5, 6

CY11001
Spring 2018

- Joule-Thompson Effect
- Second Law of Thermodynamics

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Variation of enthalpy with T and p

$$H = f(p, T)$$

$$dH = \left(\frac{\partial H}{\partial p}\right)_T dp + \left(\frac{\partial H}{\partial T}\right)_p dT$$

$$= \left(\frac{\partial H}{\partial p}\right)_T dp + C_p dT$$

Constant p process

$$dH_p = C_p dT$$

Constant T process

$$dH_T = \left(\frac{\partial H}{\partial p}\right)_T dp$$

Special case: Ideal gas

For ideal gas

$$\left(\frac{\partial H}{\partial p}\right)_T = 0 \qquad \left(\frac{\partial H}{\partial V}\right)_T = 0$$

$dH = C_p\, dT$ for ideal gas

Joule-Thompson Experiment:

Purpose is to determine $\left(\dfrac{\partial H}{\partial p}\right)_T$

Upstream pressure

Downstream pressure

Throttle

p_i

p_i, V_i, T_i
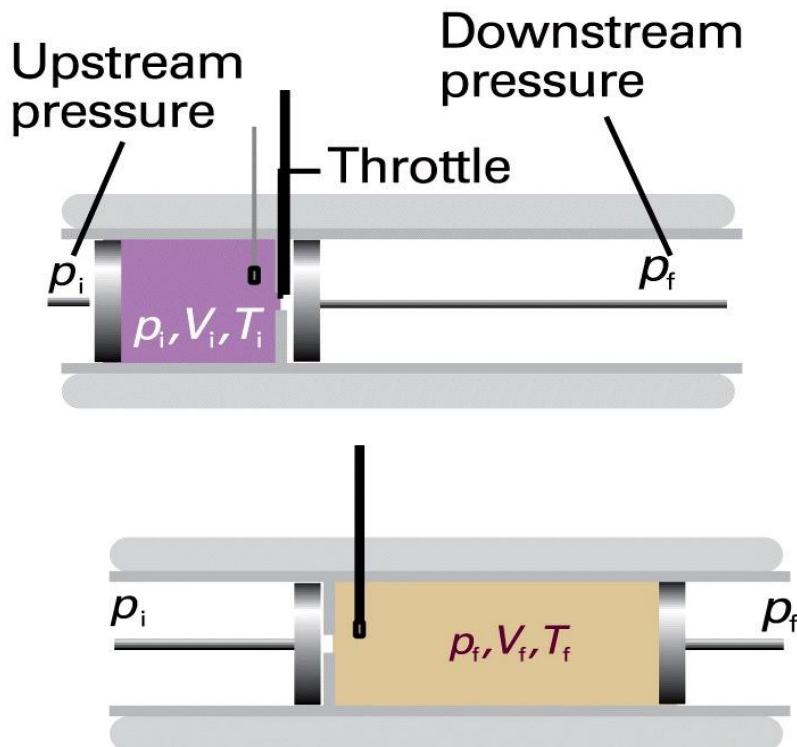
p_f

p_i

p_f, V_f, T_f

p_f

Figure 2-28
Atkins Physical Chemistry, Eighth Edition
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In this experiment

$q = 0 \qquad w = - p_f(V_f - 0) - p_i (0 - V_i) = p_i V_i - p_f V_f$

$\Delta U = U_f - U_i = q + w = - p_f V_f + p_i V_i$

$U_f + p_f V_f = U_i + p_i V_i$ **Isenthalpic process**

$H_f = H_i, \; \Delta H = 0$ **(Constant H)**

$$H = f(p,T); \quad dH = \left(\frac{\partial H}{\partial p}\right)_T dp + \left(\frac{\partial H}{\partial T}\right)_P dT$$

$$\left(\frac{\partial H}{\partial p}\right)_T = -\left(\frac{\partial H}{\partial T}\right)_P \left(\frac{\partial T}{\partial p}\right)_H = -C_p \times \mu_{JT}$$

$$dH = -\mu_{JT} C_p dp + C_p dT$$

Joule-Thompson Coefficient,

$$\mu_{JT} = \left(\frac{\partial T}{\partial p}\right)_H \approx \left(\frac{\Delta T}{\Delta p}\right)$$

Ratio of change in T to the p when a gas expands under constant H.

