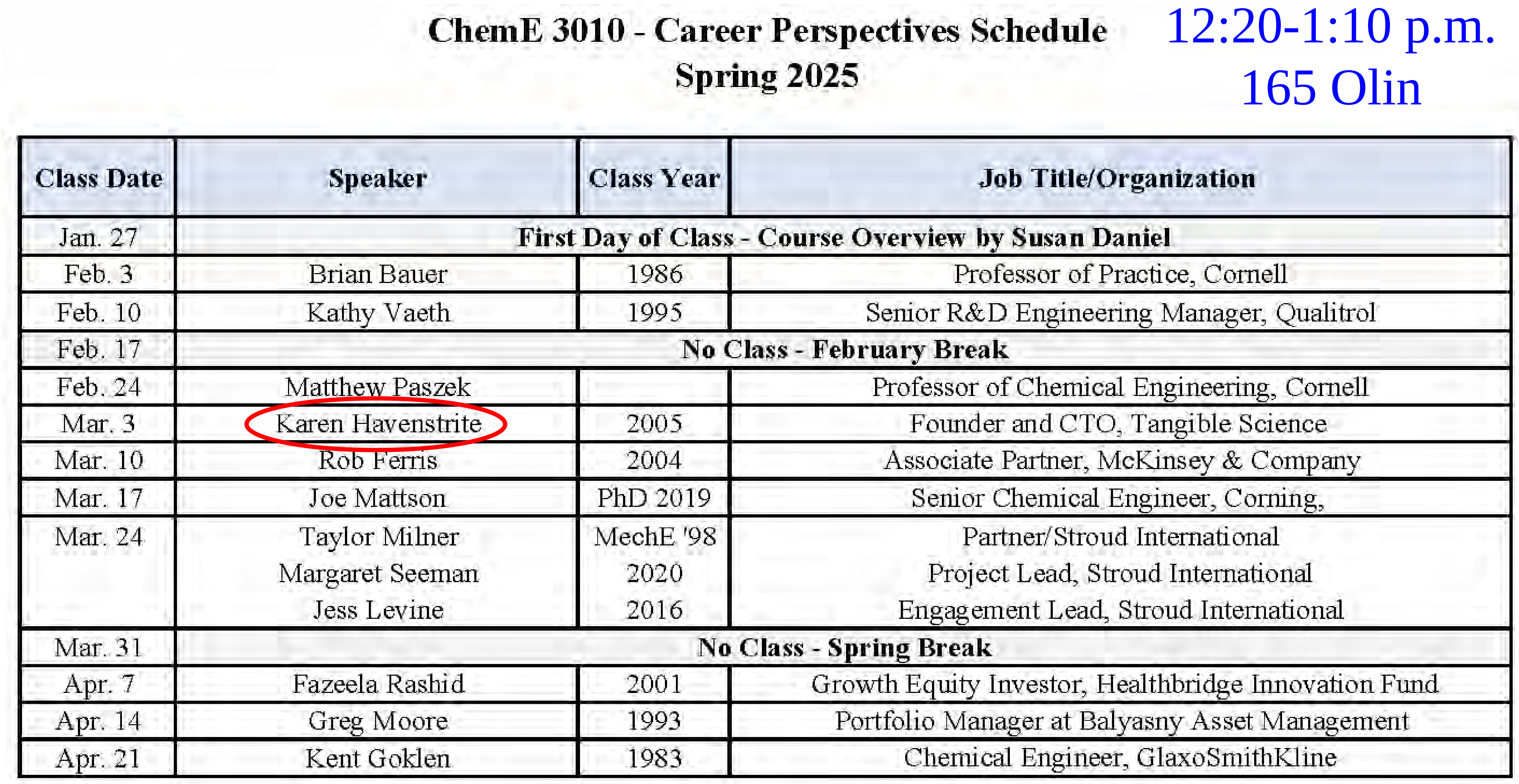
McQuarrie & Simon, Chapter 21.1-21.5, 21.7.

Reading for Thermodynamics Lecture 11:

