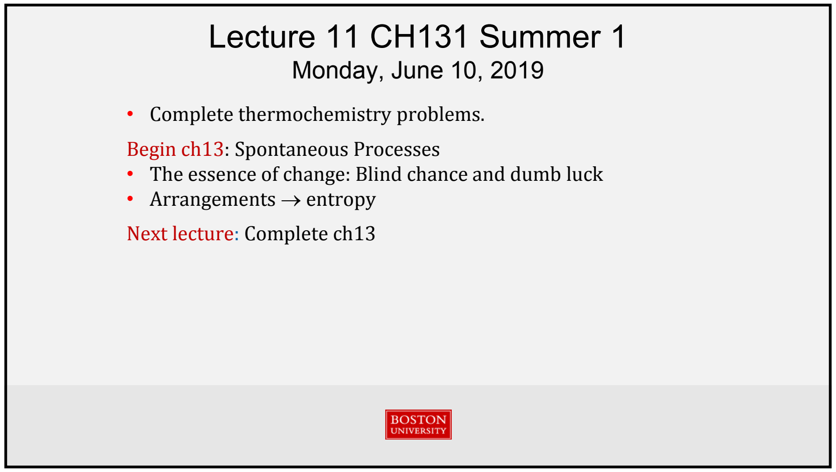

Lecture 11 CH131 Summer 1

Monday, June 10, 2019

- Complete thermochemistry problems.

Begin ch13: Spontaneous Processes

- The essence of change: Blind chance and dumb luck
- Arrangements → entropy

Next lecture: Complete ch13

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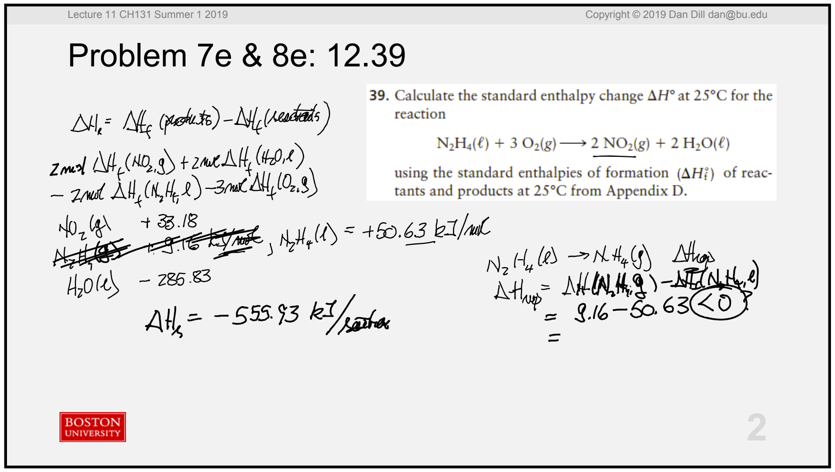

Problem 7e & 8e: 12.39

39. Calculate the standard enthalpy change ΔH° at 25°C for the reaction

$$N_2H_4(\ell) + 3\,O_2(g) \longrightarrow \underline{2\,NO_2}(g) + 2\,H_2O(\ell)$$

using the standard enthalpies of formation (ΔH_f°) of reactants and products at 25°C from Appendix D.

$\Delta H_r = \Delta H_f(\text{products}) - \Delta H_f(\text{reactants})$

$2\,\text{mol}\,\Delta H_f(NO_2,g) + 2\,\text{mol}\,\Delta H_f(H_2O,\ell)$

$-\,2\,\text{mol}\,\Delta H_f(N_2H_4,\ell) - 3\,\text{mol}\,\Delta H_f(O_2,g)$

$NO_2(g)$ $+33.18$

~~$N_2H_4(g)$ $+9.16$ kJ/mol~~, $N_2H_4(\ell) = +\underline{50.63}$ kJ/mol

$H_2O(\ell)$ -285.83

$\Delta H_r = -555.93$ kJ/reaction

$N_2H_4(\ell) \rightarrow N_2H_4(g)$ ΔH_{vap}

$\Delta H_{vap} = \Delta H(N_2H_4,g) - \Delta H_f(N_2H_4,\ell)$

$= 9.16 - 50.63\ \boxed{<0}$?