Inversion Temperature and Cooling of gases with JT expansion:

For ideal gas $\mu_{JT} = 0$
For real gas $\mu_{JT} \neq 0$

$$\mu_J = \left(\frac{\partial T}{\partial V}\right)_U \qquad \mu_{JT} = \left(\frac{\partial T}{\partial p}\right)_H \qquad \mu_T = \left(\frac{\partial H}{\partial p}\right)_T = -C_p \mu_{JT}$$

Isothermal Joule-Thomson Coefficient

Some inversion temperatures are (at 1 atm):

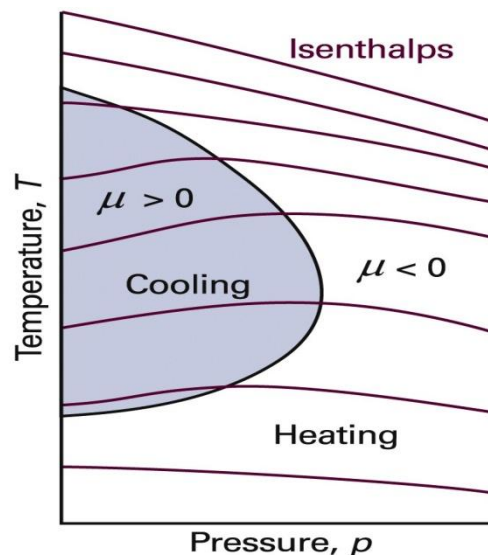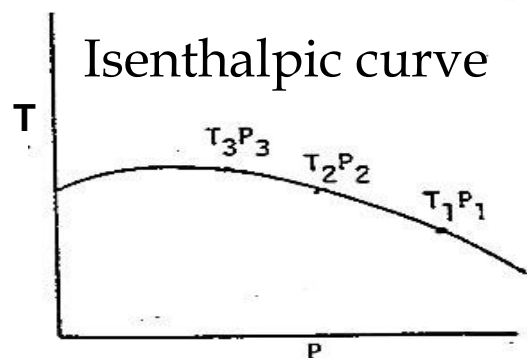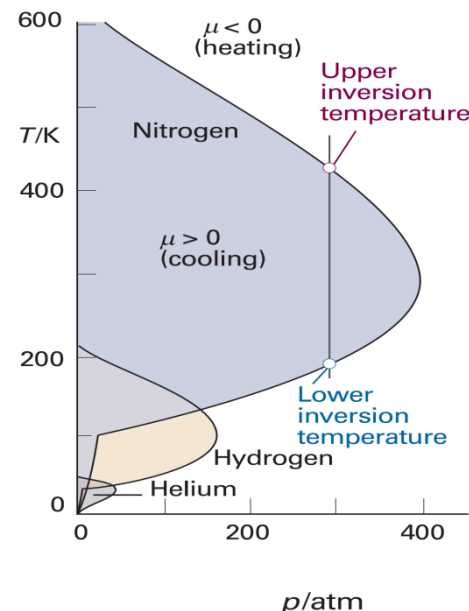|	
He	40 K
Ne	231 K
N_2	621 K
O_2	764 K

Isenthalpic curve

Figure 2-31
Atkins Physical Chemistry, Eighth Edition
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At room temperature and 1 atmp, N_2 and O_2 will cool upon expansion while He and Ne will warm upon expansion.

Calculation of thermodynamic functions for various processes

	reversible *phase change* at const. T, p	const p heating, no phase change	const V heating, no phase change
w	$-\int p\,dV = -p\Delta V$	$-\int p\,dV = -p\Delta V$	0
q	latent heat	$q_p = \Delta H$	$q_V = \Delta U$
ΔU	$q + w$	$q + w$	$= \int C_V(T)\,dT$
ΔH	$q\ (=q_p)$	$= \int C_p(T)\,dT$	$\Delta U + V\Delta p$