McQuarrie & Simon, Chapter 21.9, 22.1-22.3

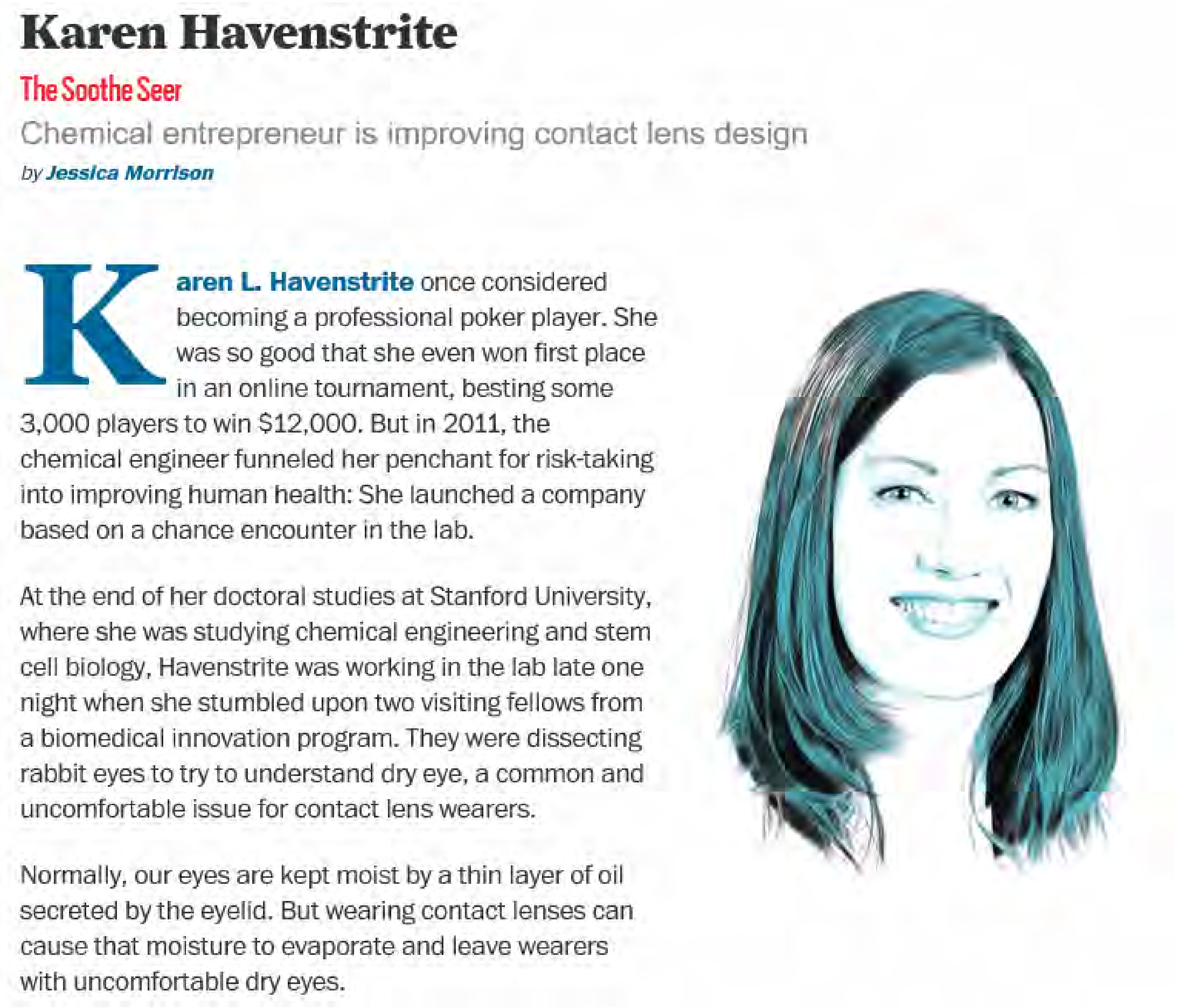
Career Guidance

Mondays
12:20-1:10 p.m.
165 Olin



ChemE 3010 - Career Perspectives Schedule
Spring 2025

Class Date	Speaker	Class Year	Job Title/Organization
Jan. 27	**First Day of Class - Course Overview by Susan Daniel**		
Feb. 3	Brian Bauer	1986	Professor of Practice, Cornell
Feb. 10	Kathy Vaeth	1995	Senior R&D Engineering Manager, Qualitrol
Feb. 17	**No Class - February Break**		
Feb. 24	Matthew Paszek		Professor of Chemical Engineering, Cornell
Mar. 3	Karen Havenstrite	2005	Founder and CTO, Tangible Science
Mar. 10	Rob Ferris	2004	Associate Partner, McKinsey & Company
Mar. 17	Joe Mattson	PhD 2019	Senior Chemical Engineer, Corning,
Mar. 24	Taylor Milner Margaret Seeman Jess Levine	MechE '98 2020 2016	Partner/Stroud International Project Lead, Stroud International Engagement Lead, Stroud International
Mar. 31	**No Class - Spring Break**		
Apr. 7	Fazeela Rashid	2001	Growth Equity Investor, Healthbridge Innovation Fund
Apr. 14	Greg Moore	1993	Portfolio Manager at Balyasny Asset Management
Apr. 21	Kent Goklen	1983	Chemical Engineer, GlaxoSmithKline



Karen Havenstrite

The Soothe Seer

Chemical entrepreneur is improving contact lens design

by **Jessica Morrison**

Karen L. Havenstrite once considered becoming a professional poker player. She was so good that she even won first place in an online tournament, besting some 3,000 players to win $12,000. But in 2011, the chemical engineer funneled her penchant for risk-taking into improving human health: She launched a company based on a chance encounter in the lab.

At the end of her doctoral studies at Stanford University, where she was studying chemical engineering and stem cell biology, Havenstrite was working in the lab late one night when she stumbled upon two visiting fellows from a biomedical innovation program. They were dissecting rabbit eyes to try to understand dry eye, a common and uncomfortable issue for contact lens wearers.

Normally, our eyes are kept moist by a thin layer of oil secreted by the eyelid. But wearing contact lenses can cause that moisture to evaporate and leave wearers with uncomfortable dry eyes.

Chemical & Engineering News, *The Talented Twelve*, 2015

1st Prelim

Tuesday, March 11, 7:30 – 9:30 p.m.

245 Olin Hall

Covers –
- Atomic Orbitals
- Molecular Orbitals
- Atomic and Molecular Spectroscopy
- Electrons in Solids
- Classical Thermodynamics through 1st Law

Covers –
- Lectures through 1st half of Monday, 2/24 (Lecture T4)
- Homework through Homework 5
- Calculation Sessions through Calculation Session 5

You may use a hand-written, double-sided reference sheet.
Reference sheets will be submitted with the Prelim.
Reference sheets will be returned Wednesday, March 12.

ChemE 2200 – Physical Chemistry II for Engineers
Calculation Session 8 – March 15, 2023 – Team Competition
How well do you know the ChemE Class of 2025?

Team
Competition
Wednesday
March 12:
“How well
Do you know
Your peers?”

Use each of the following names exactly once to match the student names with their unique traits.

Joey Armstrong
Gina Bae
Kenneth Burnett
Curtis Chen
Alina Chisti
Michael Constant
Bianca Davis
Ashlyn Dumaw
Roland Green
Anant Gupta
Derek Jiang
MG Kitahata
Daniel Korzukhin
Henry Lin
Lilah Lopez
Zach Marshall
Patrick Moore
Nhi Nguyen
Temilola Omojola
Jazmin Rodriguez
Gavi Schechter
William Shullich
Lauren da Silva
Sebastian Soto
Julia Sun
Abi Jo Wanek
Keri Yamaguchi

