

Exercise 2

Problem 1

How are Internal energy (U), Enthalpy (H), Entropy (S), Helmholtz energy (A) and Gibbs energy (G) defined?

U: The energy contained within a system: $\Delta U = Q - W$

H: The internal energy of the system + the product of the pressure and the volume, it is a mathematical property defined for convenience.

$$H = U + PV$$

S: Microscopic definition: A measure of the molecular disorder in the system, relates to the number of microscopic states that are available in a given macrostate.

$$S = k \cdot \ln W \quad \leftarrow \begin{array}{l} \text{number of ways to arrange the molecules in the system.} \\ \text{↑} \\ \text{Boltzmann's constant} \end{array}$$

A: Available useful work in a TD system at constant volume and temperature.

$$A = U - TS$$

G: Available useful work in a TD system at constant pressure and temperature
non expansion/contraction

$$G = H - TS$$

Problem 2

What is the 1st law of thermodynamic (TD) expression of?

The 1st law of TD expresses that the change in the internal energy of the system is equal to the sum of the heat and work added to the system

$$\Delta U = q + w$$

(Energy is not formed or destroyed)

Problem 3

What is the 2nd law of thermodynamic (TD) expression of?

2nd law of TD for reversible process

"The change in system entropy for a closed simple system is equal to the heat absorbed by the system along the path divided by system temp."

$$dS = \left(\frac{\partial Q}{T} \right)_{rev}$$

For irreversible process

"The change in entropy during irreversible processes is always larger than the amount of heat transferred by the system temperature."

$$dS = \left(\frac{\partial Q}{T} \right)_{irr} > \left(\frac{\partial Q}{T} \right)_{rev}$$

Problem 4

Create your own table of the TD energy functions U, H, A, G (TD potentials and the relationships between them and between their derivatives and T, p, V). Also include the U and H in non-canonical variables U(T, V) and H(T, p) and Maxwell relations. Please show the derivation work of each relations and fill in Table 1.

Apply:

- 1st law, 2nd law, the combined 1st and 2nd law (Gibbs relations)
- Definition of total differential as for a function $z(x, y)$:

$$dz = \left(\frac{\partial z}{\partial x} \right)_y dx + \left(\frac{\partial z}{\partial y} \right)_x dy$$

- The independency of the order of derivation as for a function $z(x, y)$:

$$\left(\frac{\partial^2 z}{\partial x \partial y} \right) = \left(\frac{\partial^2 z}{\partial y \partial x} \right)$$

1st law of TD

- $U = Q + W \Rightarrow dU = dq + dw$, if the process is reversible, and $P = P_{ext}$

$$\underline{dU = dq - pdV}$$

- $H = U + PV$, if the process is reversible, and $P = P_{ext}$

$$\begin{aligned} dH &= dU + pdV + Vdp \\ &= dq - pdV + pdV + Vdp \\ \underline{dH} &= \underline{dq + Vdp} \end{aligned}$$

- $A = U - TS \Rightarrow dA = dU - SdT - TdS$

$$\underline{dA = dq - pdV - SdT - TdS}$$

- $G = H - TS \Rightarrow dG = dH - TdS - SdT$

$$\underline{dG = dq + Vdp - TdS - SdT}$$

TD functions canonic variables and definitions	1st law of TD and derived relations	Combined 1st&2nd law of TD derived relations and Gibbs equations	Total differential (canonic var.)	Introducing total differential of entropy $dS(T,V)$ or $dS(T,p)$	Total differential in measurable variables (T,V) or (T,p)	Maxwell relations from Gibbs Equations
$U(S,V) =$ $U = Q - W$	$dU = dq - pdV$	$dU = TdS - pdV$	$dU = \left(\frac{\partial U}{\partial S}\right)_V dS - \left(\frac{\partial U}{\partial V}\right)_S dV$	$dU = T\left(\frac{\partial S}{\partial T}\right)_V dT + \left[T\left(\frac{\partial S}{\partial V}\right)_T - p\right] dV$	$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$	$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$
$H(S,p) =$ $H = U + pV$	$dH = dq + Vdp$	$dH = TdS + Vdp$	$dH = \left(\frac{\partial H}{\partial S}\right)_p dS + \left(\frac{\partial H}{\partial p}\right)_S dp$	$dH = T\left(\frac{\partial S}{\partial T}\right)_p dT + \left[T\left(\frac{\partial S}{\partial p}\right)_T + V\right] dp$	$dH = \left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp$	$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$
$A(T,V) =$ $A = U - TS$	$dA = dq - pdV - SdT - TdS$	$dA = -SdT - pdV$	$dA = \left(\frac{\partial A}{\partial T}\right)_V dT + \left(\frac{\partial A}{\partial V}\right)_T dV$	—	$dA = \left(\frac{\partial A}{\partial T}\right)_V dT + \left(\frac{\partial A}{\partial V}\right)_T dV$	$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial V}{\partial T}\right)_p$
$G(T,p) =$ $G = H - TS$	$dG = dq + pdV - SdT - TdS$	$dG = -SdT + Vdp$	$dG = \left(\frac{\partial G}{\partial T}\right)_p dT + \left(\frac{\partial G}{\partial p}\right)_T dp$	—	$dG = \left(\frac{\partial G}{\partial T}\right)_p dT + \left(\frac{\partial G}{\partial p}\right)_T dp$	$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$