Calculation of thermodynamic function for various processes for ideal gas

	state 1 – state 2, no phase change			rev, isothermal	rev, adiabatic
	rev	rev, const ext. p	irrev, const final p		
w	$-\int pdV$	$-p_{ex}\Delta V$	$-p_f\Delta V$	$-nRT\ln\dfrac{V_2}{V_1}$	$=\int C_V(T)dT$
q	$\Delta U - w$			$nRT\ln\dfrac{V_2}{V_1}$	0
ΔU	$=\int C_V(T)dT$			0	$=\int C_V(T)dT$
ΔH	$=\int C_p(T)dT$			0	$=\int C_p(T)dT$

Adiabatic expansion of a perfect gas into vacuum

$$q = 0 \quad \Delta U = 0 \quad w = 0 \quad \Delta H = 0$$

Limitations of the First Law of Thermodynamics

The first law assures us that the total energy of system plus surroundings remains constant during the reaction. Energy can be transferred/transformed, keeping the total energy fixed.

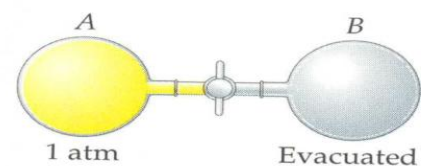$$dU_{\text{universe}} = dU_{\text{system}} + dU_{\text{surrounding}} = 0$$

Does not say:

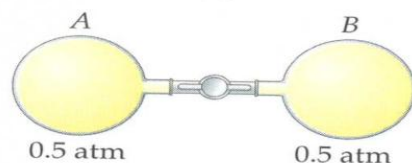Whether energy will get transferred / transformed?
If yes, in which direction?
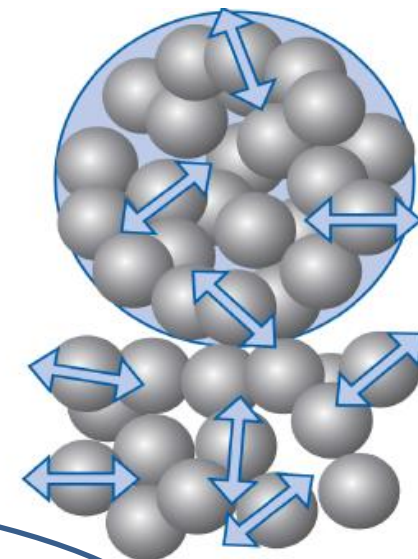If yes, how long?
If yes, how fast?

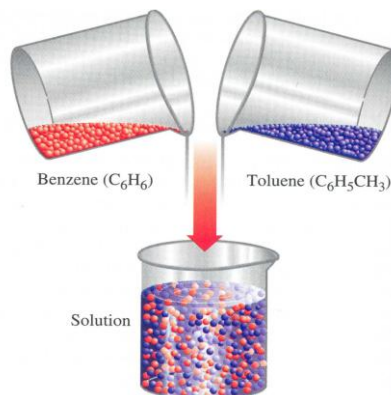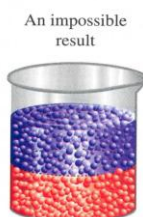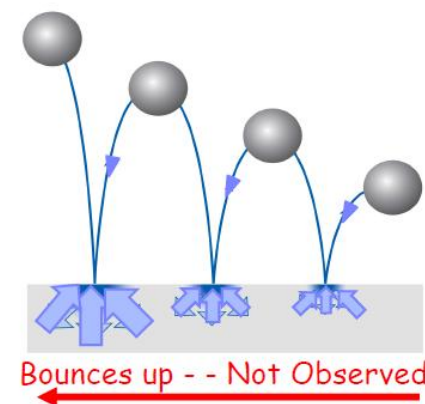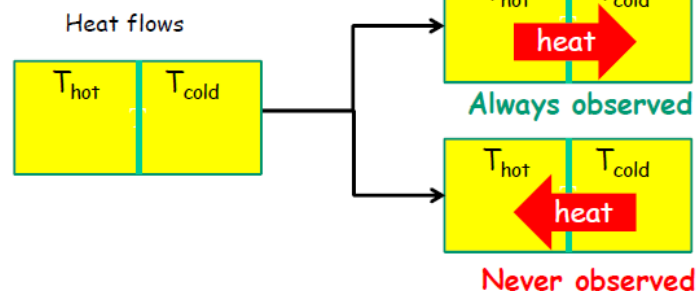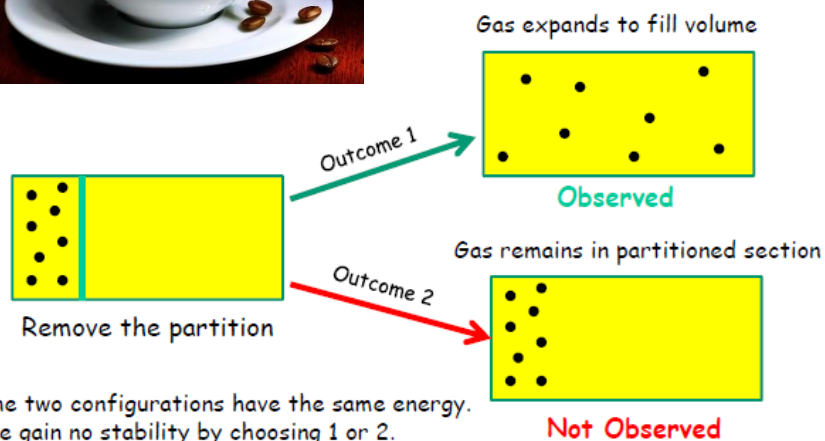In all the cases first law *allows* either outcomes, but we observe only one outcome ***spontaneously***.