=

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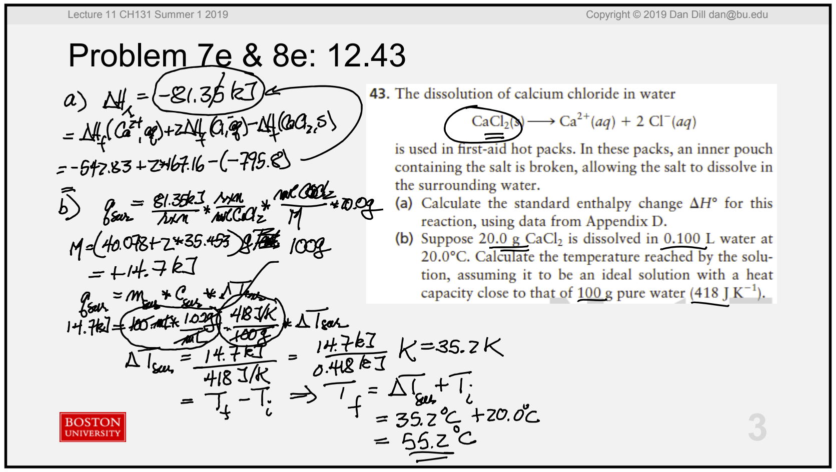

Problem 7e & 8e: 12.43

43. The dissolution of calcium chloride in water

$$\underline{CaCl_2(s)} \longrightarrow Ca^{2+}(aq) + 2\,Cl^-(aq)$$

is used in first-aid hot packs. In these packs, an inner pouch containing the salt is broken, allowing the salt to dissolve in the surrounding water.

(a) Calculate the standard enthalpy change ΔH° for this reaction, using data from Appendix D.

(b) Suppose $\underline{20.0\text{ g}}$ $CaCl_2$ is dissolved in $\underline{0.100\text{ L}}$ water at 20.0°C. Calculate the temperature reached by the solution, assuming it to be an ideal solution with a heat capacity close to that of $\underline{100\text{ g}}$ pure water ($\underline{418\text{ J K}^{-1}}$).

a) $\Delta H_r = \boxed{-81.35\text{ kJ}}$

$= \Delta H_f(Ca^{2+},aq) + 2\Delta H_f(Cl^-,aq) - \Delta H_f(CaCl_2,s)$

$= -542.83 + 2*167.16 - (-795.8)$

b) $q_{surr} = \frac{81.35\text{ kJ}}{\text{rxn}} * \frac{\text{rxn}}{\text{mol CaCl}_2} * \frac{\text{mol CaCl}_2}{M} * 20.0\text{ g}$

$M = (40.078 + 2*35.453)$ g ~~/mol~~ 100g

$= +14.7$ kJ

$q_{surr} = m_{surr} * C_{surr} * \Delta T_{surr}$

$14.7\text{ kJ} = 100\text{ mL} * \frac{1.0\text{ g}}{\text{mL}} * \frac{418\text{ J/K}}{100\text{ g}} * \Delta T_{surr}$

$\Delta T_{surr} = \frac{14.7\text{ kJ}}{418\text{ J/K}} = \frac{14.7\text{ kJ}}{0.418\text{ kJ}}\,K = 35.2\,K$

$= T_f - T_i \Rightarrow T_f = \Delta T_{surr} + T_i$

$= 35.2°C + 20.0°C$

$= \underline{55.2°C}$

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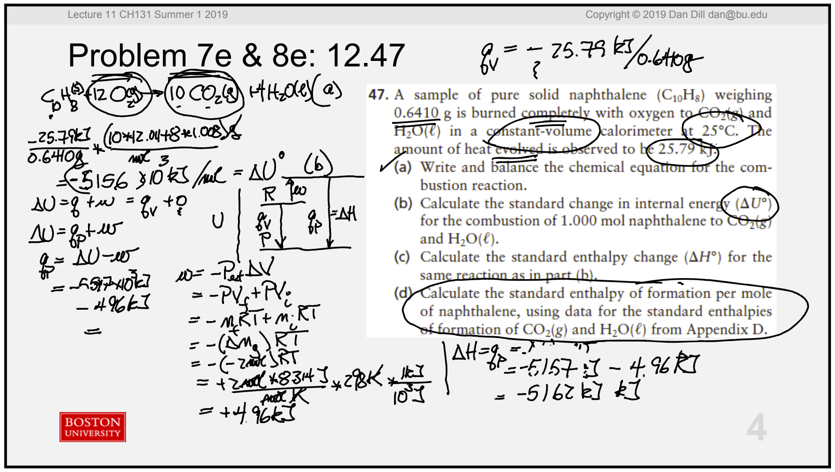

Problem 7e & 8e: 12.47

$q_V = -25.79\text{ kJ}/0.6410\text{ g}$

47. A sample of pure solid naphthalene ($C_{10}H_8$) weighing $\underline{0.6410}$ g is burned completely with oxygen to $CO_2(g)$ and $\underline{H_2O(\ell)}$ in a constant-volume calorimeter at 25°C. The amount of heat evolved is observed to be 25.79 kJ.

✓ (a) Write and balance the chemical equation for the combustion reaction.

