

Helmholtz Energy

$$dU = \delta q + \delta w$$

$$\delta w = -P_{\text{ext}} dV$$

$$\text{when } dV = 0 \quad \delta w = 0$$

$$dS \geq \frac{\delta q}{T} \quad \text{Clausius inequality}$$

$$dU \leq TdS$$

$$\text{Thus, } dU - TdS \leq 0$$

At constant T, V

$$d(U - TS) \leq 0$$

$\uparrow$
 $A \rightarrow$ Helmholtz Energy

$$dA \leq 0 \quad \text{at constant } T, V$$

For a system held at constant V and T , spontaneous processes occur until A reaches a minimum at equilibrium

(Similar to $dS \geq 0$ for an isolated system undergoing a spontaneous process)

For an isothermal change

$$\Delta A = \Delta U - T\Delta S$$

$$\Delta A \leq 0 \quad (\text{at constant } T, V)$$

$$\Delta A < 0 \quad \text{for an irreversible, spontaneous change}$$

$$\Delta A = 0 \quad \text{for a reversible change}$$

Consider the mixing of two gases (ideal) at constant T

$$\Delta U = 0, \quad \Delta \bar{S} = -x_1 R \ln(x_1) - x_2 R \ln(x_2)$$

$$\Delta \bar{A} = \underbrace{x_1 RT \ln(x_1)}_{< 0} + \underbrace{x_2 RT \ln(x_2)}_{< 0}$$

$$\Delta \bar{A} < 0$$

isothermal mixing of two ideal gases is a spontaneous process.

$$\Delta A = \Delta U - T\Delta S$$

for a spontaneous, irreversible process

$$\Delta A < 0$$

Calculating ΔS over a reversible path

$$q_{\text{rev}} = T\Delta S$$

$$\Delta A = \underbrace{\Delta U - q_{\text{rev}}}_{= w_{\text{rev}}} \quad (\text{First Law})$$

$$\Delta A = w_{\text{rev}} \quad (\text{isothermal, reversible})$$

When $\Delta A < 0$, the process occurs spontaneously

w_{rev} represents the work done that can be done by the system by carrying out the change reversibly.

When $\Delta A > 0$, the process does not occur spontaneously

$w_{\text{rev}} \rightarrow$ work done on the system to carry out the change reversibly

In both cases, in the presence of irreversibility

$$w > w_{\text{rev}}$$

Gibbs Free Energy

Most reactions occur at constant P rather than constant V .

Again, from the Clausius inequality

$$dS \geq \frac{\delta q}{T}$$

$$\text{at constant pressure} \quad \delta w = -PdV$$

$$dU \leq TdS - PdV$$

$$dU - TdS + PdV \leq 0$$

at constant T, P

$$d(U - TS + PV) \leq 0$$

$$G = U - TS + PV = H - TS = A + PV$$

Gibbs free energy

$$\Delta G = \Delta H - T\Delta S \leq 0 \quad \text{at constant } T, P$$

$$G = U - TS + PV$$

$$dG = dU - TdS - SdT + PdV + VdP$$

$$dU = TdS + \delta w_{\text{rev}}$$

$$dG = \delta w_{\text{rev}} - SdT + VdP + PdV$$

$$= \delta w_{\text{rev}} + PdV - SdT + VdP$$

$$= \underbrace{\delta w_{\text{rev}} - \delta w_{\text{PV}}}_{\delta w_{\text{non PV}}} - SdT + VdP$$

$\delta w_{\text{non PV}} \rightarrow$ work that is not Pressure-Volume work

$$dG = \delta w_{\text{non PV}} - SdT + VdP$$

For a reversible process at constant T, P

$$dG = \delta w_{\text{non PV}}$$

$$\Delta G = w_{\text{non PV}}$$

When $\Delta G < 0$ the process occurs spontaneously

$w_{\text{non PV}} \rightarrow$ work done by the system carrying out the process reversibly. Examples of non-PV work include electric work, chemical work etc.

Maxwell Relations

Provides useful expressions for quantities that cannot be measured directly to those that can.

$$dA = dU - TdS - SdT$$

For a reversible process

$$dU = TdS - PdV, \text{ therefore}$$

$$dA = -PdV - SdT$$

$$A = f(V, T)$$

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

Comparing with

$$\left(\frac{\partial A}{\partial V} \right)_T = -P \quad \left(\frac{\partial A}{\partial T} \right)_V = -S$$

$$\left(\frac{\partial^2 A}{\partial V \partial T} \right) = \left(\frac{\partial^2 A}{\partial T \partial V} \right)$$

implies

$$\left(\frac{\partial P}{\partial T} \right)_V = \left(\frac{\partial S}{\partial V} \right)_T$$

Thus,

$$\Delta S = \int_{V_1}^{V_2} \left(\frac{\partial P}{\partial T} \right)_V dV \quad \text{at constant } T$$