Spontaneity:

A <u>spontaneous process</u> occurs naturally and needs no external source of work. A <u>non-spontaneous process</u>, although allowed by first law of TD, requires an external source of work to drive it.

Who drives, a spontaneous process?

Entropy

- The thermodynamic property of a system that is related to its degree of randomness or disorder is called **entropy (S).**

- The **entropy** S and the **entropy change** $\Delta S = S_2 - S_1$ are **state functions.**

- The **entropy** S has a unique value, once the pressure p, the temperature T and the composition n of the system are specified, $S=S(p,T,n)$.

- The **entropy is an extensive property**, i.e., increases with the amount of matter in the system. $S_m = S/n$ (molar entropy).

Thermodynamic definition of entropy

dS_{syst} = Change in entropy that occurs during a chemical or physical process

= $dq_{rev} \,/\, T$ (q_{rev} is the heat supplied *reversibly*)

$$\Delta S_{\text{system}} = \int_1^2 \frac{dq_{rev}}{T}$$

surrounding   system
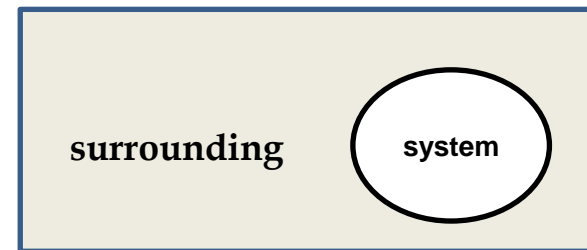
For surroundings,

$dS_{\text{surr}} = -\, dq/T_{\text{surr}}$

$$\Delta S_{surr} = \frac{-q}{T_{surr}}$$

Large change in entropy occurs when heat is dissipated to surrounding at low temperature.

How do you calculate entropy change?

For surrounding

$$dS_{surr} = - dq / T_{surr}$$

$$\Delta S_{surr} = \frac{-q}{T_{surr}}$$

surrounding   system

Calculate the actual q for the process from state 1 to state 2 and apply the above formula

For system

- Find out state 1 and state 2
- Construct reversible pathway(s) from state 1 and state 2
- Apply the formula

$$\Delta S = \int_{1}^{2} \frac{dq_{rev}}{T}$$

•Calculate the entropy change in the surroundings when 1.0 mole of $H_2O(l)$ is formed from its elements under standard conditions at 25° C (298.15 K).

$H_2(g) + 1/2\ O_2(g) = H_2O\ (l)$ $\Delta_f H = -286$ kJ/mol.