(b) Calculate the standard change in internal energy (ΔU°) for the combustion of 1.000 mol naphthalene to $CO_2(g)$ and $H_2O(\ell)$.

(c) Calculate the standard enthalpy change (ΔH°) for the same reaction as in part (b).

(d) Calculate the standard enthalpy of formation per mole of naphthalene, using data for the standard enthalpies of formation of $CO_2(g)$ and $H_2O(\ell)$ from Appendix D.

$C_{10}H_8(s) + 12\,O_2(g) \rightarrow 10\,CO_2(g) + 4\,H_2O(\ell)$ (a)

$\frac{-25.79\text{ kJ}}{0.6410\text{ g}} * \frac{(10*12.011+8*1.008)\text{ g}}{\text{mol}}$

$= -5.156\times10^3\text{ kJ/mol} = \Delta U^\circ$ (b)

$\Delta U = q + w = q_V + 0$

$\Delta U = q_P + w$

$q_P = \Delta U - w$

$= -5.157\times10^3\text{ kJ}$

$-\,4.96\text{ kJ}$

=

U

R w

q_V P

$q_P = \Delta H$

$w = -P_{ext}\Delta V$

$= -PV_f + PV_i$

$= -n_fRT + n_iRT$

$= -(\Delta n_g)RT$

$= -(-2\text{ mol})RT$

$= +2\text{ mol} * \frac{8.314\text{ J}}{\text{mol K}} * 298\text{ K} * \frac{1\text{ kJ}}{10^3\text{ J}}$

$= +4.96\text{ kJ}$

$\Delta H = q_P = -5157\text{ kJ} - 4.96\text{ kJ}$

$= -5162\text{ kJ}$

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$C_{10}H_8(s) + 12O_2(g) \rightleftharpoons 10\,CO_2(g) + 4H_2O(l)$

$\Delta H_r = -51\overset{62}{\cancel{57}}$ kJ/mol

$\cancel{\Delta H_f(C_{10}H_8,s) = ?} = 10\Delta H_f(CO_2,g) + 4\Delta H_f(H_2O,l) - \Delta H_f(C_{10}H_8,s)$

$\Delta H_f(C_{10}H_8,s) = -\Delta H_r + 10\Delta_f(CO_2,g) + 4\Delta H_f(H_2O,l)$

$= +5162\text{ kJ} - 4*285.83\text{ kJ} - 10*393.51$

$= +83.85\text{ kJ}$

[Quiz] The enthalpy diagram shows changes associated with the reaction
$Na_2(g) + Br_2(g) \rightarrow 2\,NaBr(g)$.
The uppermost line corresponds to the species ...

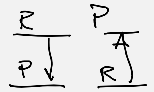
0% 1. ~~$2\,Na(s) + Br_2(l)$~~ X

94% 2. $2\,Na(g) + 2\,Br(g)$

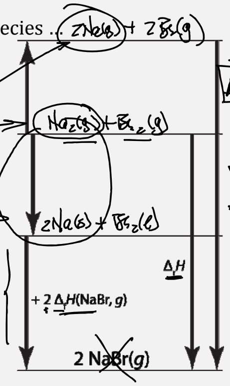
6% 3. ~~$Na_2(g) + Br_2(g)$~~ X

$2\,Na(s) \rightarrow 2Na(l) \rightarrow \cancel{2}Na_2(g) \rightarrow 2\,Na(g)$

?



$2Na(s) + Br_2(l) \rightarrow 2\,NaBr(g)$



$\Delta U = q + w$

$\Delta U = q_V + w_V$

$\boxed{\Delta U = q_V}$

$\Delta U = q_p + w_p$

$q_p = \Delta U - w_p = \Delta H$

$\boxed{\Delta H = q_p}$

The essence of change

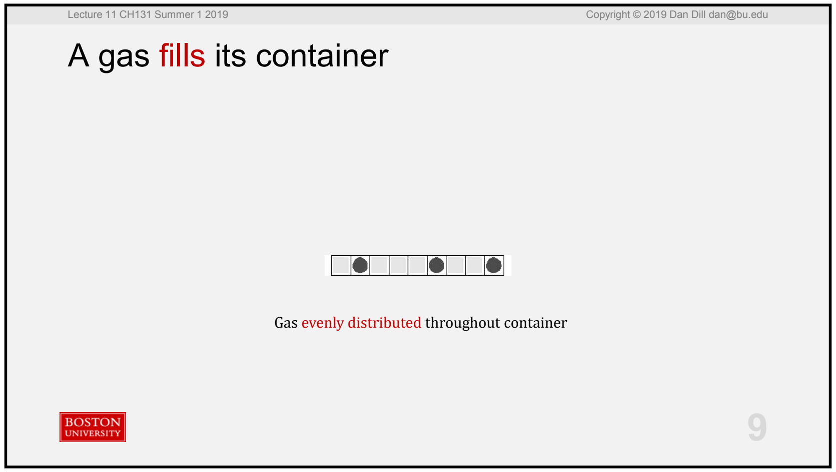
all complexity is an illusion ...

things happen simply because they can happen and because they are statistically most likely to happen."