Lauren da Silva	I have 15 piercings.
Derek Jiang	I have tried 25 Cornell Dairy Ice Cream Flavors.
Abi Jo Wanek	I lived on a boat for a year.
Keri Yamaguchi	I used to be Biomedical Engineering.
Daniel Korzukhin	I am the Fall 2021 intramural soccer champ.
Curtis Chen	I was born in Canada, go to school in the United States, and live in England.
Ashlyn Dumaw	I have never had a glass of milk.
William Shullich	I have owned an orange cat my entire life.
Alina Chisti	I was detained by the police for trespassing senior year of high school.
Bianca Davis	I went to an all-girls high school.
Anant Gupta	I have traveled through 6 states in under 24 hours.
Michael Constant	I played trumpet on top of the clocktower.
Jazmin Rodriguez	Lebron James handed me a basketball on the Cleveland Cavaliers court when I was little.
Roland Green	I am a member of the Cornell Bee Club.
Nhi Nguyen	One of my eye is short-sighted, the other one is long-sighted so it makes no difference if I wear my glasses or not (I still wear them sometimes just for fun).
Joey Armstrong	I have a blue belt in Brazilian jiu-jitsu.
Henry Lin	I have a black belt in Shinko-Ryu karate.
Patrick Moore	One of my favorite small possessions is a duck band from a hen mallard.
Sebastian Soto	My three biggest fears in order are: the sky, the ocean, and ants.
Lilah Lopez	I can stand on my head, shoulders, and elbows.
MG Kitahata	I have no wisdom teeth but have had over 15 cavities so far.
Temilola Omojola	I went to a boarding school in the Netherlands for high school.
Gavi Schechter	I was stung by a stingray in Panama last winter break.
Julia Sun	I made Physics 1112 Curious Cats Tshirts and sold it to 10 people.
Kenneth Burnett	I won a “Most Outstanding Soloist” award for my jazz drum set solo.
Gina Bae	My family drove from southern California to Ithaca to drop me off for college.
Zach Marshall	I accidentally applied to Cal Poly Pomona instead of Cal Poly when applying to colleges.

Combined Results from the 1st & 2nd Laws – $U(T,V)$ and $S(T,V)$

We need to calculate ΔS to predict spontaneity for isolated systems.

To calculate ΔS, we need equations in terms of
measurable, controllable quantities – P, V, T, and N.

$$1^{\text{st}}\ \text{Law:}\quad dU = \delta q_{\text{rev}} + \delta w_{\text{rev}} \qquad \delta w_{\text{rev}} = -PdV$$

$$2^{\text{nd}}\ \text{Law:}\quad dS = \frac{\delta q_{\text{rev}}}{T} \qquad \delta q_{\text{rev}} = TdS$$

$$\therefore \boxed{dU = TdS - PdV \quad \text{for reversible processes with } PV \text{ work}}$$

Write the total differential for $U = U(T,V)$

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$TdS - PdV = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

Solve for dS

$$dS = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V dT + \frac{1}{T}\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] dV$$

Combined Results from the 1st & 2nd Laws – $U(T,V)$ and $S(T,V)$

From the previous slide

$$dS = \boxed{\frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V dT} + \boxed{\frac{1}{T}\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] dV}$$

Write the total differential for $S = S(T,V)$.

$$dS = \boxed{\left(\frac{\partial S}{\partial T}\right)_V dT} + \boxed{\left(\frac{\partial S}{\partial V}\right)_T dV}$$

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V$$

$$\boxed{\left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T}\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]}$$

0 for an ideal gas

$$\boxed{\left(\frac{\partial S}{\partial T}\right)_V = \frac{1}{T} C_V}$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T}\left[P + \cancel{\left(\frac{\partial U}{\partial V}\right)_T}\right] = \frac{P}{T} = \frac{\frac{nRT}{V}}{T} = \frac{nR}{V}$$

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

$$\int dS = \int_{T_1}^{T_2} \frac{C_V}{T} dT + \int_{V_1}^{V_2} \frac{nR}{V} dV$$

For an ideal gas,

$$dS = \frac{C_V}{T} dT + \frac{nR}{V} dV$$

$$\boxed{\Delta S = C_V \ln\frac{T_2}{T_1} + nR\ln\frac{V_2}{V_1}}$$

For an isolated ideal gas with C_V independent of T.

Combined Results from the 1st & 2nd Laws – $H(T,P)$ and $S(T,P)$

$$dH = d(U+PV) = dU + PdV + VdP \quad \text{for reversible processes}$$

Substitute $dU = TdS - PdV \;\Rightarrow\; dH = (TdS - \cancel{PdV}) + \cancel{PdV} + VdP$

$$\boxed{dH = TdS + VdP \quad \text{for reversible processes}}$$

Write the total differential for $H = H(T,P)$

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

$$TdS + VdP = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

Solve for dS

$$dS = \boxed{\frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_P dT} + \boxed{\frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right] dP}$$

Write the total differential for $S = S(T,P)$

$$dS = \boxed{\left(\frac{\partial S}{\partial T}\right)_P dT} + \boxed{\left(\frac{\partial S}{\partial P}\right)_T dP}$$

0 for an ideal gas

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_P = \frac{1}{T}C_P \qquad \left(\frac{\partial S}{\partial P}\right)_T = \frac{1}{T}\left[\cancel{\left(\frac{\partial H}{\partial P}\right)_T} - V\right] = -\frac{V}{T} = \frac{\frac{-nRT}{P}}{T} = -\frac{nR}{P}$$

Combined Results from the 1st & 2nd Laws – $H(T,P)$ and $S(T,P)$

From the previous slide $$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

For an ideal gas, $$dS = \frac{C_P}{T} dT - \frac{nR}{P} dP$$

$$\int dS = \int_{T_1}^{T_2} \frac{C_P}{T} dT - \int_{P_1}^{P_2} \frac{nR}{P} dP$$

$$\boxed{\Delta S = C_P \ln \frac{T_2}{T_1} - nR \ln \frac{P_2}{P_1}}$$

For an isolated ideal gas with C_P independent of T.

Useful equations from the previous slide:

$$\boxed{\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}} \qquad \boxed{\left(\frac{\partial S}{\partial P}\right)_T = \frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]}$$

Combined Results from the 1st & 2nd Laws

In general,
$$dU(T,V) = C_{\mathrm{V}}dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right]dV$$

$$dS(T,V) = \frac{C_{\mathrm{V}}}{T}dT + \frac{1}{T}\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]dV$$

For an ideal gas,
$$dU(T,V) = C_{\mathrm{V}}dT$$

$$dS(T,V) = \frac{C_{\mathrm{V}}}{T}dT + \frac{nR}{V}dV$$

In general,
$$dH(T,P) = C_{\mathrm{P}}dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right]dP$$

$$dS(T,P) = \frac{C_{\mathrm{P}}}{T}dT + \frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]dP$$

For an ideal gas,
$$dH(T,P) = C_{\mathrm{P}}dT$$

$$dS(T,P) = \frac{C_{\mathrm{P}}}{T}dT - \frac{nR}{P}dP$$

How Entropy Changes with Temperature

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} \quad \Rightarrow \quad dS = \frac{C_V}{T}\,dT \quad \text{at constant } V$$

$$\Delta S = \int_{S_1}^{S_2} dS = \int_{T_1}^{T_2} \frac{C_V}{T}\,dT \quad \text{at constant } V$$

