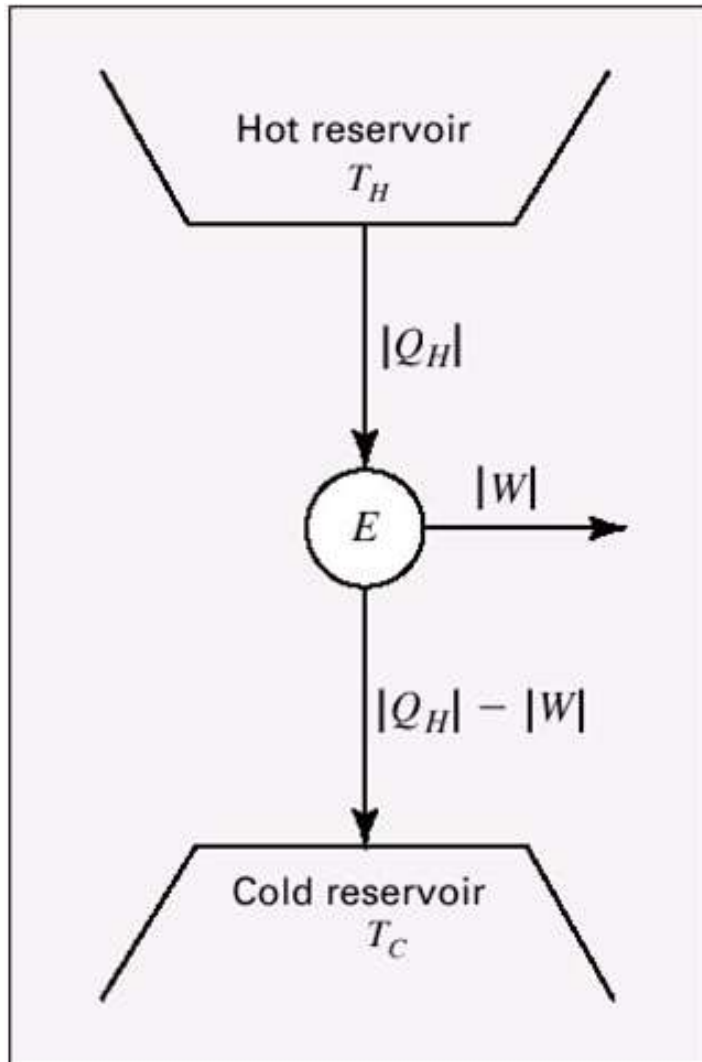# CH365 Chemical Engineering Thermodynamics

Lesson 25
3rd Law and Entropy from the Microscopic Viewpoint

What is Entropy?

Implications

$$\eta = \frac{|W|}{|Q_H|} = 1 - \frac{T_C}{T_H}$$

(Eq. 5.8)

Third Law of Thermodynamics

The absolute entropy is zero for all perfect crystalline substances at absolute zero temperature.

$$S = S(T) = \int_0^{T_f} \frac{(C_P)_S}{T} dT + \frac{\Delta H_f}{T_f} + \int_{T_f}^{T_v} \frac{(C_P)_L}{T} dT + \frac{\Delta H_v}{T_V} + \int_{T_V}^{T} \frac{(C_P)_G}{T} dT$$

(Eq. 5.40)