Michael Munowitz, "Principles of Chemistry," W. W. Norton, 2000

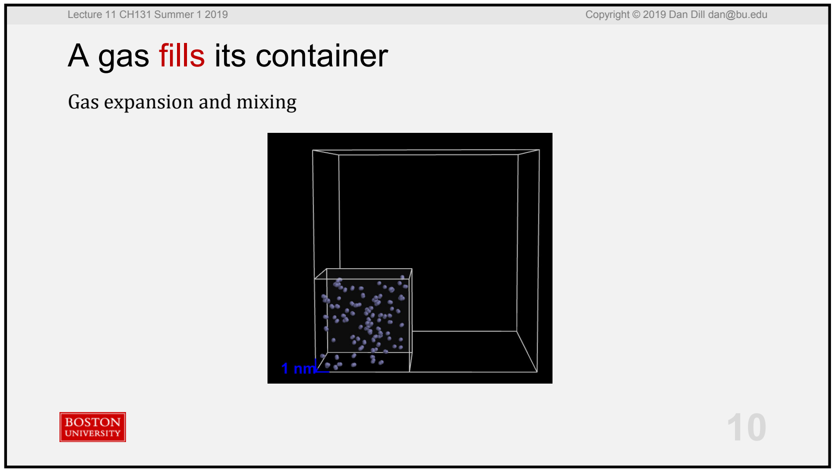
A gas fills its container

Gas all on left of container



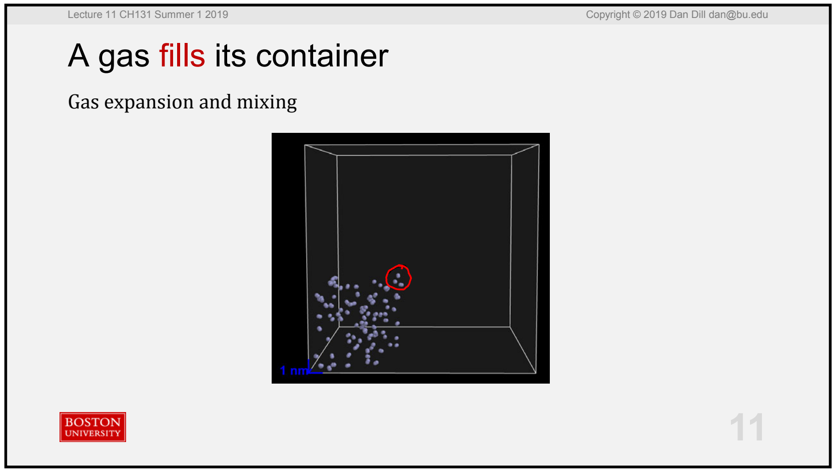
A gas fills its container

Gas evenly distributed throughout container



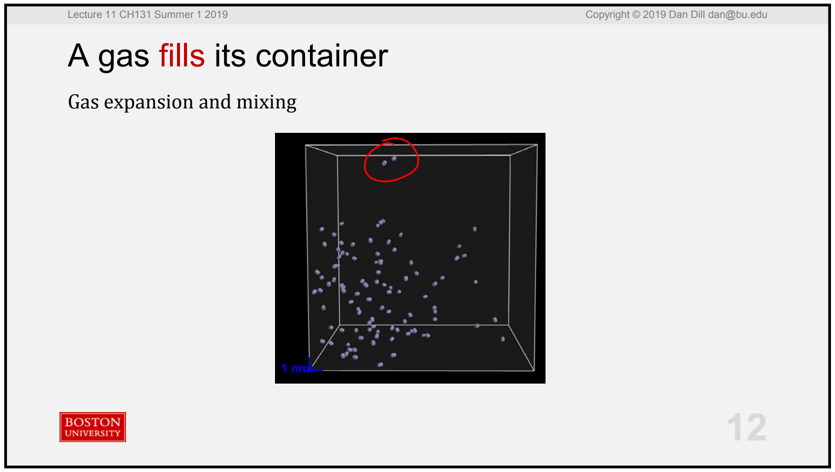
A gas fills its container

Gas expansion and mixing



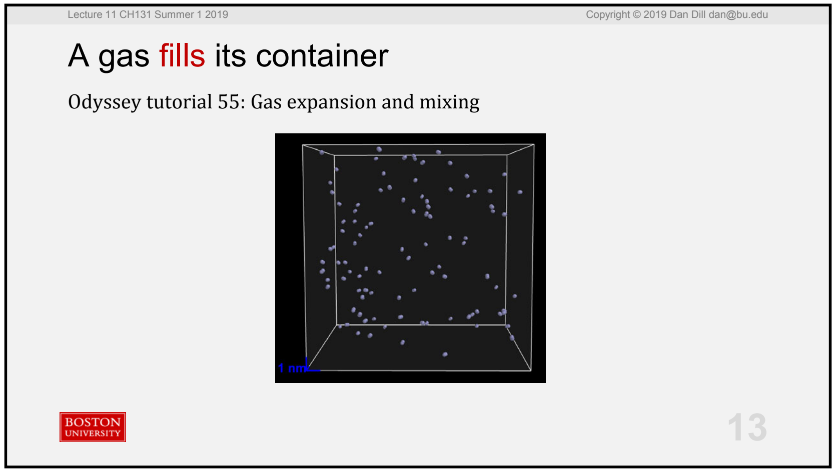
A gas fills its container