For an ideal gas

$$\begin{aligned} \left(\frac{\partial P}{\partial T} \right)_V &= \left(\frac{\partial}{\partial T} \right)_V (PV) = \frac{\partial}{\partial T} (nRT) \\ &= \frac{nR}{V} \end{aligned}$$

$$\Delta S = \int_{V_1}^{V_2} \frac{nR dV}{V} = nR \ln \frac{V_2}{V_1}$$

Another example, consider

$$A = U - TS$$

$$\begin{aligned} \left(\frac{\partial A}{\partial V}\right)_T &= \left(\frac{\partial U}{\partial V}\right)_T - T\left(\frac{\partial S}{\partial V}\right)_T \quad \rightarrow \left(\frac{\partial P}{\partial T}\right)_V \\ &= \left(\frac{\partial U}{\partial V}\right)_T - T\left(\frac{\partial P}{\partial T}\right)_V \end{aligned}$$

$$-P = \left(\frac{\partial U}{\partial V} \right)_T - T \left(\frac{\partial P}{\partial T} \right)_V$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

For an ideal gas

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{nRT}{V} = P$$

Thus, $\left(\frac{\partial U}{\partial V}\right)_T = P - P = 0$

Earlier we noted:

$$\begin{aligned} C_p - C_v &= \left[P + \left(\frac{\partial U}{\partial V} \right)_T \right] \left(\frac{\partial V}{\partial T} \right)_P \\ &= \left[P + T \left(\frac{\partial P}{\partial T} \right)_V - P \right] \left(\frac{\partial V}{\partial T} \right)_P \\ &= T \left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_P \end{aligned}$$

See Problem 5 from the “Work and Energy” lecture notes.

Alternatively, given that

$$V = f(P, T)$$

$$dV = \left(\frac{\partial V}{\partial T} \right)_P dT + \left(\frac{\partial V}{\partial P} \right)_T dP$$

At constant volume,

$$0 = \left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V$$

Thus,

$$\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial V}\right)_T$$

$$C_p - C_v = -T \left(\frac{\partial V}{\partial T}\right)_P^2 \left(\frac{\partial P}{\partial V}\right)_T$$

$$\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T \quad \text{isothermal compressibility}$$

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P \quad \text{co-efficient of thermal expansion}$$

$$C_p - C_v = \frac{\alpha^2 TV}{\kappa}$$

P, V dependence of A, G

$$dA = -PdV - SdT = -PdV \quad (\text{at constant } T)$$

$$\Delta A = -\int_{V_1}^{V_2} PdV = -nRT \ln \frac{V_2}{V_1}$$

since $\Delta A = -T\Delta S$ and $\Delta U = 0$ at constant T for an ideal gas

$$-T\Delta S = -nRT \ln \frac{V_2}{V_1}$$

$$\Delta S = nR \ln \frac{V_2}{V_1} \quad \text{as before}$$

$$dG = -SdT + VdP$$

Remembering,

$$G = f(T, P)$$

$$dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP$$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \quad \text{Thus } G \text{ increases with decreasing temperature. } S \geq 0$$

$$\left(\frac{\partial G}{\partial P}\right)_T = V \quad G \text{ increases with increasing pressure since } V > 0$$

$$\left(\frac{\partial G}{\partial T \partial P}\right) = -\left(\frac{\partial S}{\partial P}\right)_T$$

$$\left(\frac{\partial G}{\partial P \partial T}\right) = \left(\frac{\partial V}{\partial T}\right)_P$$

Thus,

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$

$$\Delta S = -\int_{P_1}^{P_2} \left(\frac{\partial V}{\partial T}\right)_P dP$$

For an ideal gas,

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{P}$$

$$\Delta S = -\int_{P_1}^{P_2} \frac{nR}{P} dP = -nR \ln \frac{P_2}{P_1}$$

Again, remembering

$$dG = dH - TdS \quad \text{at constant } P, T$$

$$\left(\frac{\partial G}{\partial P}\right)_T = \left(\frac{\partial H}{\partial P}\right)_T - T\left(\frac{\partial S}{\partial P}\right)_T \quad \begin{matrix} \nearrow \left(\frac{\partial V}{\partial T}\right)_P \\ \searrow V \end{matrix}$$

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P$$

Thermodynamic equation of state.

Summarizing

U: $dU = TdS - PdV$ S, V are natural variables for U

Maxwell Relations

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

For a system at constant S, V

$$dU = 0$$

$dU < 0$ for a spontaneous process

H: $dH = TdS + VdP$ S, P are natural variables for H

Maxwell Relations

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

For a system at constant S, P

$$dH = 0$$

$dH < 0$ for a spontaneous process.

