Chapter 02

Review of Thermo Basics
2 The Language of Thermo

• today. key words
state functions
thermodynamic properties
1\textsuperscript{st} and 2\textsuperscript{nd} law of thermo

• announce. No class Mon 31\textsuperscript{aug}2009 (Labor Day).
1\textsuperscript{st} exam (8 am on Fri 18\textsuperscript{sep}2009, 111 Wartik).
Midterm exam Mon 05\textsuperscript{oct}2009 from 6:30-9:30.

• assignments. HW 01 due before class Wed 02\textsuperscript{sep}2009.
reading: Ch 02
Example. Energy required to heat an ideal gas

I heat 3 mol of an idea gas from 24 C to 37 C at constant volume. How much energy is required?

\[ dU = \delta Q + \delta W \]

\[ dU = C_v dT \]

\[ \Delta U = C_v \Delta T \]

\[ C_v = \frac{s}{2} R = \frac{5}{2} \left( 8.314 \text{ J/mol} \cdot \text{K} \right) \]

\[ = 20.79 \text{ J/mol} \cdot \text{K} \]

\[ Q = \Delta U = 3 \text{ mol} \left[ \frac{20.79 \text{ J}}{\text{mol} \cdot \text{K}} \right] (37 - 24 \text{ C}) = \boxed{811 \text{ J}} \]
universe = system + surroundings

closed system = no mass transfer with surroundings
adiabatic system = no heat transfer with surroundings
isolated system = no “communication”
Equilibrium happens with no transport

- ChE 330: Fluid flow happens with a gradient of $\nabla \rho$

- ChE 350: Heat transfer happens with a gradient of $\nabla T$

- ChE 410: Diffusion happens with a gradient of $\nabla C$, $\nabla \mu$

Equilibrium requires gradients $= 0$ for ... $\nabla \rho = 0$
$\nabla T = 0$
$\nabla C = 0$
Intensive versus extensive properties

Intensive properties … do NOT depend on size. T, p, density

Extensive properties … depend on size (or extent). mass, volume, total energy

To make extensive → intensive, divide by mass or moles
State functions ... only end points matter

\[ dF = \left( \frac{\partial F}{\partial X} \right)_{Y, z} dX + \left( \frac{\partial F}{\partial Y} \right)_{X, z} dY + \left( \frac{\partial F}{\partial z} \right)_{X, Y} dz \]

\[ \Delta F_{AB} = \int_{A}^{B} dF = \int_{A}^{B} \left[ \left( \frac{\partial F}{\partial X} \right)_{Y} dX + \left( \frac{\partial F}{\partial Y} \right)_{X} dY \right] \]

\[ \Delta F_{AB} = F_{B} - F_{A} \]

Choose simplest path ...
Example. Molar volume

Estimate the size of a water molecule, and its molar volume.

\[ V_1 = \frac{1}{\rho} \cdot \frac{\text{MW}}{N_A} = \frac{\text{m}^3}{\text{kg}} \cdot \frac{0.018 \text{ kg}}{1000 \text{ kg}} \cdot \frac{\text{mol}}{6.02 \times 10^{23}} \]

\[ = 2.99 \times 10^{-29} \text{ m}^3 \]

\[ V_1 = L^3 \Rightarrow 0.31 \text{ nm} = 3.1 \times 10^{-10} \text{ m} \]

\[ V = \frac{\text{MW}}{\rho} = \frac{\text{m}^3}{\text{kg}} \cdot \frac{0.018 \text{ kg}}{1000 \text{ kg}} = 1.8 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1} \]

\[ = 18 \text{ mL} \text{ mol}^{-1} \]
Some thermodynamic variables

compressibility

\[ Z = \frac{PV}{RT} \]

internal energy

\[ U \quad \text{(quantum level, molecular)} \]

enthalpy

\[ H \equiv U + PV \]

entropy

\[ dS = \frac{dQ_{\text{rev}}}{T} \]
Some thermodynamic variables

Gibbs energy

\[ G \equiv H - TS \]

\[ U + PV - TS \]

“heat” capacities

\[ C_V \equiv \left( \frac{\partial U}{\partial T} \right)_V \]

\[ \rightarrow \Delta U = \int_{T_1}^{T_2} C_V dT \]

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

\[ \Delta H = \int_{T_1}^{T_2} C_P dT \]

For an ideal gas, \( C_V = \frac{5R}{2} = 20.79 \text{ J/mol-K} \)
\( C_P = \frac{7R}{2} = 29.10 \text{ J/mol-K} \)