Gas expansion and mixing



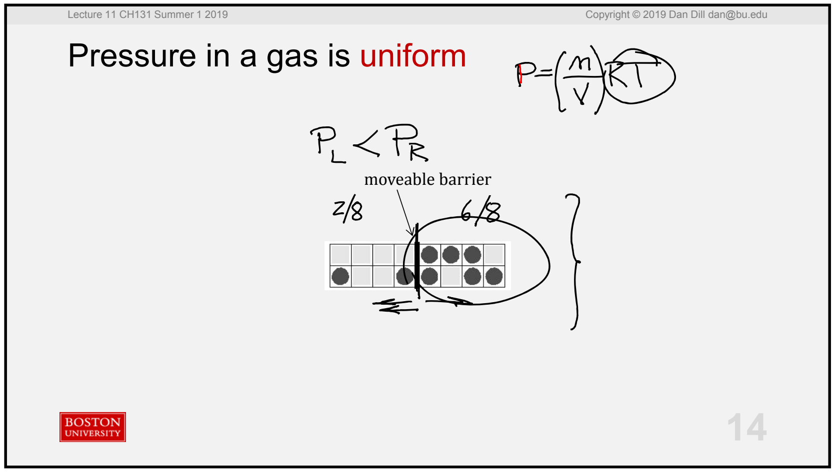
A gas fills its container

Gas expansion and mixing



A gas fills its container

Odyssey tutorial 55: Gas expansion and mixing



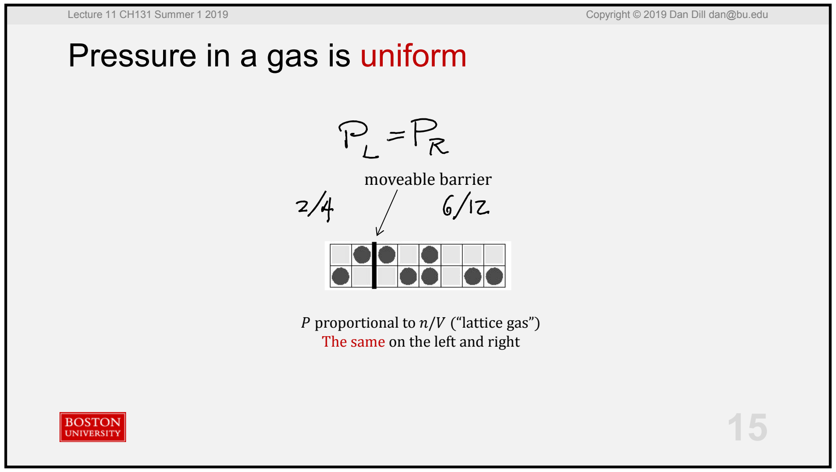
Pressure in a gas is uniform

$P = \left(\frac{n}{V}\right)RT$

$P_L < P_R$

moveable barrier

$2/8$ $6/8$



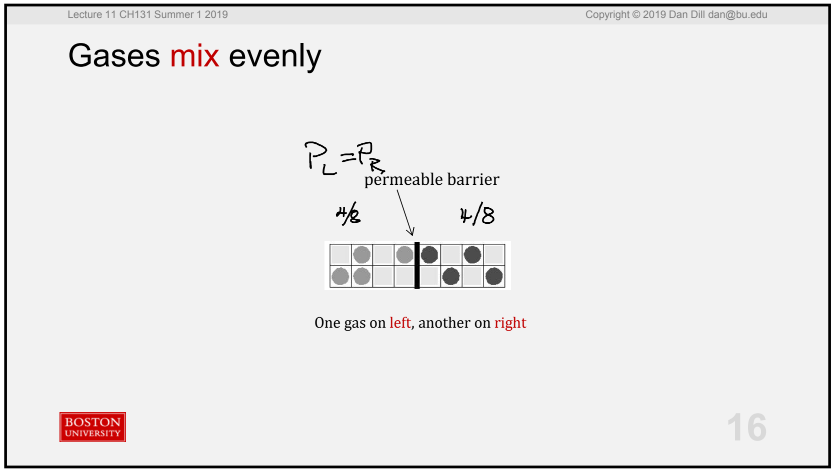
Pressure in a gas is uniform

$P_L = P_R$