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T} \quad \Rightarrow \quad dS = \frac{C_P}{T}\,dT \quad \text{at constant } P$$

$$\Delta S = \int_{S_1}^{S_2} dS = \int_{T_1}^{T_2} \frac{C_P}{T}\,dT \quad \text{at constant } P$$

To calculate an absolute *S*, we need to know *S* at 0K …

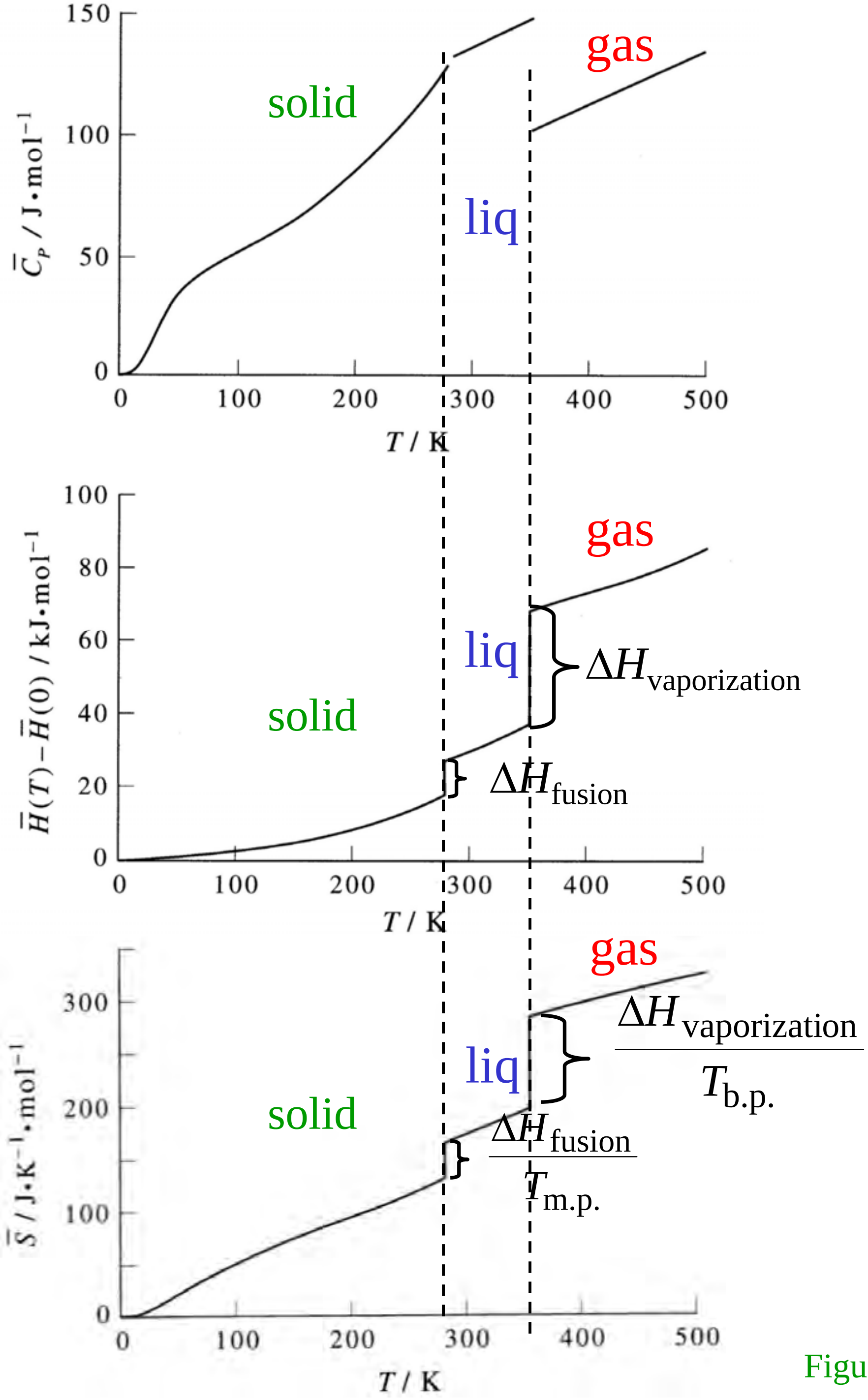
The 3rd Law of Thermodynamics: $S(0\text{K}) = 0$ for a perfect crystal.

Calculate the absolute entropy for a gas at temperature T at 1 atm.

$$S(T, 1\,\text{atm}) = \int_{0\text{K}}^{T_{\text{m.p.}}} \frac{C_{P,\,\text{solid}}}{T}\,dT + \frac{\Delta H_{\text{fusion}}}{T_{\text{m.p.}}} + \int_{T_{\text{m.p.}}}^{T_{\text{b.p.}}} \frac{C_{P,\,\text{liquid}}}{T}\,dT + \frac{\Delta H_{\text{vaporization}}}{T_{\text{b.p.}}} + \int_{T_{\text{b.p.}}}^{T} \frac{C_{P,\,\text{vapor}}}{T}\,dT$$

heat solid to melting point	melt solid	heat liquid to boiling point	evaporate liquid	heat vapor to T.

Calculating Enthalpy and Entropy for a Pure Substance: Benzene



heat capacity, C_P

enthalpy, ΔH

$$\text{slope} = \left(\frac{\partial \overline{H}}{\partial T}\right)_P = \overline{C}_P$$

entropy, S

$$\text{slope} = \left(\frac{\partial \overline{S}}{\partial T}\right)_P = \frac{\overline{C}_P}{T}$$

Figures 19.6, 19.7, and 21.2 from McQuarrie & Simon

Example Calculation – from Prelim 2, 2024

An inventor claims to have a device that separates
a 50/50 gas mixture of A + B into two gases:
(1) a gas with 20. mol% A and 80. mol% B and
(2) a gas with 80. mol% A and 20. mol% B.

No heat is delivered to the device. No work is done on the gas.

Is the inventor's device viable?
You must specify your criterion(ia) and justify your conclusion.

The input is 2.00 mol/min of a mixture with
50. mol% A and 50. mol% B at 3.00 atm and 298 K.
The two output streams are at 1.00 atm and 298 K.
You may assume mixtures of A and B are ideal diatomic gases.