भारतीय प्रौद्योगिकी संस्थान खड़गपुर
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Calculation of Entropy Changes (A few special cases)

$$\Delta S_{\text{system}} = \int_1^2 \frac{dq_{rev}}{T}$$

1. Cyclic Process $\Delta S_{\text{syst}} = 0$ (S is a state function)

2. Reversible adiabatic process $\Delta S_{\text{syst}} = 0$ ($dq_{\text{rev}} = 0$)

3. Reversible phase-change at constant p and T

$$\Delta S_{\text{syst}} = \int_1^2 \frac{dq_{rev}}{T} = \frac{1}{T} \int_1^2 dq_{rev} = \frac{q_{rev}}{T} = \frac{\Delta H}{T}$$

4. Constant p heating (reversibly) with no phase change:

$$dq_{rev} = dq_p = C_p dT$$

$$\Delta S_{\text{syst}} = \int_{T_1}^{T_2} \frac{dq_{rev}}{T} = C_p \int_{T_1}^{T_2} \frac{dT}{T} = C_p \ln\left(\frac{T_2}{T_1}\right)$$

5. Reversible isothermal process:

$$\Delta S_{\text{syst}} = \int_1^2 \frac{dq_{rev}}{T} = \frac{1}{T} \int_1^2 dq_{rev} = \frac{q_{rev}}{T}$$

6. For ideal gas:

$$dS = \frac{dq_{rev}}{T} = \frac{dU - w_{rev}}{T} = \frac{C_V dT + pdV}{T} = C_V \frac{dT}{T} + nR \frac{dV}{V}$$

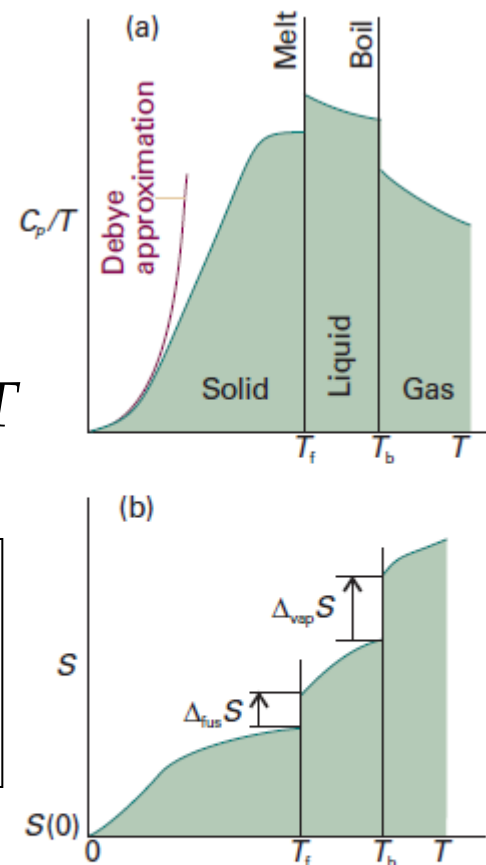$$\Delta S = C_V \ln\frac{T_2}{T_1} + nR \ln\frac{V_2}{V_1}$$

$$\Delta S = C_p \ln\frac{T_2}{T_1} + nR \ln\frac{p_1}{p_2}$$

Calculation of Entropy at *any* temperature

Heating at constant pressure/Volume

$$\Delta S_p = \int \frac{C_p}{T} dT = C_p \ln \frac{T_2}{T_1}$$

$$\Delta S_V = \int \frac{C_V}{T} dT = C_V \ln \frac{T_2}{T_1}$$

Debye approx:
$C_p \propto T^3$ at low T

(a) Melt Boil

C_p/T Debye approximation

Solid Liquid Gas

T_f T_b T

Entropy at any temperature,

$$S(T) = S(0) + \int_0^{T_f} \frac{C_p(s)}{T} dT + \frac{\Delta H_{\text{fus}}}{T_{\text{fus}}} + \int_{T_f}^{T_b} \frac{C_p(l)}{T} dT + \frac{\Delta H_{\text{vap}}}{T_{\text{vap}}} + \int_{T_b}^{T} \frac{C_p(g)}{T} dT$$

(b)