This equation allows calculation of absolute entropy.
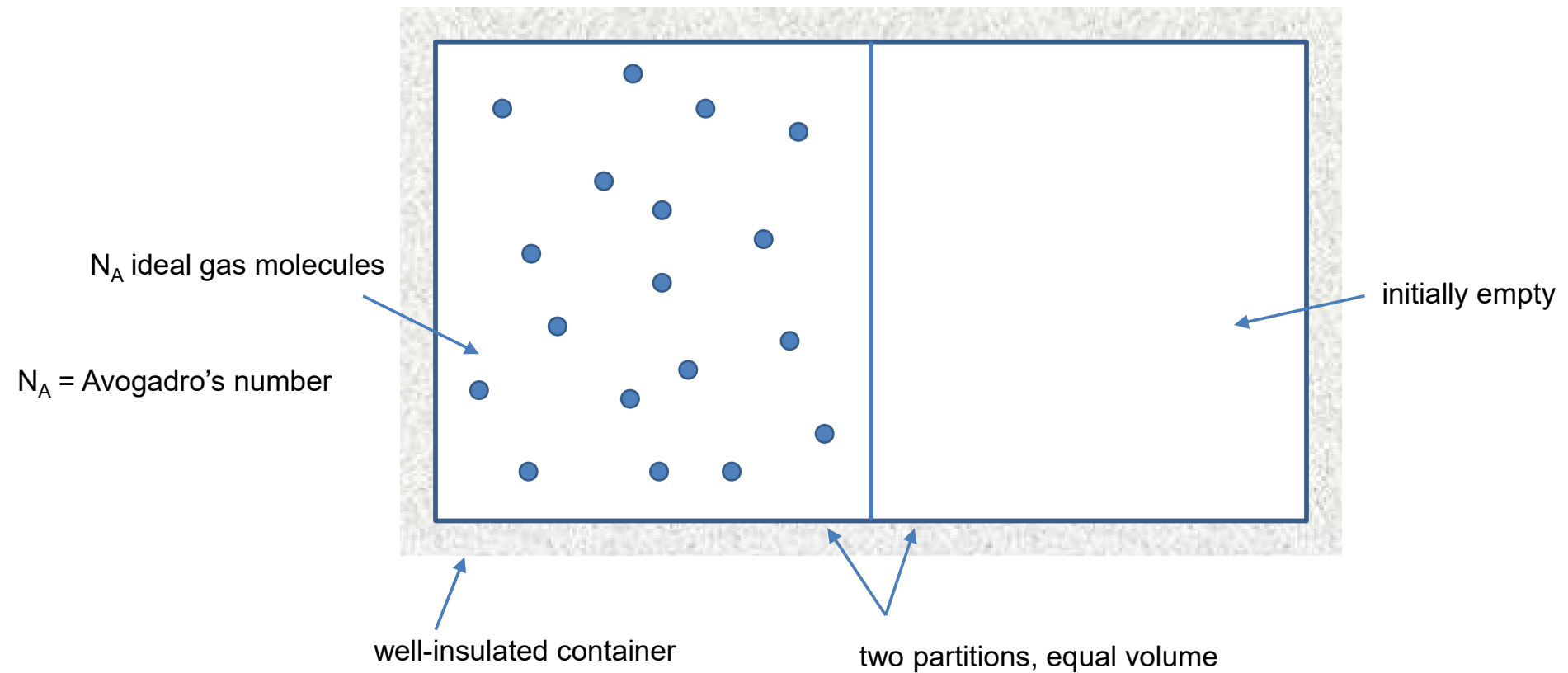
In[1]:= (*CaO(s) m.p. 2845 K*)

(*Cp from Appendix C page 670*)

$Cp = 6.104 + .443*10^{-3}*T - 1.047*10^{5}*T^{-2};$

In[2]:= $\int_{0}^{273} \frac{Cp}{T} \, dT$

Statistical Interpretation

- ideal gas

  - molecules do not interact

  - internal energy resides within the individual molecules

N_A ideal gas molecules

N_A = Avogadro's number

initially empty

well-insulated container

two partitions, equal volume

$$U = U(T, V)$$

ch. 4, p. 138, (un-numbered equation)

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

0 → Because molecules don't interact

$$\frac{\Delta S}{R} = \int_{T_{before}}^{T_{after}} \frac{C_P^{ig}}{R} \frac{dT}{T} - \ln\left(\frac{P_{final}}{P_{initial}}\right)$$