moveable barrier

$2/4$ $6/12$

P proportional to n/V (“lattice gas”)
The same on the left and right



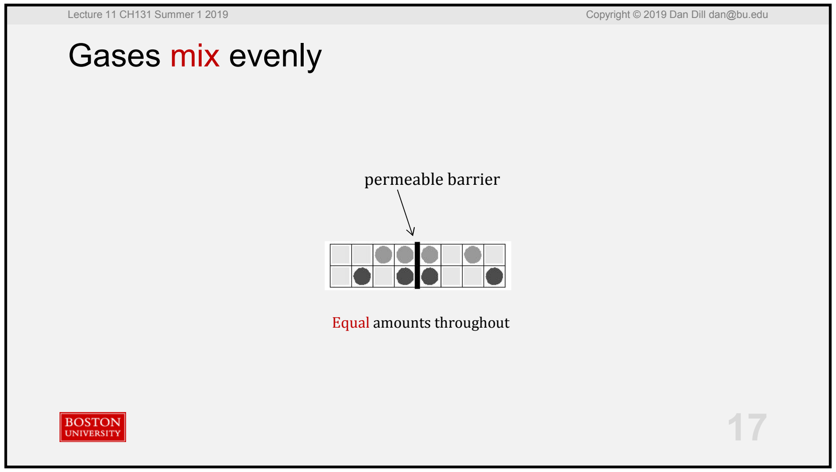
Gases mix evenly

$P_L = P_R$

permeable barrier

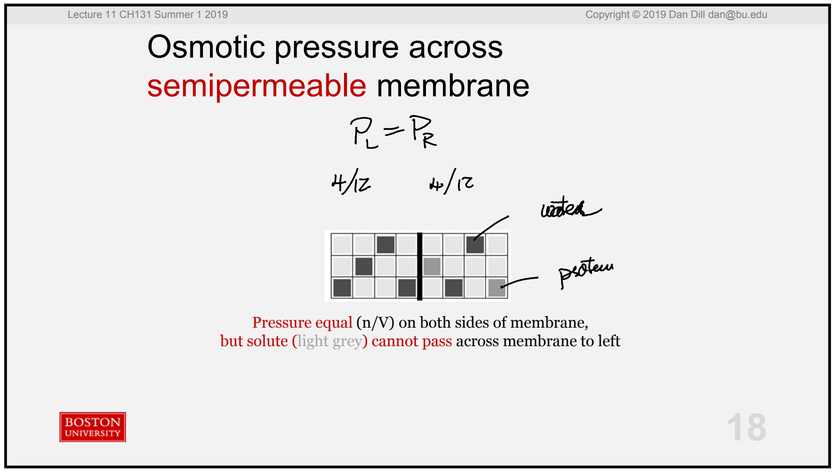
$4/8$ $4/8$

One gas on left, another on right



Gases mix evenly

Equal amounts throughout

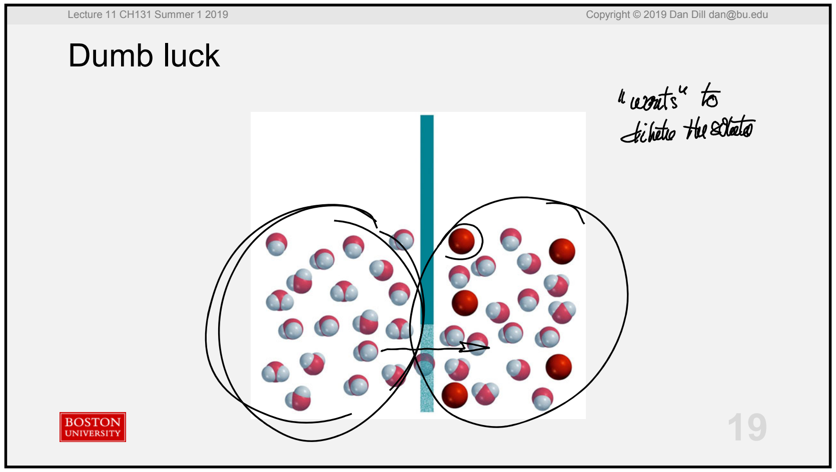


Osmotic pressure across semipermeable membrane

$P_L = P_R$