\( \text{N}_2 \) has \( C_P = 1040 \text{ J/kg-K} = 29.12 \text{ J/mol-K} \)

\( \text{gold} \) has \( C_P = 131.6 \text{ J/kg-K} = 25.4 \text{ J/mol-K} \)

\( \text{water} \) has \( C_V \approx C_P = 4184 \text{ J/kg-K} = 75.3 \text{ J/mol-K} \)
Story CENTER: Entrepreneurship

Character
Excellence
Ownership
Tenacity
Entrepreneurship
Relationship

Rowland Hill
Example. Energy required to heat an ideal gas

I heat 3 mol of an idea gas from 24 C to 37 C at constant volume. How much energy is required?
ChE has 4 magic “conservation equations”

\[ \text{Accumulation} = \text{in} - \text{out} + \text{gen} \]

- Mass balance (MB)
- Energy balance (EB, 1st law of therm)
- Entropy balance (EnB, 2nd law)
- Momentum balance (MoB, F=ma, Newton's 2nd law, Navier-Stokes)

\[ \Delta U = \delta Q + \delta W \]

\[ \frac{\Delta U}{\Delta t} = \dot{Q} + V \]
1st law of thermodynamics

Closed system

\[ dU = dQ + dW \]

Open system

\[ dU^t = \sum_{\text{all streams}} \left\{ \left( H + \frac{v^2}{2} + gz \cdots \right) dm \right\} + dQ^t + dW^t \]

\[ \frac{dU^t}{dt} = \sum_{\text{all streams}} \left\{ \left( H + \frac{v^2}{2} + gz \cdots \right) dm \right\} + \dot{Q} + \dot{W} \]
2\textsuperscript{nd} law of thermodynamics

\[ \Delta S^t_{\text{universe}} \geq 0 \]

Ludwig Boltzmann  
(1844 - 1906)
2nd law of thermodynamics

Energy distributes …
Thermodynamics: laws → measurable variables

- Temperature: $T$
- Pressure: $p$
- Volume: $v$
- Concentrations (mol frxn): $x_i$
- Internal energy: $U$
- Heat: $Q$
- Work: $W$
- Entropy: $S$
- Enthalpy: $H$
- Gibb’s free energy: $G$
- Helmholtz free energy: $A$
- Chemical potential: $\mu$
- Fugacity: $f$

$\{\}$ intensive state variables

$\{\}$ 1st and 2nd laws
Example. Compressing air in different ways

Air is compressed from an initial condition of 1 bar and 25 C to a final state of 5 bar and 25 C by three different mechanically-reversible processes, in a closed system.

a  Heat at const V, followed by cooling at const P
b  Isothermal compression
c  Adiabatic compression, then cooling at const V

For each process, calculate

$\Delta U$ and $\Delta H$.
$W$ and $Q$
blank
Summary

\[
\frac{dU^t}{dt} = \sum_{\text{all streams}} \left\{ \left( H + \frac{v^2}{2} + gz \cdots \right) \dot{m} \right\} + \dot{Q} + \dot{W}
\]

\[
\Delta S^t_{\text{universe}} \geq 0
\]

Character
Excellence
Ownership
Tenacity
Entrepreneurship
Relationship

Entrepreneurship.
List of symbols for 02

\[ C_V = \text{constant volume heat capacity } [=] \text{ J/mol-K} \]
\[ C_P = \text{constant pressure heat capacity } [=] \text{ J/mol-K} \]
\[ G = \text{Gibbs energy } = H - TS [=] \text{ J} \]
\[ H = \text{enthalpy } [=] \text{ J} \]
\[ k = \text{Boltzmann constant } = \frac{R}{N_A} = 1.38 \times 10^{-23} \text{ J/K} \]
\[ m = \text{mass} \]
\[ MW = \text{molecular weight } [=] \text{ kg/mol} \]
\[ N_A = \text{Avogadro’s number } = 6.022 \times 10^{23}/\text{mol} \]
\[ P = \text{pressure } [=] \text{ Pa or N/m}^2 \]
List of symbols for 02

Q = heat [=] J
\( \rho \) = density [=] kg/m\(^3\)
R = gas constant = 8.314 J/mol-K
S = entropy [=] J/K
t = time
T = temperature [=] C or K
U = internal energy [=] J
v = speed [=] m/s
\( v_{rms} \) = “root-mean-square” speed = \(<v^2>^{1/2}\)
V = volume [=] m\(^3\)
W = work [=] J
Z = compressibility factor = PV/RT [=] none