$\underbrace{\qquad}$ 0, no change in T

$\underbrace{\qquad}$ P drops by half

(Eq. 5.10)

definition of C_V

ch. 3, p. 79, (Eq. 3.13a)
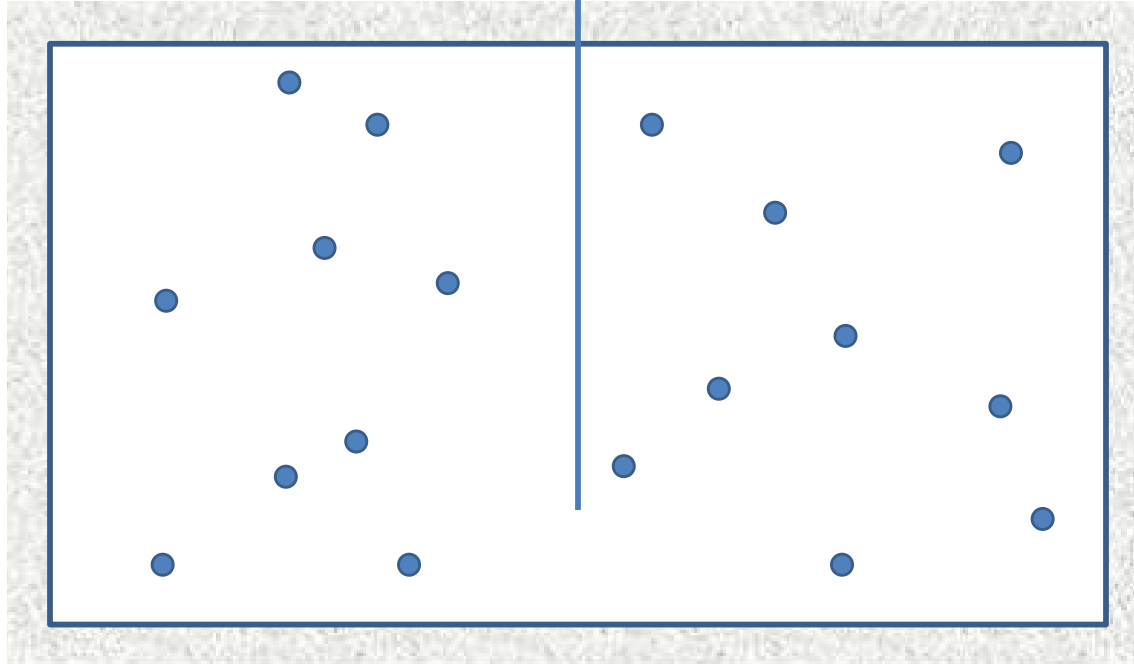
$$dU = C_V dT$$

Recall:

ch. 3, p. 79, (Eq. 3.14a)

$$dH = C_P dT$$

definition of C_P:

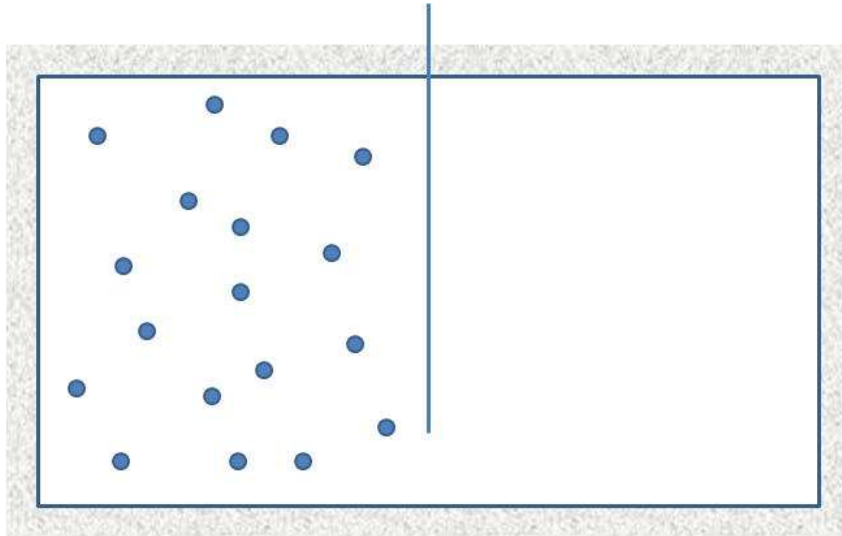$$C_P \equiv \left(\frac{\partial H}{\partial T}\right)_P$$

$$\Delta U = C_V \Delta T = 0$$

But if ΔU=0, then T does not change.