Ignore the internal mechanism of the device.
State any additional assumptions.

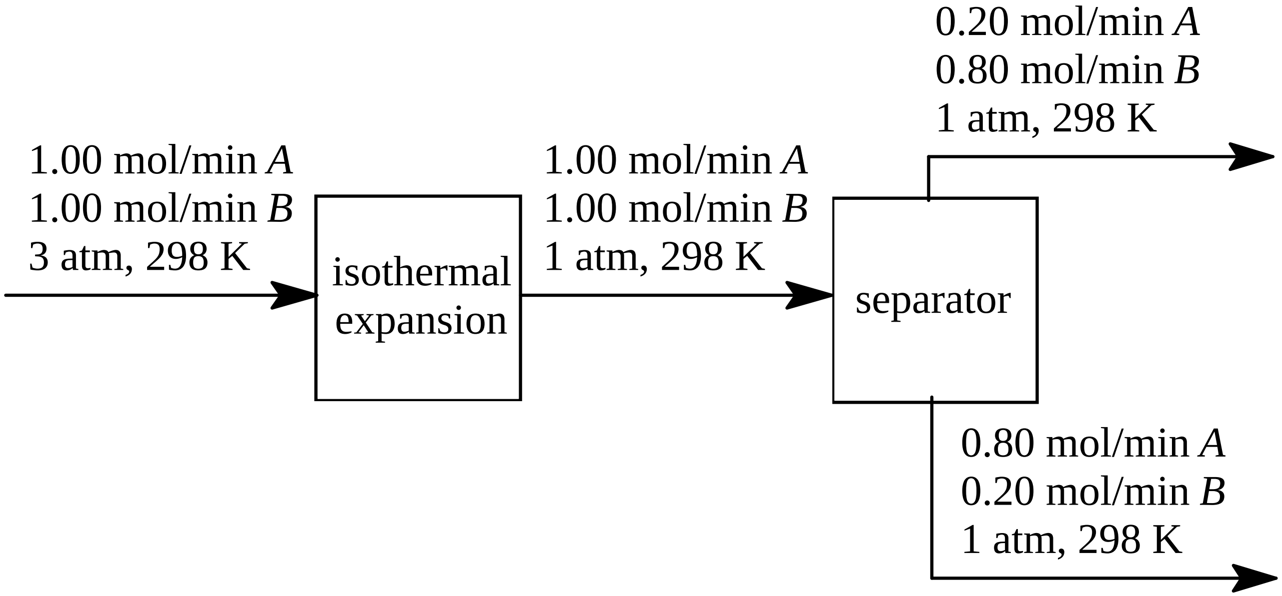
Analysis of a Partial Separator

Is the inventor’s device viable?
You must specify your criterion(ia) and justify your conclusion.

Criteria:

1. Must satisfy the 1st Law of Thermodynamics.
2. Must satisfy the 2nd Law of Thermodynamics.

Assume steady state. Sketch an equivalent unit.



1.00 mol/min *A*
1.00 mol/min *B*
3 atm, 298 K

isothermal
expansion

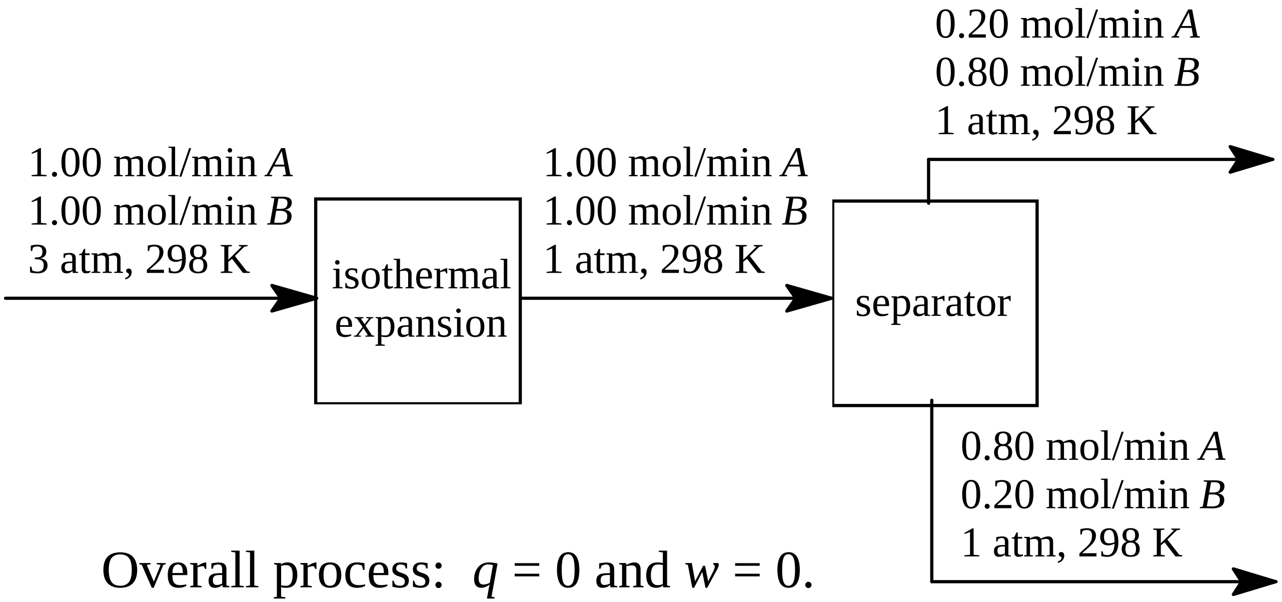
1.00 mol/min *A*
1.00 mol/min *B*
1 atm, 298 K

separator

0.20 mol/min *A*
0.80 mol/min *B*
1 atm, 298 K

0.80 mol/min *A*
0.20 mol/min *B*
1 atm, 298 K

Partial Separator – 1st Law Analysis



1.00 mol/min *A*
1.00 mol/min *B*
3 atm, 298 K

isothermal expansion

1.00 mol/min *A*
1.00 mol/min *B*
1 atm, 298 K

separator

0.20 mol/min *A*
0.80 mol/min *B*
1 atm, 298 K

0.80 mol/min *A*
0.20 mol/min *B*
1 atm, 298 K

Overall process: $q = 0$ and $w = 0$.

$$\Rightarrow \Delta U_{\text{overall}} = q + w = 0$$

1st Law Analysis of isothermal expander: $q = 0$ and $w = 0$.