Table 1: Thermodynamic functions and its derived property relations

1st & 2nd law of TD

- $U = Q + W \Rightarrow dU = dq + dw$, if the process is reversible, and $P = P_{ext}$

$$dU = dq - PdV, \quad dS = \frac{dq}{T}$$

$$dU = TdS - PdV$$

- $H = U + PV$, if the process is reversible, and $P = P_{ext}$

$$dH = dU + pdV + Vdp$$

$$= TdS - pdV + pdV + Vdp$$

$$dH = TdS + Vdp$$

- $A = U - TS \Rightarrow dA = dU - SdT - TdS$

$$dA = TdS - pdV - SdT - TdS$$

$$dA = -SdT - pdV$$

- $G = H - TS \Rightarrow dG = dH - TdS - SdT$

$$dG = TdS + Vdp - TdS - SdT$$

$$dG = -SdT + Vdp$$

Total differentials

Just using the definition of total differentials

Introducing the total differential of S

$$dS(T,V) = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

$$dS(T,p) = \left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp$$

$$dU = TdS - pdV$$

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

$$dH = TdS + Vdp$$

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

Total differentials in measurable variables

For A and G , it is the same, they already are in T, P

(which might be wrong, I might have inserted dU too early)

- by introducing S , we now have $dU(T, V)$ and $dH(T, p)$

which allows us to write the total differentials

Maxwell relations

Comparing the 3rd and 4th columns gives us:

$$U: T = \left(\frac{\partial U}{\partial S}\right)_V, -p = \left(\frac{\partial U}{\partial V}\right)_S$$

$$H: T = \left(\frac{\partial H}{\partial S}\right)_p, V = \left(\frac{\partial H}{\partial p}\right)_S$$

$$A: -S = \left(\frac{\partial A}{\partial T}\right)_V, -p = \left(\frac{\partial A}{\partial V}\right)_T$$

$$G: -S = \left(\frac{\partial G}{\partial T}\right)_p, V = \left(\frac{\partial G}{\partial p}\right)_T$$

Euler's theorem

$$\frac{\partial}{\partial y} \left(\frac{\partial F}{\partial x} \right)_y = \frac{\partial}{\partial x} \left(\frac{\partial F}{\partial y} \right)_x$$

$$U: \underbrace{\frac{\partial}{\partial V} \left(\frac{\partial U}{\partial S} \right)_V}_T = \underbrace{\frac{\partial}{\partial S} \left(\frac{\partial U}{\partial V} \right)_S}_{-p} \Rightarrow \left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial p}{\partial S} \right)_V$$

$$H: \underbrace{\frac{\partial}{\partial p} \left(\frac{\partial H}{\partial S} \right)_p}_T = \underbrace{\frac{\partial}{\partial S} \left(\frac{\partial H}{\partial p} \right)_S}_V \Rightarrow \left(\frac{\partial T}{\partial p} \right)_S = \left(\frac{\partial V}{\partial S} \right)_p$$

$$A: \underbrace{\frac{\partial}{\partial V} \left(\frac{\partial A}{\partial T} \right)_V}_{-S} = \underbrace{\frac{\partial}{\partial T} \left(\frac{\partial A}{\partial V} \right)_T}_{-p} \Rightarrow \left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial p}{\partial T} \right)_V$$

$$G: \underbrace{\frac{\partial}{\partial p} \left(\frac{\partial G}{\partial T} \right)_p}_{-S} = \underbrace{\frac{\partial}{\partial T} \left(\frac{\partial G}{\partial p} \right)_T}_V \Rightarrow \left(\frac{\partial S}{\partial p} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_p$$

Problem 5

Derive "useful" relations for $U(T, V)$ and $H(T, p)$ by introducing the definitions of heat capacities C_V and C_p .