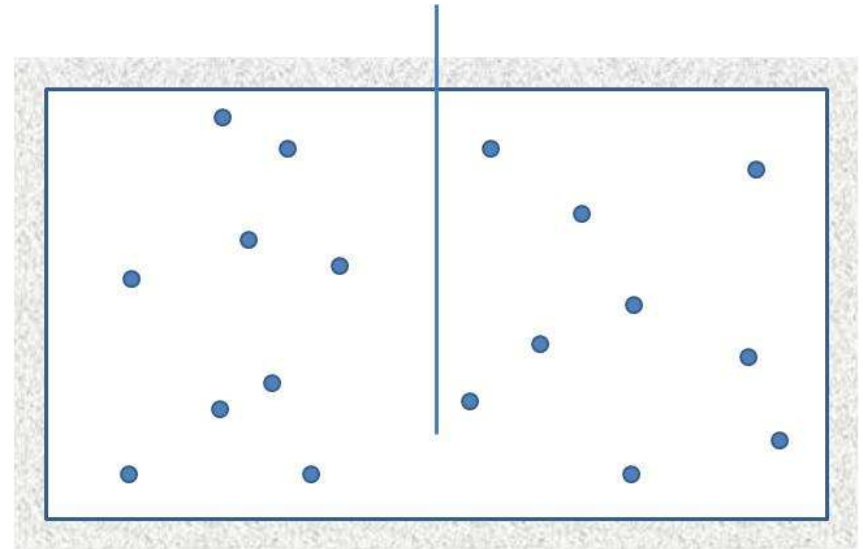$$\Delta S = -R \cdot \ln\left(\frac{P_{after}}{P_{before}}\right) = R \cdot \ln(2)$$

$\underbrace{\qquad}$ >0 (irreversible)

Result of *classical* thermodynamics

more ordered → less random → less disordered

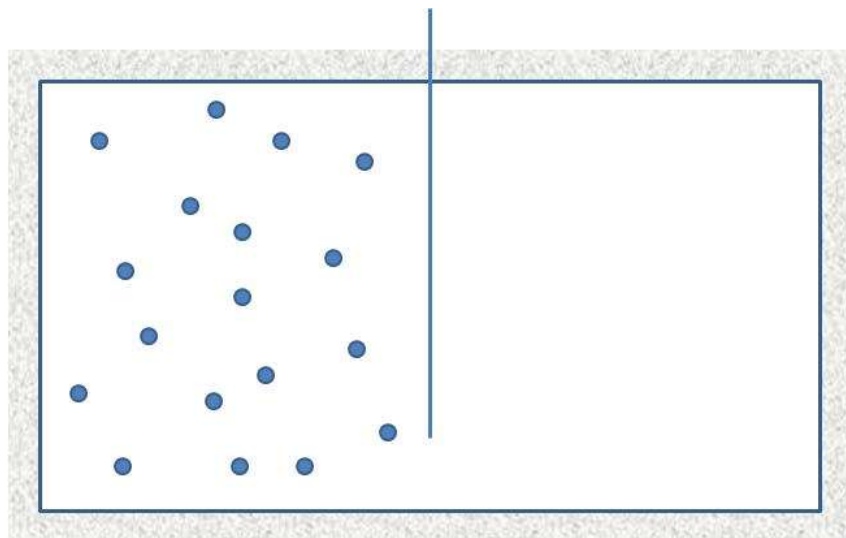less ordered → more random → more disordered

- immediately after opening

- molecules are not randomly distributed over the total volume

- crowded into half the space

Increasing disorder (or decreasing structure) on the molecular level corresponds to increasing entropy.

Expression for disorder postulated by J.W. Gibbs and L. Boltzmann, 1878.

