Thermodynamics

Remedial Lecture 2

02 – 24 – 2022

Course outline

- 5 sessions:
  - 1 Basics, (state) functions, ideal gas, internal energy, work, heat
  - **2 Energy, Entropy,**
  - 3 Energy chemical reactions
  - 4 Electrochemistry
  - 5 Colligative properties & statistical thermo

Course today

- Different Energy equations
  - Definitions
  - When to use

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  - Definitions
  - When to use
- Entropy
  - Definition
  - Function in Thermodynamics

Entropy & Energy

- Study guide (page 6 – 13)
- Atkins (see study guide)

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$$\mathrm{d}S = \frac{\mathrm{d}Q^{rev}}{T} \geq \frac{\mathrm{d}Q}{T}$$

$$\mathrm{d}S_{tot} = \mathrm{d}S + \mathrm{d}S_{env} \geq 0$$

$$\mathrm{d}U = -P\mathrm{d}V + T\mathrm{d}S + \sum_i \mu_i \mathrm{d}n_i$$

$$H = U + PV$$

$$\mathrm{d}H = V\mathrm{d}P + T\mathrm{d}S + \sum_i \mu_i \mathrm{d}n_i$$

$$A = U - TS$$

$$\mathrm{d}A = -P\mathrm{d}V - S\mathrm{d}T + \sum_i \mu_i \mathrm{d}n_i$$

$$G = H - TS$$

$$\mathrm{d}G = V\mathrm{d}P - S\mathrm{d}T + \sum_i \mu_i \mathrm{d}n_i$$

Entropy: S

Entropy of a system S_{sys} is a state function,
entropy of the surroundings S_{sur} is NOT a state function.
The total entropy ($S_{tot} = S_{sys} + S_{sur}$) is also NOT a state function.
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2nd law of thermodynamics:
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We saw in the first session that at constant pressure Q = H and since H is a state function, $H^{rev} = H^{irr}$

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$$\Delta S = \int_{T_A}^{T_{fus}} \frac{c_{p,solid}}{T}\,\mathrm{d}T + \frac{\Delta_{fus} H}{T_{fus}} + \int_{T_{fus}}^{T_{vap}} \frac{c_{p,liquid}}{T}\,\mathrm{d}T + \frac{\Delta_{vap} H}{T_{vap}} + \int_{T_{vap}}^{T_X} \frac{c_{p,gas}}{T}\,\mathrm{d}T$$

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We can also see on the formula sheet:

$S = kln(W)$ this is about statistical thermodynamics and we will come back to that in the last remedial

Entropy

Definition: $$\mathrm{d}S \equiv \frac{\mathrm{d}Q^{rev}}{T}$$

Second Law, spontaneous process:

- $dS_{tot} = dS + dS_{sur} \geq 0$,
- In isolated system, Clausius inequality

$$\mathrm{d}S \geq \frac{\mathrm{d}Q}{T} \quad \text{or} \quad \mathrm{d}Q \leq T\mathrm{d}S \quad \text{or} \quad \mathrm{d}Q \leq \mathrm{d}Q^{rev}.$$

Different energy functions & when to choose
1: Internal Energy

- Internal Energy: U
  - U ≡ Q + W
  - $\mathrm{d}U = \mathrm{d}Q + \mathrm{d}W = \mathrm{d}Q - P_{ext}\mathrm{dV} + \mathrm{d}W'$
  - dU = TdS − PdV

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- We can also use internal energy U if we deal with a mono-atomic perfect gas: U = 3/2 nRT or ΔU = 3/2 nRΔT. For an isothermic process the ΔU than is 0!

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2: Enthalpy

- Enthalpy: H
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4: Helmholtz free energy

- Helmholtz free energy: A
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A lump of gold of 200 g and 120.0 °C is placed in an adiabatic container with 25.0 g water at a temperature of 10.0 °C. The system is left alone until equilibrium is achieved.

$C_p(Au) = 0.131\ Jg^{-1}K^{-1}$ and $C_p(H_2O) = 4{,}15\ Jg^{-1}K^{-1}$ and independent of temperature.

a) Determine the equilibrium temperature of the system

b) Determine the entropy change ΔS of the gold

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T_f = 32° C

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$$0.131 \cdot 200 \cdot ln \frac{305}{393} = -6.64\, J/K$$

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$\Delta S_{H2O} = C_{p_{H2O}} \cdot m_{H2O} \cdot ln\frac{T_f}{T_i} = 4.15 \cdot 25 \cdot ln\frac{305}{283} = 7.77\ J/K$

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$\Delta S_{tot} = -6.64 + 7.77 > 0$

c) Give the meaning of all symbols in the following formula as well as a description of its use in thermodynamic problems.

$$\Delta S = -nR\left(x_A \ln x_A + x_B \ln x_B\right)$$

Question 2 (test 2011) Ammonia solidifies at a temperature of 195.4 K. The heat of fusion, which is the amount of heat needed to melt ammonia at that temperature and a pressure of 1 atm, is 5 652 J/mol.

cp (solid ammonia) = 30.0 J mol-1 K-1 and cp (liquid ammonia) = 75.3 J mol-1 K-1 . Both can be considered independent of temperature. A vessel containing 1 mole supercooled liquid ammonia is put in a bath at constant temperature.

Pressure = 1 atm and temperature vessel = temperature ammonia = temperature bath = 185.4 K.

A bright PhD student shouts “Crystallize!” at the vessel and the liquid crystallizes immediately.

a) Draw a reversible path as an alternative for the process at 185.4 K.
b) Calculate the heat of fusion of ammonia at 185.4 K.
c) Calculate the change of entropy due to the crystallization.
d) Show that the result agrees with the second law of thermodynamics