Problem 6

Simplify the relations (from Problem 5) assuming ideal gas.

The definitions: $C_V = \left(\frac{\partial U}{\partial T} \right)_V$

$$C_p = \left(\frac{\partial H}{\partial T} \right)_p$$

From problem 4:

$$dU = \underbrace{T \left(\frac{\partial S}{\partial T} \right)_V}_{= C_V} dT + \underbrace{T \left(\frac{\partial S}{\partial V} \right)_T}_{\text{Maxwell relation} = \left(\frac{\partial p}{\partial T} \right)_V} dV - p dV = C_V dT + \underbrace{\left[T \left(\frac{\partial p}{\partial T} \right)_V - p \right]}_{=0} dV = C_V dT$$

Ideal gas law:

$$p = \frac{nRT}{V}$$

$$\Rightarrow \left(\frac{\partial p}{\partial T} \right)_V = \frac{nR}{V} \Rightarrow T \left(\frac{\partial p}{\partial T} \right)_V = \frac{nRT}{V} = p$$

$$dH = T \left(\frac{\partial S}{\partial T} \right)_P dT + T \left(\frac{\partial S}{\partial P} \right)_T dP + V dP = C_P dT + \underbrace{\left[V - \left(\frac{\partial V}{\partial T} \right)_P \cdot T \right]}_{\substack{\text{Maxwell} \\ = - \left(\frac{\partial V}{\partial T} \right)_P \cdot T}} dP = C_P dT$$

$\underbrace{T \left(\frac{\partial S}{\partial T} \right)_P}_{= \left(\frac{\partial H}{\partial T} \right)_P = C_P}$
 $\underbrace{T \left(\frac{\partial S}{\partial P} \right)_T}_{= - \left(\frac{\partial V}{\partial T} \right)_P \cdot T}$
 $\underbrace{\left[V - \left(\frac{\partial V}{\partial T} \right)_P \cdot T \right]}_{=0, \text{ same calculation as for } dU}$

• For problem 5

$$dU = C_V dT + \left[T \left(\frac{\partial P}{\partial T} \right)_V - P \right] dV$$

$$dH = C_P dT + \left[V - \left(\frac{\partial V}{\partial T} \right)_P \cdot T \right] dP$$

• For problem 6

$$dU = C_V dT$$

$$dH = C_P dT$$

Problem 7

10 mol of an ideal gas with $C_V = 20.8 \text{ J/mol}\cdot\text{K}$ at $T_0 = 300 \text{ K}$ and $P_0 = 0.3 \text{ MPa}$ occupy the left half of an insulated vessel as shown in Figure 1. The other half is evacuated. At time $t = 0$, a 1 kW electrical heating element is turned on. After 30 s, the partition dividing the vessel ruptures and the heating element is turned off. Calculate

(a) The final temperature T_f and pressure P_f of the gas in the vessel

(b) The entropy change of the gas during the process

$$a) \quad \Delta U = q + W = n \cdot C_V \cdot \Delta T$$

$$q + W = n \cdot C_V \cdot (T_f - T_0) \quad , \quad W = 0 \text{ (no work done)}$$

$$T_f = T_0 + \frac{q}{n C_V} = 300 \text{ K} + \frac{30 \text{ s} \cdot 1000 \text{ J/s}}{10 \text{ mol} \cdot 20.8 \text{ J/mol}\cdot\text{K}}$$

$$\underline{T_f = 444 \text{ K}}$$

$nR = \text{constant}$, using ideal gas law:

$$\frac{P_0 V_0}{T_0} = \frac{P_f V_f}{T_f} \quad , \quad V_f = 2 \cdot V_0$$

$$\Rightarrow P_f = \frac{P_0 \cdot T_f}{2 \cdot T_0} = \frac{0.3 \text{ MPa} \cdot 444 \text{ K}}{2 \cdot 300 \text{ K}} = 0.222 \text{ MPa}$$