Quantitative Expression of Disorder

more ordered = less random = less disordered

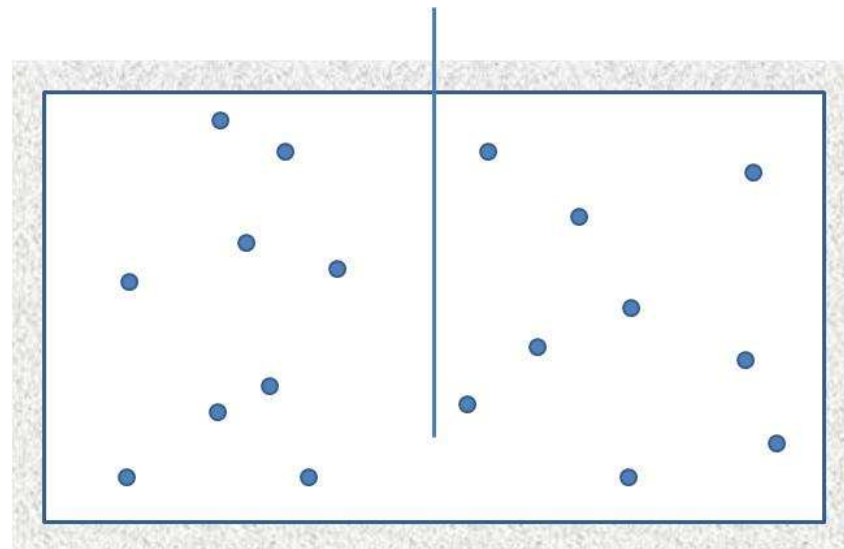less ordered = more random = more disordered

All molecules are in one of the two states.

$$\Omega_{initial} = \frac{N_A!}{(N_A!)(0!)}$$

$$= \frac{18!}{(18!)(0!)}$$

$$= 1$$

$$\Omega_{final} = \frac{N_A!}{\left(\dfrac{N_A}{2}!\right)\left(\dfrac{N_A}{2}!\right)}$$

$$= \frac{18!}{9! \cdot 9!}$$

$$= 48,620$$
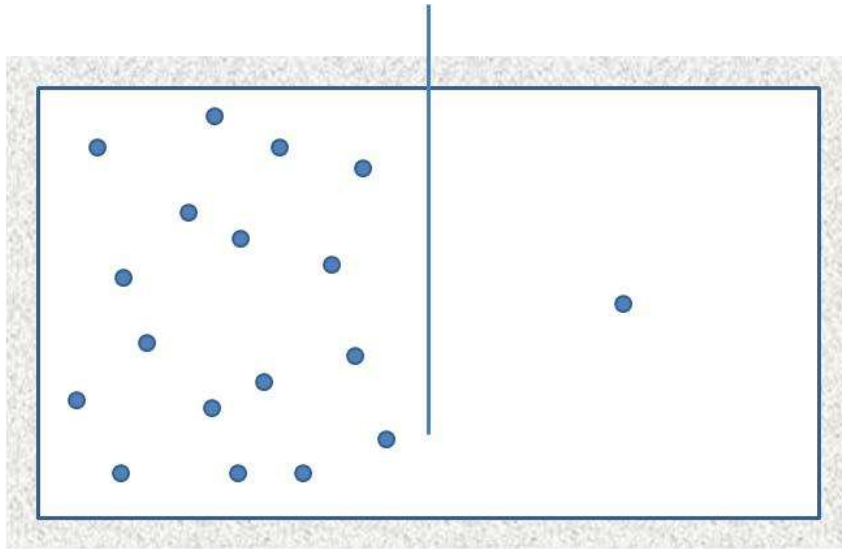
$$\Omega_1 = \frac{18!}{(17!)(1!)} = 18$$
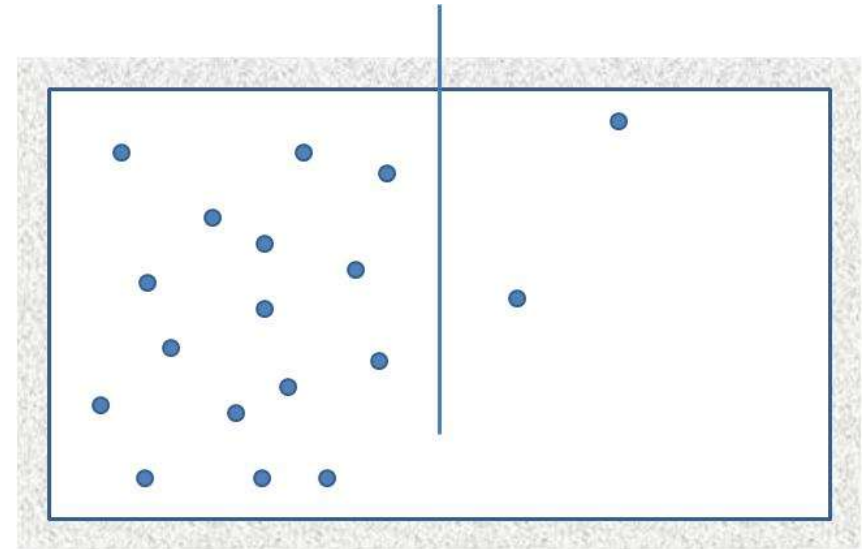
$$\Omega_2 = \frac{18!}{(16!)(2!)} = 153$$