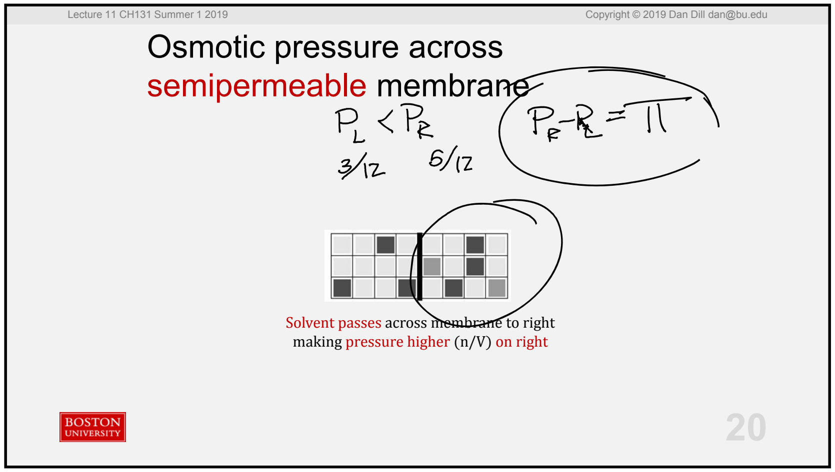
4/12 4/12

Pressure equal (n/V) on both sides of membrane,
but solute (light grey) cannot pass across membrane to left



Dumb luck

"wants" to
dilute the solute



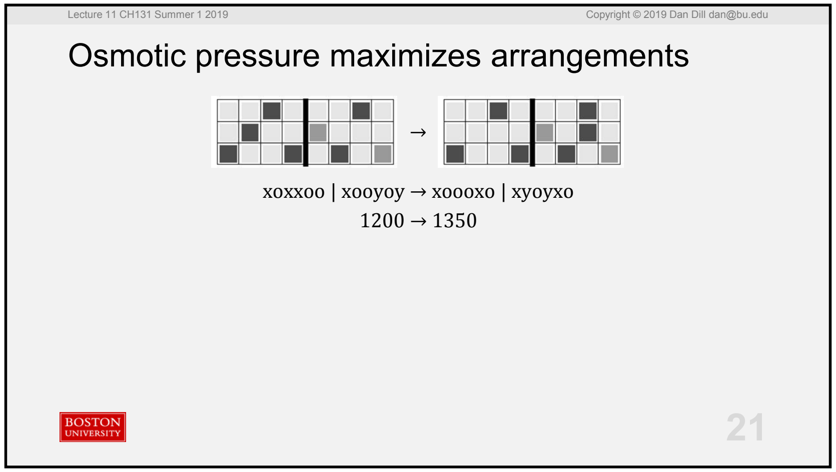
Osmotic pressure across semipermeable membrane

$P_L < P_R$

3/12 6/12

$P_R - P_L = \Pi$

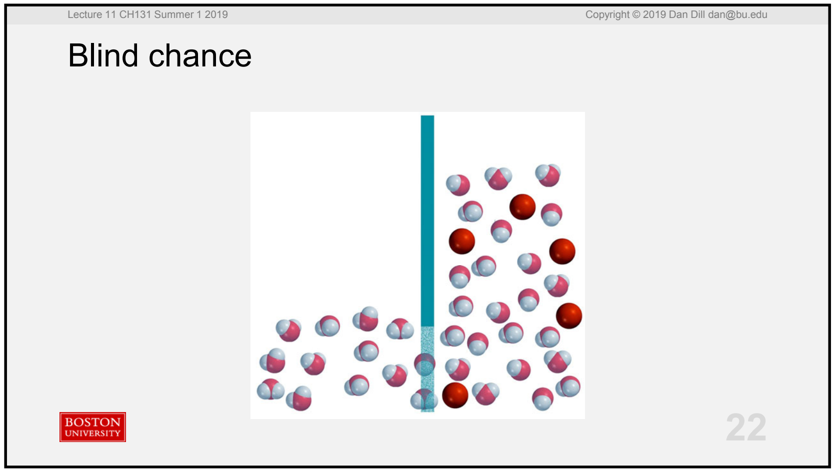
Solvent passes across membrane to right
making pressure higher (n/V) on right