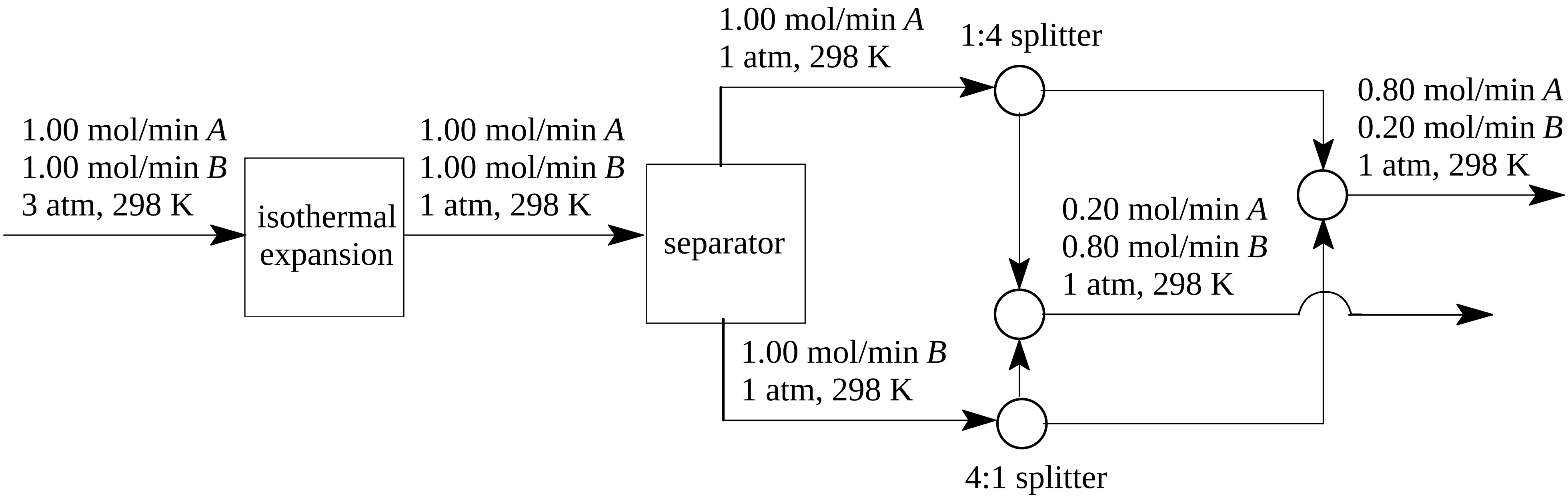
$$\text{Temperature is constant} \Rightarrow \Delta U_{\text{expansion}} = 0$$ ✓

1st Law Analysis of separator: $q = 0$ and $w = 0$.

$$\text{Temperature is constant} \Rightarrow \Delta U_{\text{separation}} = 0$$ ✓

$$\Rightarrow \Delta U_{\text{overall}} = \Delta U_{\text{expansion}} + \Delta U_{\text{separation}} = 0$$ ✓

Partial Separator – 2nd Law Analysis



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1.00 mol/min *B*
3 atm, 298 K

isothermal expansion

1.00 mol/min *A*
1.00 mol/min *B*
1 atm, 298 K

separator

1.00 mol/min *A*
1 atm, 298 K

1:4 splitter

1.00 mol/min *B*
1 atm, 298 K

4:1 splitter

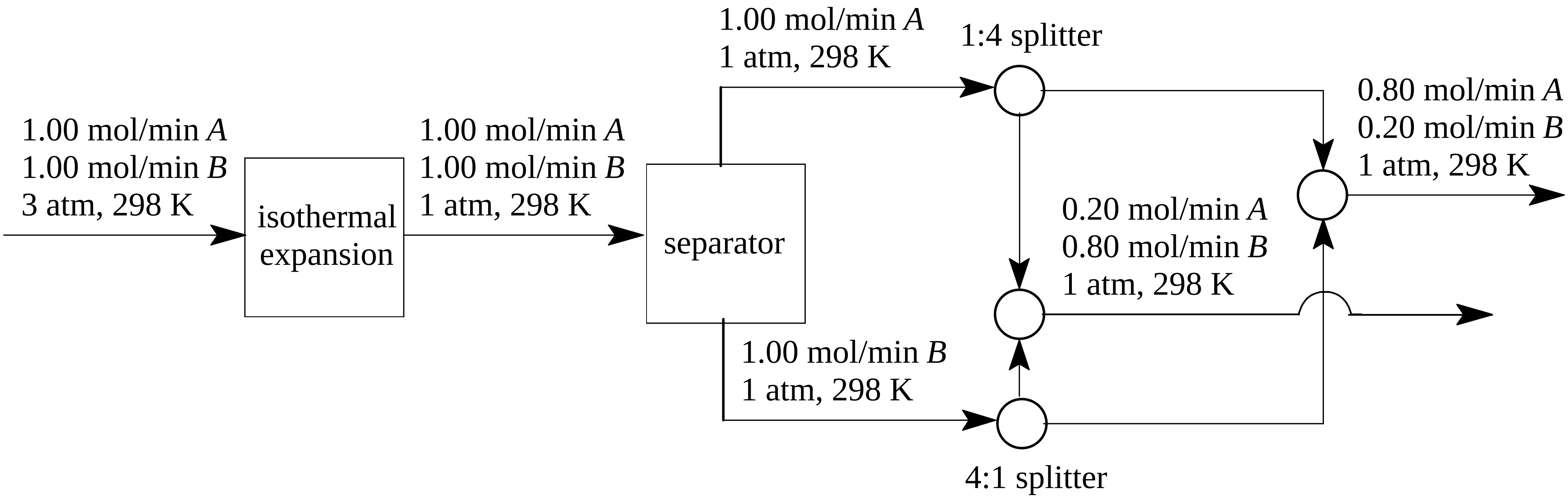
0.80 mol/min *A*
0.20 mol/min *B*
1 atm, 298 K

0.20 mol/min *A*
0.80 mol/min *B*
1 atm, 298 K

$$\Delta S_{\text{expansion}} = nR\ln\frac{V_2}{V_1} = nR\ln\frac{P_1}{P_2} = (2\ \text{mol/min})(8.314\ \text{J}/\text{K}\cdot\text{mol})\ln\frac{3\ \text{atm}}{1\ \text{atm}}$$

$$\Delta S_{\text{expansion}} = +18.27\ \text{J/K}\cdot\text{min}$$

Partial Separator – 2nd Law Analysis, cont'd



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1 atm, 298 K

separator

1.00 mol/min *A*
1 atm, 298 K

1:4 splitter

1.00 mol/min *B*
1 atm, 298 K

4:1 splitter

0.80 mol/min *A*
0.20 mol/min *B*
1 atm, 298 K

0.20 mol/min *A*
0.80 mol/min *B*
1 atm, 298 K

Calculate Δ*S* for the reversible unmixing of 50/50 *A*+*B* to pure *A* and pure *B*.