$$\underline{P_f = 0.222 \text{ MPa}}$$

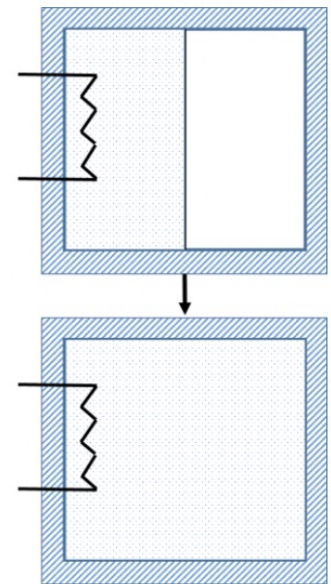


Figure 2: Schematic of process for Problem 7

b) From problem 4

1 mole basis: $dU = TdS - PdV = C_v dT$

$$\Rightarrow dS = \frac{dU}{T} + \frac{P}{T} dV$$

$$dS = \frac{C_v}{T} dT + \frac{P}{T} dV \quad / \text{ideal gas law}$$

$$dS = \frac{C_v}{T} dT + \frac{R}{V} dV \quad / \text{"Integrating"}$$

$$\Delta S = C_v \cdot \ln\left(\frac{T_f}{T_i}\right) + R \cdot \ln\left(\frac{V_f}{V_i}\right)$$

$\underbrace{\ln\left(\frac{V_f}{V_i}\right)}_{=2} \quad (V_f = 2V_i)$

For 10 moles: $\Delta S = 10 \text{ mol} \left(20,8 \frac{\text{J}}{\text{mol} \cdot \text{K}} \cdot \ln\left(\frac{444}{300}\right) + 8,314 \frac{\text{J}}{\text{mol} \cdot \text{K}} \cdot \ln 2 \right)$

$$\underline{\underline{\Delta S = 139,2 \text{ J/K}}}$$

Problem 8

An inventor is proposing a 'black box' for producing electrical power that operates on a stream of compressed air at $P_1 = 4 \text{ bar}$, $T_1 = 300 \text{ K}$. The input stream is split into two equal flows of $P_2 = P_3 = 1 \text{ bar}$ at $T_2 = 280 \text{ K}$ and $T_3 = 260 \text{ K}$, respectively. The claim is made that power is produced at a steady state rate of $W = 3.4 \text{ kJ/mol}$ of air flowing through the device. Assuming that unlimited heat exchange with the environment at $T_{\text{env}} = 300 \text{ K}$ is allowed, you are asked to provide an analysis of the thermodynamic feasibility of such a device (proving that entropy changes for the system is non-zero). Assume that air can be approximated as an ideal gas with $C_p = 29.1 \text{ J/mol} \cdot \text{K}$, independent of temperature.

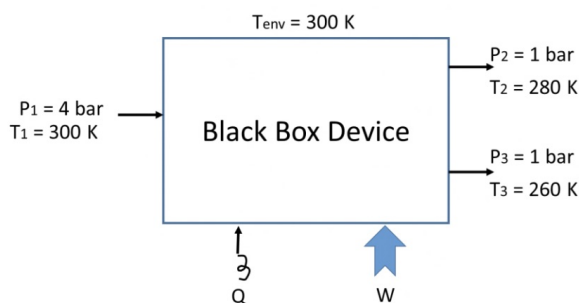


Figure 3: Schematic of process Problem 8

Energy balance for steady-state:

1 mol basis:

$$H_1 - \frac{H_2}{2} - \frac{H_3}{2} + q + W = 0$$

/ Using reference state so $H=0$ at $T=0$
 $\Delta H = C_p \Delta T \Rightarrow H = C_p \cdot T$

$$C_p(T_1 - \frac{1}{2}(T_2 + T_3)) + q + W = 0$$

$$q = -C_p(T_1 - \frac{1}{2}(T_2 + T_3)) - W = -29,1 \frac{\text{J}}{\text{mol} \cdot \text{K}} \left(300 - \frac{1}{2}(280 + 260) \right) \text{K} - (-3,4 \frac{\text{kJ}}{\text{mol}})$$

$$\underline{\underline{q = 2527 \text{ J/mol}}}$$

Entropy balance

$$\frac{dS}{dt} = \sum s^{\text{in}} \cdot \dot{n}^{\text{in}} - \sum s^{\text{out}} \cdot \dot{n}^{\text{out}} + \underbrace{\sum \frac{\dot{q}}{T_{\text{sys}}}}_{\text{Only surrounding}} + \dot{S}_{\text{gen}} = 0 \quad \text{steady state}$$