$\Delta_{\text{vap}} S$

S

$\Delta_{\text{fus}} S$
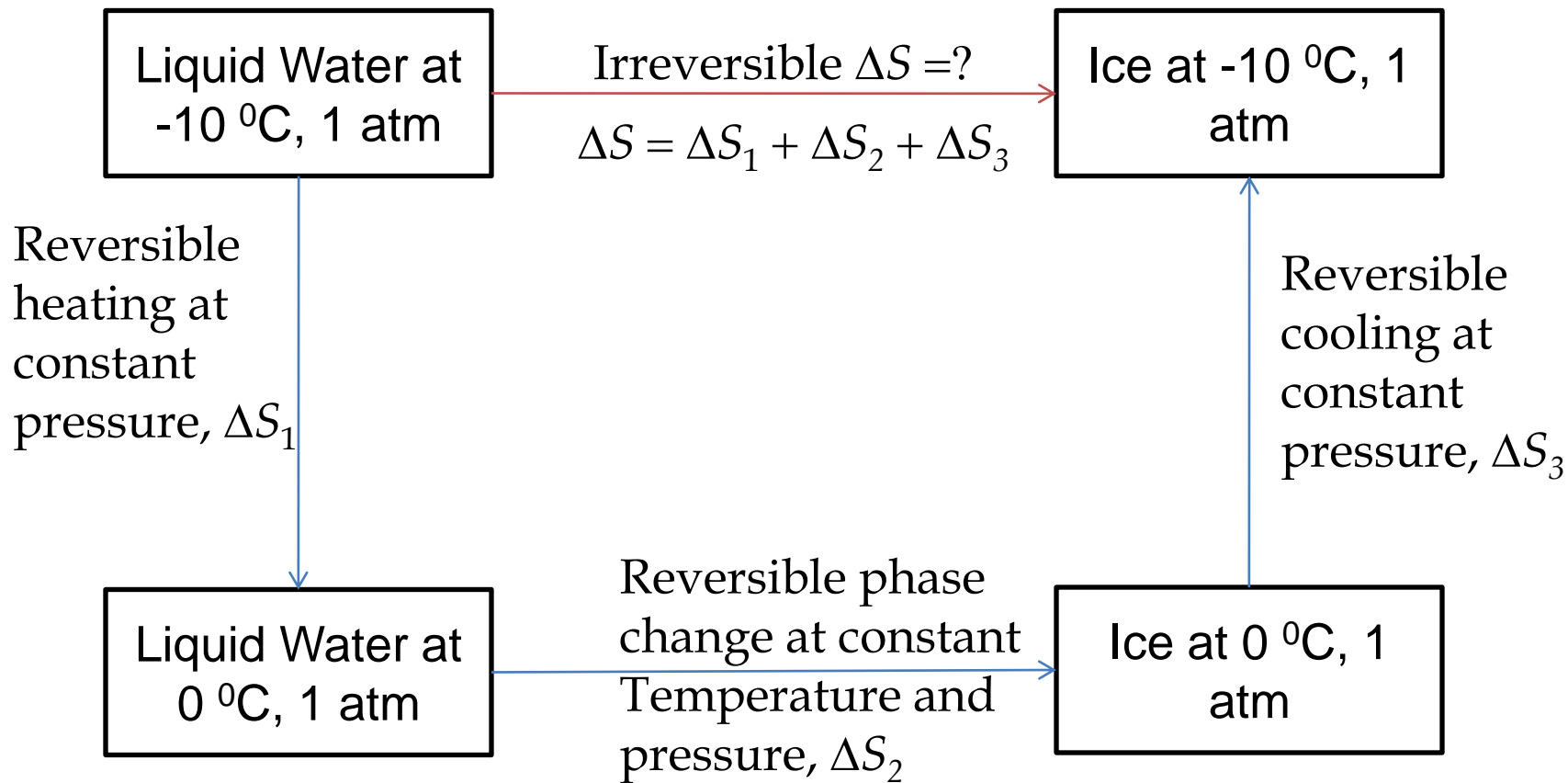
$S(0)$

0 T_f T_b T

Fig. 3.14 The calculation of entropy from heat capacity data. (a) The variation of C_p/T with the temperature for a sample. (b) The entropy, which is equal to the area beneath the upper curve up to the corresponding temperature, plus the entropy of each phase transition passed.