unbounded as N_A increases

for the 18 particles, $\Omega_{final} = 48,620$

How about $N_A = 10^{23}$?
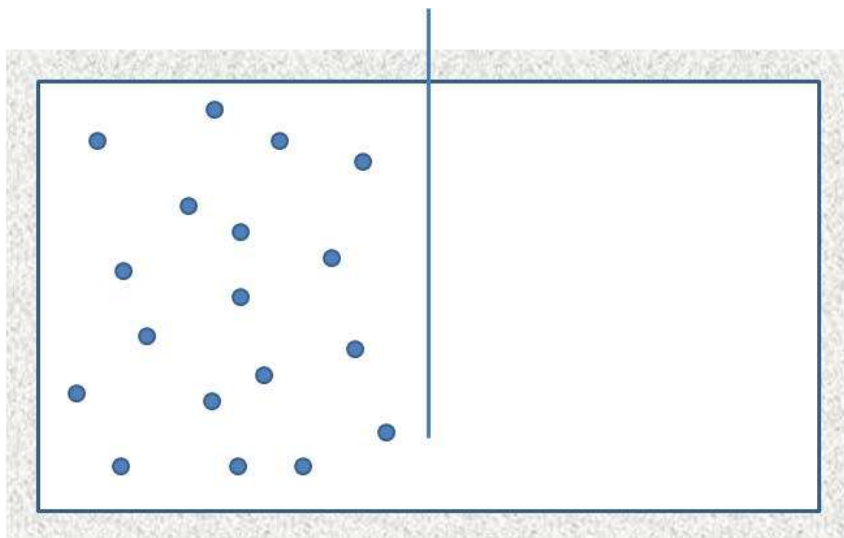
Boltzmann's thought process:

Boltzmann's thought process, continued:

more ordered = less random = less disordered

less ordered = more random = more disordered
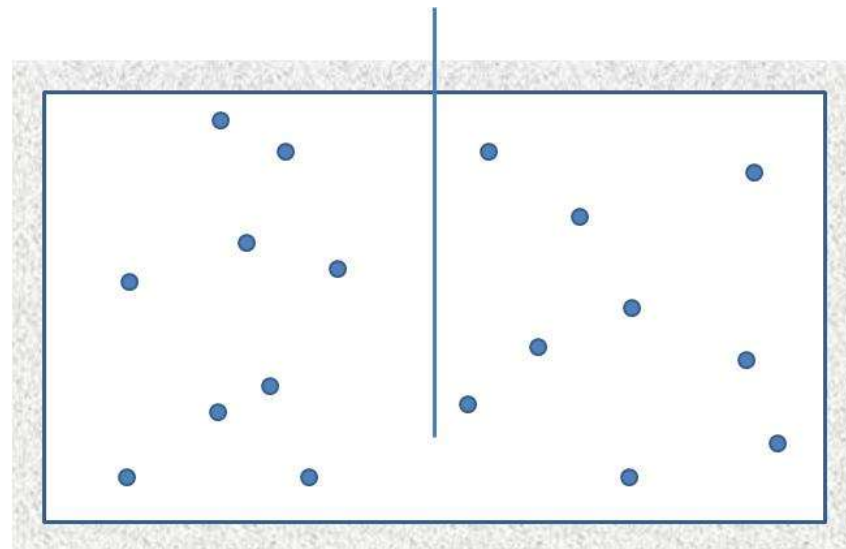
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Increasing disorder (or decreasing structure) on the molecular level corresponds to increasing entropy.