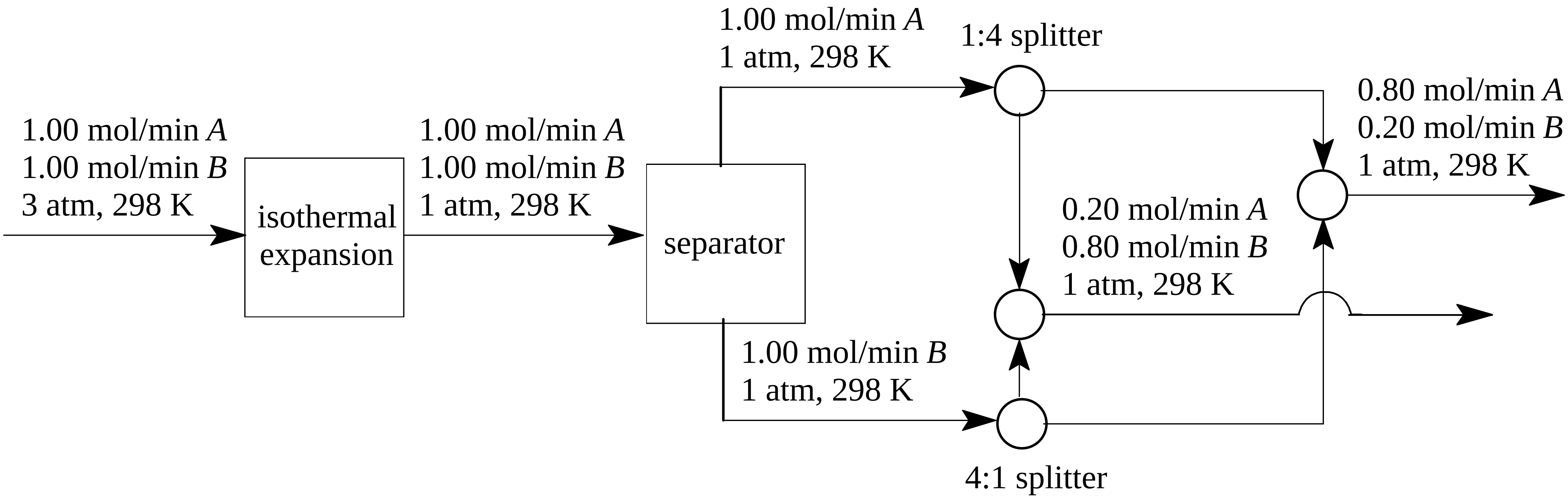
Δ*S* is the reverse of mixing pure *A* and pure *B* to form a 50/50 mixture.

$$\Delta S_{\text{unmixing}} = +R\left[n_{\text{A}}\ln\frac{n_{\text{A}}}{n_{\text{A}}+n_{\text{b}}} + n_{\text{B}}\ln\frac{n_{\text{A}}}{n_{\text{A}}+n_{\text{b}}}\right]$$

$$= +R\left[(1\,\text{mol/min})\ln\frac{1}{1+1} + (1\,\text{mol/min})\ln\frac{1}{1+1}\right]$$

$$\Delta S_{\text{unmixing}} = -11.53\ \text{J/K}\cdot\text{min}$$

Partial Separator – 2nd Law Analysis, cont'd



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1.00 mol/min *B*
3 atm, 298 K

isothermal expansion

1.00 mol/min *A*
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1 atm, 298 K

separator

1.00 mol/min *A*
1 atm, 298 K

1:4 splitter

1.00 mol/min *B*
1 atm, 298 K

4:1 splitter

0.80 mol/min *A*
0.20 mol/min *B*
1 atm, 298 K

0.20 mol/min *A*
0.80 mol/min *B*
1 atm, 298 K

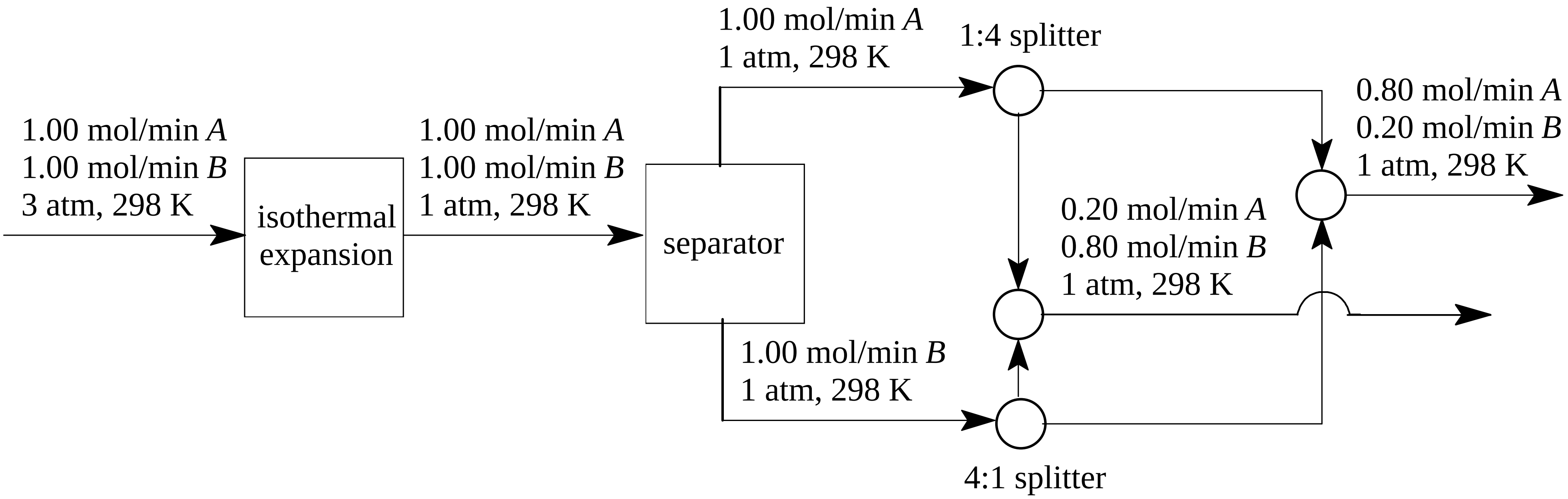
Calculate Δ*S* for the reversible mixing
of 0.2 mol/min of pure *A* and 0.8 mol/min of pure *B* to form 20/80 *A*+*B*.