Trouton's Rule

A wide range of liquid give approx. the same standard entropy of vaporization ~ 85 J K^{-1} mol^{-1} . Exception: water, it is 109 J/K/mol

Construction of Reversible Steps to Describe an Irreversible Process:

Example 1:

Liquid Water at -10 ^{0}C, 1 atm	Irreversible $\Delta S =?$ $\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3$	**Ice at -10 ^{0}C, 1 atm**

Reversible heating at constant pressure, ΔS_1

Reversible cooling at constant pressure, ΔS_3

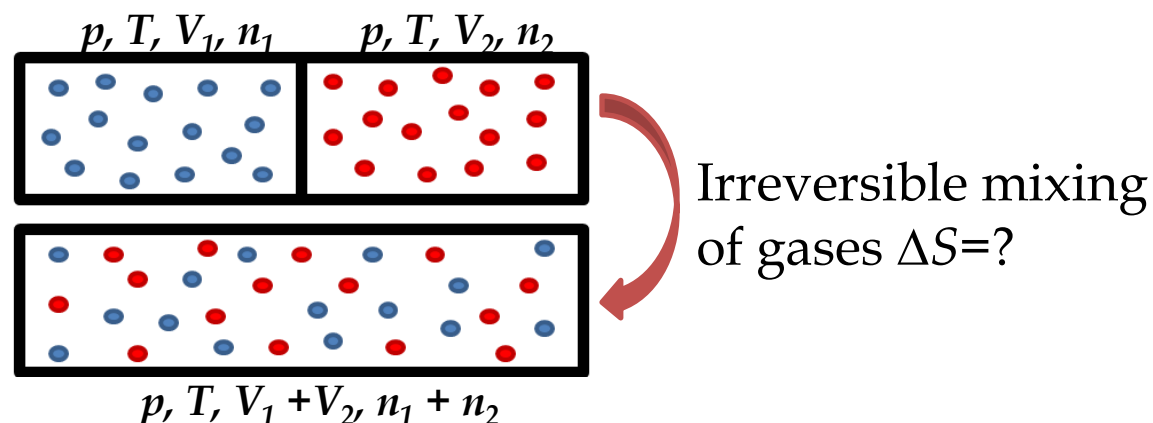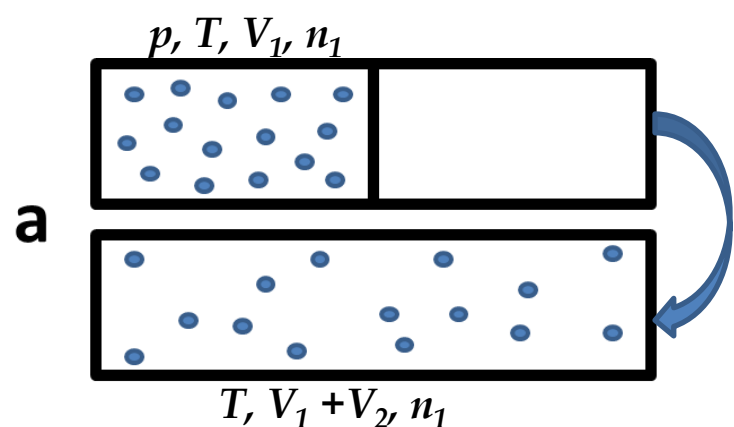|		
Liquid Water at 0 ^{0}C, 1 atm	Reversible phase change at constant Temperature and pressure, ΔS_2	**Ice at 0 ^{0}C, 1 atm**

Home work

Entropy is an extensive property. $\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3$

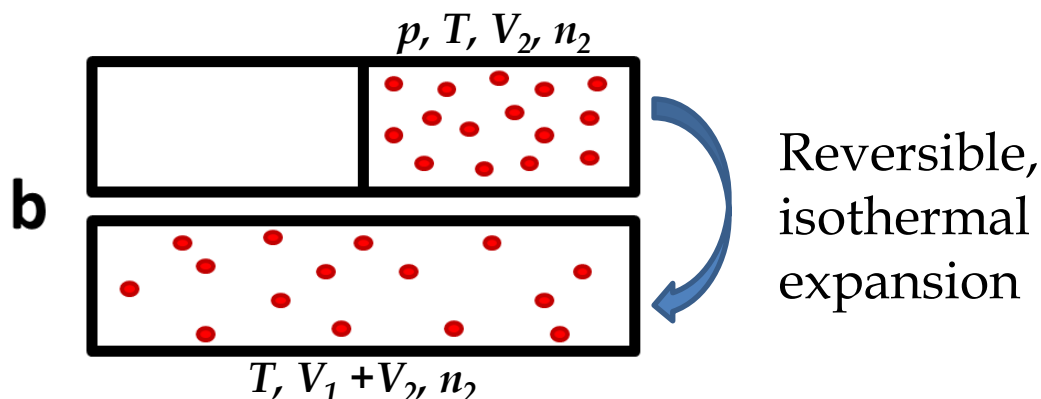# Construction of Reversible Steps to Describe an Irreversible Process:

Example 2: **Entropy of Mixing of ideal gases**

$$\Delta S_{mix} = \Delta S_1 + \Delta S_2$$

p, T, V$_1$, n$_1$ p, T, V$_2$, n$_2$

Irreversible mixing of gases ΔS=?

p, T, V$_1$ +V$_2$, n$_1$ + n$_2$

p, T, V$_1$, n$_1$

a

T, V$_1$ +V$_2$, n$_1$

p, T, V$_2$, n$_2$

b

T, V$_1$ +V$_2$, n$_2$

Reversible, isothermal expansion
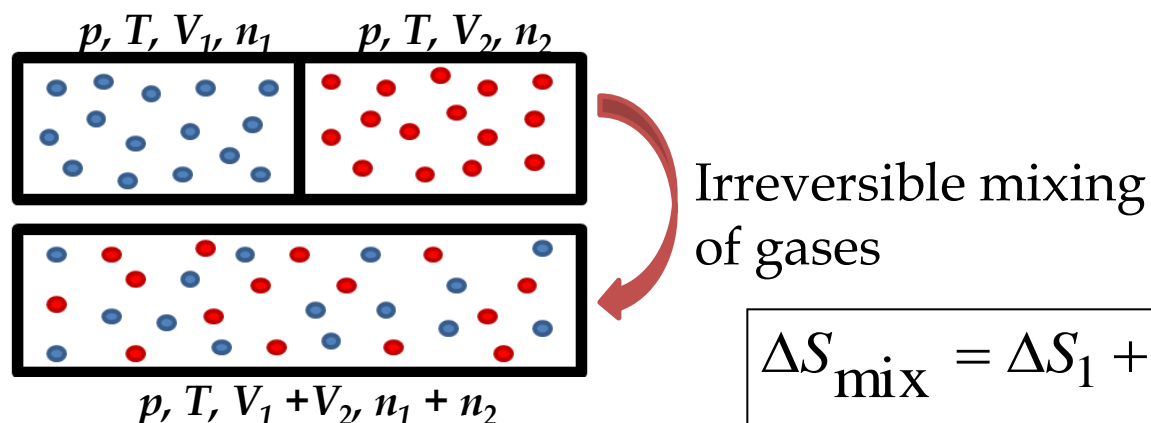
$$\Delta S_1 = n_1 R \ln \frac{V_1 + V_2}{V_1}$$

$$\Delta S_2 = n_2 R \ln \frac{V_1 + V_2}{V_2}$$

Construction of Reversible Steps to Describe an Irreversible Process:

Example 2: **Entropy of Mixing of ideal gases**

p, T, V$_1$, n$_1$ *p, T, V$_2$, n$_2$*

p, T, V$_1$ +V$_2$, n$_1$ + n$_2$

Irreversible mixing of gases

$$\Delta S_{\mathrm{mix}} = \Delta S_1 + \Delta S_2$$

$$\Delta S_1 = n_1 R \ln \frac{V_1 + V_2}{V_1}, \Delta S_2 = n_2 R \ln \frac{V_1 + V_2}{V_2}$$

$$\frac{V_1}{V_1 + V_2} = \frac{\dfrac{n_1 RT}{p}}{\dfrac{n_1 RT}{p} + \dfrac{n_2 RT}{p}} = \frac{n_1}{n_1 + n_2} = X_1$$

$$\Delta S_{\mathrm{mix}} = -n_1 R \ln X_1 - n_2 R \ln X_2$$

$$= -nR(X_1 \ln X_1 + X_2 \ln X_2)$$

*Find out X$_1$ for which ΔS_{mix} is maximum.

Home work