Questions?

Homework

Problem 5.44

A nuclear power plant generates 750 MW; the reactor temperature is 315 deg C and a river with water temperature of 20 deg C is available.

(a) What is the maximum possible thermal efficiency of the plant, and what is the minimum rate at which heat must be discarded to the river?

(b) If the actual thermal efficincy of the plant is 60% of the maximum, at what rate must heat be discarded to the river, and what is the temperature rise of the river if it has a flow rate of 165 cubic meters per second?

Problem 5.50

Ethylene vapor is cooled at atmospheric pressure from 830 to 35 deg C by direct heat transfer to the surroundings at 25 deg C. With respect to this surroundings temperature, what is the lost work of the process in kJ/mol?

Show that the same result is obtained as the work which can be derived from reversible heat engines operating with the ethylene vapor as the heat source and the surroundings as the sink.

The heat capacity of ethylene is given in Table C.1 of App. C.

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Problem 5.17

A Carnot engine operates between temperature levels of 600 K and 300 K. It drives a Carnot refrigerator, which provides cooling at 250 K and discards heat at 300 K. Determine a numerical value for the ratio of heat extracted by the refrigerator ("cooling load") to the heat delivered to the engine ("heating load").

Problem 5.17
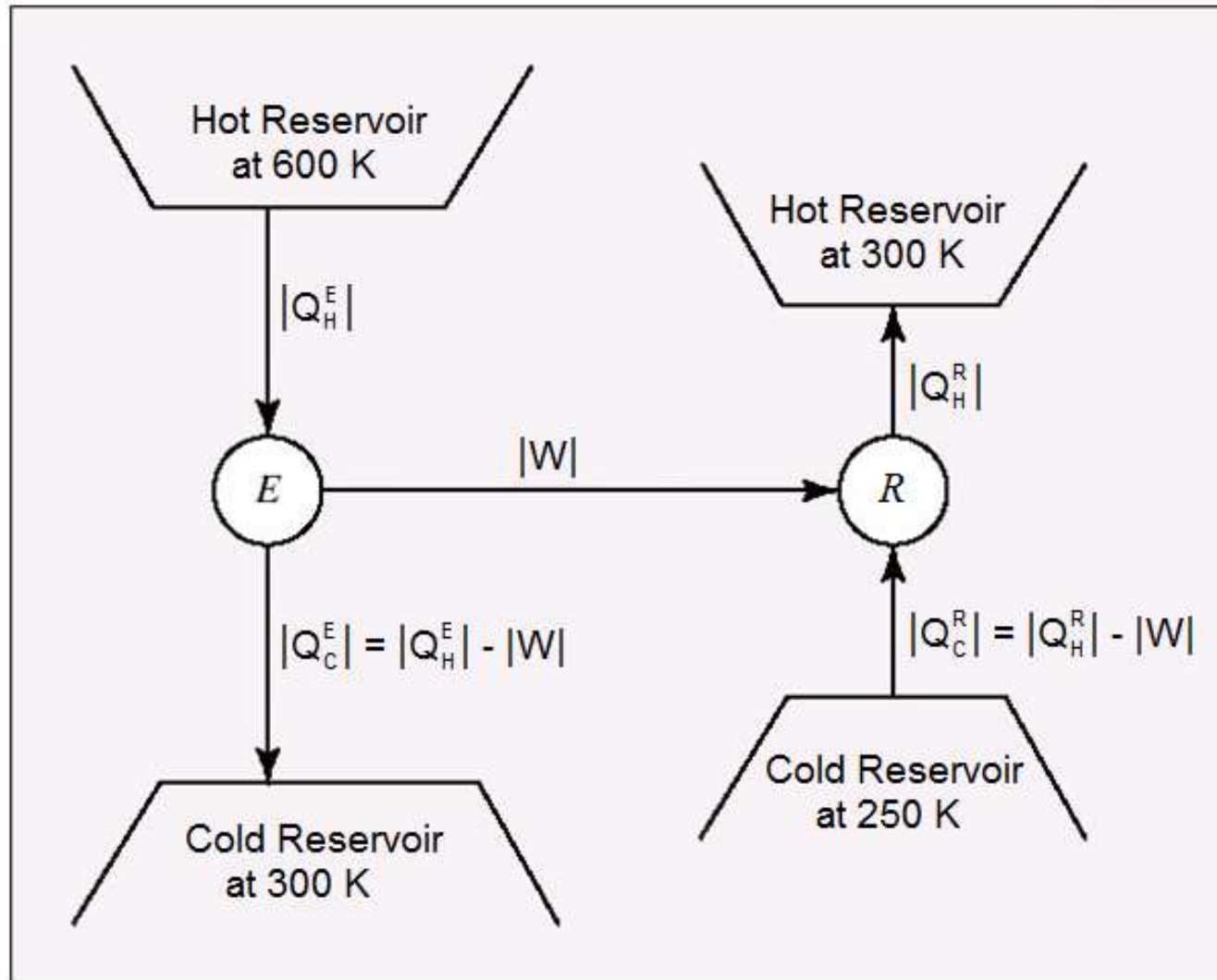
Problem 5.17 - COP

absorbs $\left|Q_H^E\right|$, discards $\left|Q_C^E\right|$, and produces $\left|W\right|$	absorbs $\left|Q_C^R\right|$, discards $\left|Q_H^R\right|$, and consumes $\left|W\right|$
$\left|W\right| = \left|Q_H^E\right| - \left|Q_C^E\right|$ (page 175) 1st Law	$\left|W\right| = \left|Q_H^R\right| - \left|Q_C^R\right|$ 1st Law
$\eta \equiv \dfrac{\left|W\right|}{\left|Q_H^E\right|}$ (Eq. 5.2) definition of efficiency	$\omega \equiv \dfrac{\left|Q_C^R\right|}{\left|W\right|}$ (page 179) definition of coefficient of performance (or COP)
$\eta = \dfrac{\left|Q_H^E\right| - \left|Q_C^E\right|}{\left|Q_H^E\right|}$	$\omega = \dfrac{\left|Q_C^R\right|}{\left|Q_H^R\right| - \left|Q_C^R\right|} \Rightarrow \dfrac{1}{\omega} = \dfrac{\left|Q_H^R\right| - \left|Q_C^R\right|}{\left|Q_C^R\right|} = \dfrac{\left|Q_H^R\right|}{\left|Q_C^R\right|} - 1$
$\dfrac{\left|Q_C^E\right|}{\left|Q_H^E\right|} = \dfrac{T_C^E}{T_H^E}$ (Eqn. 5.4) introduce Kelvin scale and simplify for ideal gases	$\dfrac{\left|Q_H^R\right|}{\left|Q_C^R\right|} = \dfrac{T_H^R}{T_C^R}$ (page 179) introduce Kelvin scale and simplify for ideal gases
$\eta = 1 - \dfrac{T_C^E}{T_H^E}$	$\dfrac{1}{\omega} = \dfrac{T_H^R}{T_C^R} - 1 = \dfrac{T_H^R - T_C^R}{T_C^R} \Rightarrow \omega = \dfrac{T_C^R}{T_H^R - T_C^R}$