$$\Delta S_{\text{mixing}\,1} = -R\left[n_{\text{A}} \ln \frac{n_{\text{A}}}{n_{\text{A}} + n_{\text{b}}} + n_{\text{B}} \ln \frac{n_{\text{A}}}{n_{\text{A}} + n_{\text{b}}} \right]$$

$$= -R\left[(0.2\text{ mol/min}) \ln \frac{0.2}{0.2 + 0.8} + (0.8\text{ mol/min}) \ln \frac{0.8}{0.8 + 0.2} \right]$$

$$\Delta S_{\text{mixing}\,1} = +4.16\text{ J/K} \cdot \text{min}$$

Partial Separator – 2nd Law Analysis, cont’d



1.00 mol/min *A*
1.00 mol/min *B*
3 atm, 298 K

isothermal expansion

1.00 mol/min *A*
1.00 mol/min *B*
1 atm, 298 K

separator

1.00 mol/min *A*
1 atm, 298 K

1:4 splitter

1.00 mol/min *B*
1 atm, 298 K

4:1 splitter

0.80 mol/min *A*
0.20 mol/min *B*
1 atm, 298 K

0.20 mol/min *A*
0.80 mol/min *B*
1 atm, 298 K

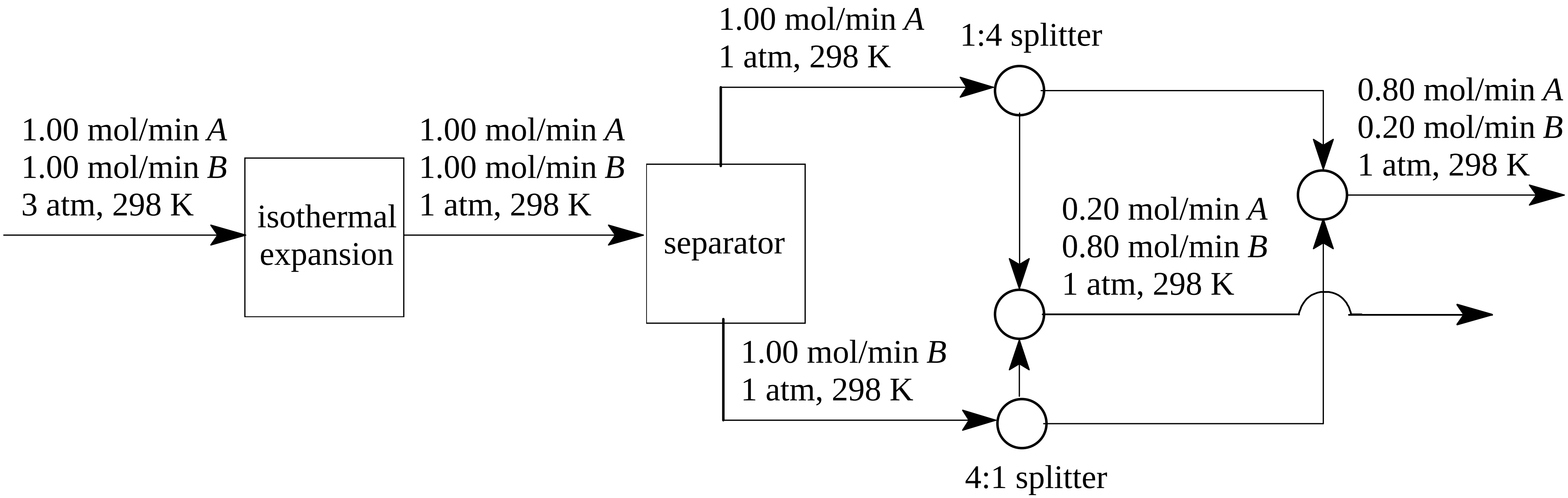
Calculate Δ*S* for the reversible mixing
of 0.8 mol/min of pure *A* and 0.2 mol/min of pure *B* to form 80/20 *A*+*B*.

$$\Delta S_{\text{mixing 2}} = -R\left[n_{\text{A}} \ln \frac{n_{\text{A}}}{n_{\text{A}} + n_{\text{b}}} + n_{\text{B}} \ln \frac{n_{\text{A}}}{n_{\text{A}} + n_{\text{b}}} \right]$$

$$= -R\left[(0.8\,\text{mol/min}) \ln \frac{0.8}{0.8 + 0.2} + (0.8\,\text{mol/min}) \ln \frac{0.2}{0.2 + 0.8} \right]$$

$$\Delta S_{\text{mixing 2}} = +4.16\ \text{J/K} \cdot \text{min}$$

Partial Separator – 2nd Law Analysis of Total Process



1.00 mol/min *A*
1.00 mol/min *B*
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isothermal expansion

1.00 mol/min *A*
1.00 mol/min *B*
1 atm, 298 K

separator

1.00 mol/min *A*
1 atm, 298 K

1:4 splitter

1.00 mol/min *B*
1 atm, 298 K

4:1 splitter

0.20 mol/min *A*
0.80 mol/min *B*
1 atm, 298 K

0.80 mol/min *A*
0.20 mol/min *B*
1 atm, 298 K

$$\Delta S_{\text{process}} = \Delta S_{\text{expansion}} + \Delta S_{\text{unmixing}} + \Delta S_{\text{mixing 1}} + \Delta S_{\text{mixing 2}}$$

$$= 18.27 + -11.53 + 4.16 + 4.16 \text{ J/K} \cdot \text{min}$$

$$\Delta S_{\text{process}} = +15.1 \text{ J/K} \cdot \text{min}$$

Because $\Delta S_{\text{process}} > 0$, process is spontaneous. ✓