Osmotic pressure maximizes arrangements

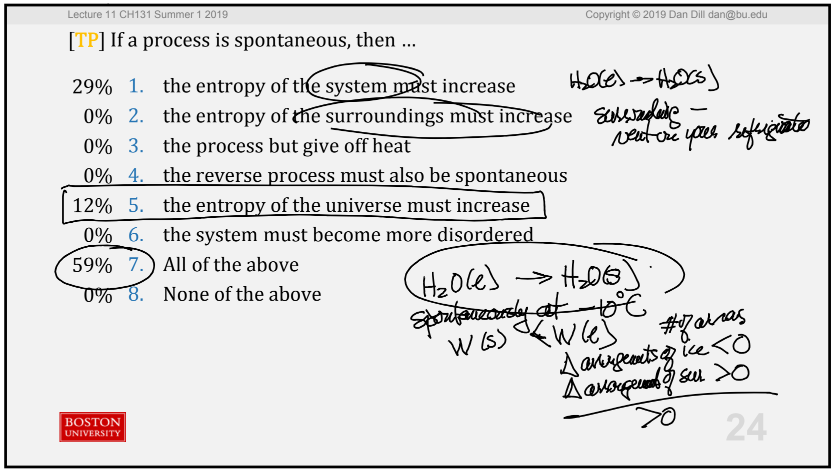
xoxxoo | xooyoy → xoooxo | xyoyxo

1200 → 1350



Blind chance

Arrangements → entropy



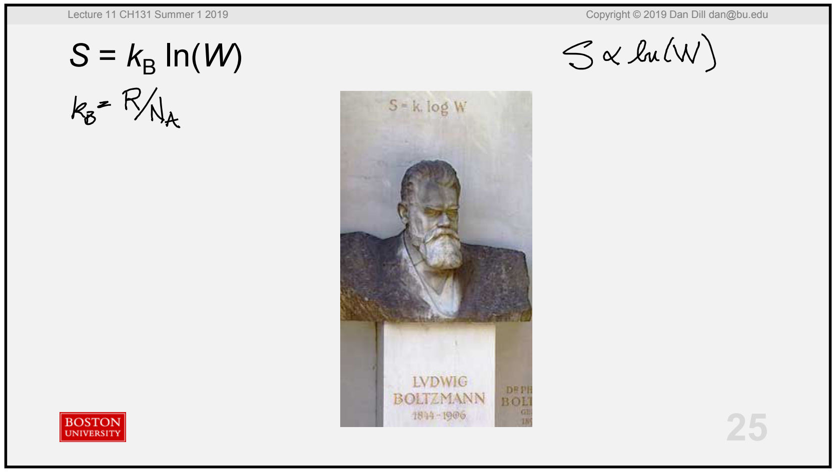
[TP] If a process is spontaneous, then …

29% 1. the entropy of the system must increase
0% 2. the entropy of the surroundings must increase
0% 3. the process but give off heat
0% 4. the reverse process must also be spontaneous
[✓ 12% 5. the entropy of the universe must increase]
0% 6. the system must become more disordered
[✓ 59% 7.] All of the above
0% 8. None of the above

$H_2O(l) \to H_2O(s)$

surroundings –
next to your refrigerator

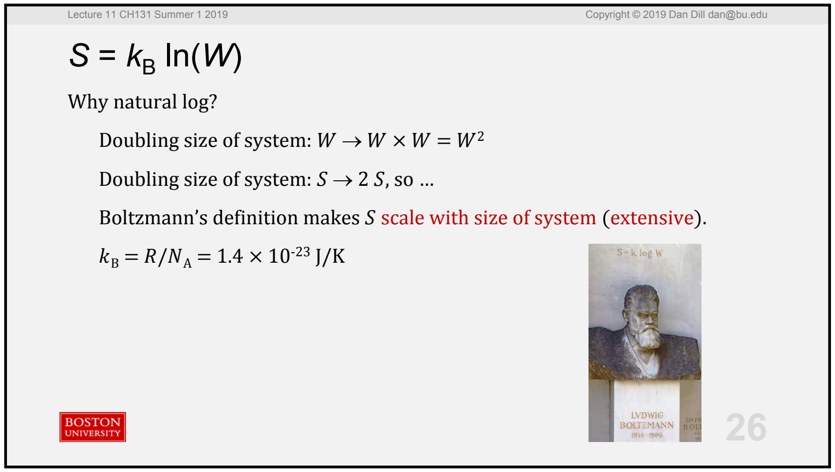
$H_2O(l) \to H_2O(s)$
spontaneously at −10°C
$W(s) < W(l)$
# of arras
Δ arrangements of ice < 0
Δ arrangements of sur > 0
> 0



$S = k_B \ln(W)$

$S \propto \ln(W)$

$k_B = R/N_A$



$S = k_B \ln(W)$

Why natural log?

Doubling size of system: $W \rightarrow W \times W = W^2$

Doubling size of system: $S \rightarrow 2\,S$, so …

Boltzmann's definition makes S scale with size of system (extensive).

$k_B = R/N_A = 1.4 \times 10^{-23}$ J/K