$\dot{S}_{\text{gen}} = \Delta S_{\text{univ}}$

$$\Delta S_{\text{univ}} = \sum s^{\text{out}} \cdot \dot{n}^{\text{out}} - \sum s^{\text{in}} \cdot \dot{n}^{\text{in}} - \frac{\dot{q}}{T_{\text{env}}}$$

$$= \frac{1}{2}(s_2 + s_3) - s_1 - \frac{\dot{q}}{T_{\text{env}}} \quad / \text{ From problem 4:}$$

$$= \frac{1}{2}(s_2 + s_3 - 2s_1) - \frac{\dot{q}}{T_{\text{env}}}$$

$$= \frac{1}{2} \left(C_p \left(\ln \frac{T_2}{T_{\text{ref}}} + \ln \frac{T_3}{T_{\text{ref}}} - \ln \left(\frac{T_1}{T_{\text{ref}}} \right)^2 \right) - R \cdot \left(\ln \frac{P_2}{P_{\text{ref}}} + \ln \frac{P_3}{P_{\text{ref}}} - \ln \left(\frac{P_1}{P_{\text{ref}}} \right)^2 \right) \right) - \frac{\dot{q}}{T_{\text{env}}}$$

$$= \frac{1}{2} \left(C_p \cdot \ln \left(\frac{T_2 \cdot T_3 \cdot T_{\text{ref}}^2}{T_1^2 \cdot T_{\text{ref}}^2} \right) - R \cdot \ln \left(\frac{P_2 \cdot P_3 \cdot P_{\text{ref}}^2}{P_1^2 \cdot P_{\text{ref}}^2} \right) \right) - \frac{\dot{q}}{T_{\text{env}}}$$

$$\Delta S_{\text{univ}} = \frac{1}{2} \left(C_p \ln \left(\frac{T_2 \cdot T_3}{T_1^2} \right) - R \cdot \ln \left(\frac{P_2 \cdot P_3}{P_1^2} \right) \right) - \frac{\dot{q}}{T_{\text{env}}}$$

$$\Delta S_{\text{univ}} = \frac{1}{2} \left(29.1 \frac{\text{J}}{\text{mol} \cdot \text{K}} \ln \left(\frac{280 \cdot 260}{300^2} \right) - 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} \ln \left(\frac{1 \cdot 1}{4^2} \right) \right) - \frac{2527 \text{ J/mol}}{300 \text{ K}}$$

$$\underline{\Delta S_{\text{univ}} = 0.02 \frac{\text{J}}{\text{mol} \cdot \text{K}}} \quad \text{The entropy change is } > 0 \Rightarrow \underline{\text{It is possible}}$$

$$dH = TdS + Vdp = C_p dT$$

$$dS = \frac{dH}{T} - \frac{V}{T} dp \quad / \text{ ideal gas law}$$

$$dS = C_p \frac{dT}{T} - \frac{R}{p} dp \quad / \text{ integrating}$$

$$S_i - S_{\text{ref}} = C_p \ln \left(\frac{T_i}{T_{\text{ref}}} \right) - R \ln \left(\frac{P_i}{P_{\text{ref}}} \right)$$

Problem 9

1. Show how you derive the relations for entropy in terms of heat capacities below. You may derive from first law energy balances, total differentials for state functions, relations for heat capacities that links dS.

$$a. \quad dS = \frac{C_V}{T} dT + \left(\frac{\partial P}{\partial T} \right)_V dV$$

$$b. \quad dS = \frac{C_P}{T} dT - \left(\frac{\partial V}{\partial T} \right)_P dP$$

$$a) \quad \text{From } dU = TdS - PdV = C_V dT$$

$$dS = \frac{C_V}{T} dT - \frac{P}{T} dV, \text{ Total differential} \Rightarrow \frac{P}{T} = \left(\frac{\partial S}{\partial V} \right)_T \stackrel{\uparrow}{=} \left(\frac{\partial P}{\partial T} \right)_V$$

Maxwell relation

$$\Rightarrow \underline{dS = \frac{C_V}{T} dT - \left(\frac{\partial P}{\partial T} \right)_V dV}$$

$$b) \quad \text{From } dH = TdS + Vdp = C_P dT$$

$$dS = \frac{C_P}{T} dT + \frac{V}{T} dp, \text{ Total differential} \Rightarrow \frac{V}{T} = \left(\frac{\partial S}{\partial p} \right)_T \stackrel{\uparrow}{=} - \left(\frac{\partial V}{\partial T} \right)_P$$

Maxwell relation

$$\Rightarrow \underline{dS = \frac{C_P}{T} dT - \left(\frac{\partial V}{\partial T} \right)_P dp}$$