A: $dA = -SdT - PdV$ T, V are natural variables for A

Maxwell Relations

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$dA = 0 \quad \text{at constant } T, V$$

$dA < 0$ for a spontaneous process

G: $dG = -SdT + VdP$ T, P are natural variables for G

Maxwell Relations

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

$$dG = 0 \quad \text{at constant } T, P$$

$dG < 0$ for a spontaneous process

Taking the above example.

$$G = f(P, T)$$

$$dG = \left(\frac{\partial G}{\partial P} \right)_T dP + \left(\frac{\partial G}{\partial T} \right)_P dT$$

$$\text{Thus, } \left(\frac{\partial G}{\partial P} \right)_T = V$$

$$\left(\frac{\partial G}{\partial T} \right)_P = -S$$

$$\begin{aligned} \left(\frac{\partial G}{\partial P \partial T} \right) &= \left(\frac{\partial V}{\partial T} \right)_P \\ \left(\frac{\partial G}{\partial T \partial P} \right) &= - \left(\frac{\partial S}{\partial P} \right)_T \end{aligned} \quad \begin{array}{l} \text{Maxwell} \\ \text{relations} \end{array}$$

The Gibbs-Helmholtz Equation

$$G = H - TS$$

$$\text{or } \frac{G}{T} = \frac{H}{T} - S$$

$$\left(\frac{\partial (G/T)}{\partial T} \right)_P = -\frac{H}{T^2} + \frac{1}{T} \left(\frac{\partial H}{\partial T} \right)_P - \left(\frac{\partial S}{\partial T} \right)_P$$

$$\left(\frac{\partial S}{\partial T} \right)_P = \frac{C_p(T)}{T}$$

$$\begin{aligned} \left(\frac{\partial (G/T)}{\partial T} \right)_P &= -\frac{H}{T^2} + \frac{C_p(T)}{T} - \frac{C_p(T)}{T} \\ &= -\frac{H}{T^2} \end{aligned}$$

Thus,

$$\left(\frac{\partial (\Delta G/T)}{\partial T} \right)_P = -\frac{\Delta H}{T^2}$$

Problem 1

Using $A = U - TS$ and the natural variables of A , find $(\partial U/\partial V)_T$ for a gas that obeys an equation of state that has the form

$$Pf(V) = RT$$

Also use the Maxwell relations for A .

$$A = U - TS$$

Differentiating with respect to V at constant T ,

$$\left(\frac{\partial A}{\partial V}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T - T\left(\frac{\partial S}{\partial V}\right)_T$$

$$dA = -SdT - PdV$$

$$A = f(V, T)$$

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

Thus, comparing co-efficients of dV

$$\left(\frac{\partial A}{\partial V}\right)_T = -P$$

Thus,

$$-P = \left(\frac{\partial U}{\partial V}\right)_T - T\left(\frac{\partial S}{\partial V}\right)_T$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P$$

From the Maxwell relations of A

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

Thus,

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

For the equation of state

$$Pf(V) = RT$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{f(V)}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{RT}{f(V)} - P = P - P = 0$$

Problem 2

Show that

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

Use $G = H - TS$ and the Maxwell equations and natural variables for G .

Since we have dP , dT in the above equation

we write $H = f(T, P)$

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP = C_p(T) + \left(\frac{\partial H}{\partial P}\right)_T dP$$

Now, $G = H - TS$

$$\left(\frac{\partial G}{\partial P}\right)_T = \left(\frac{\partial H}{\partial P}\right)_T - T\left(\frac{\partial S}{\partial P}\right)_T$$

$$\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial G}{\partial P}\right)_T + T\left(\frac{\partial S}{\partial P}\right)_T$$

$$dG = -SdT + VdP$$

$$G = f(P, T)$$

$$dG = \left(\frac{\partial G}{\partial P}\right)_T dP + \left(\frac{\partial G}{\partial T}\right)_P dT$$

Comparing the co-efficients of dP

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

From the Maxwell Equations

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

Thus,

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P$$

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

Problem 3

Derive an expression for ΔS for the reversible, isothermal expansion of a Van der Waals gas (1 mole). Use the Maxwell relations for A.

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

For a Van der Waals gas,

$$P = \frac{RT}{V - b} - \frac{a}{V^2}$$

For 1 mole of a gas,

$$P = \frac{RT}{V - b} - \frac{a}{V^2}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V - b}$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{R}{V - b}$$

$$\Delta S = \int_{V_1}^{V_2} \frac{R dV}{V - b} = R \ln \frac{V_2 - b}{V_1 - b}$$

Problem 4

Derive an expression for the change in entropy for the pressure change of a real gas from an initial pressure P_1 to a final pressure P_2 at constant T . Use the Maxwell relations for G .

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

For a real gas,

$$PV = nRT$$

$$P\left(\frac{\partial V}{\partial T}\right)_P = nR$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{P}$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\frac{nR}{P}$$

$$\begin{aligned}\Delta S &= -nR \int_{P_1}^{P_2} \frac{dP}{P} = -nR \ln \frac{P_2}{P_1} \\ &= nR \ln \frac{P_1}{P_2}\end{aligned}$$

$\Delta S > 0$ for a compression, i.e. $P_1 > P_2$

Problem 5

One mole of CO_2 expands reversibly and isothermally at 300 K from 2.00 L to 10.00 L. Treating it as a Van der Waals gas with $b = 0.04267 \text{ L mol}^{-1}$, calculate ΔS . Compare your answer with the value for an ideal gas.

From Problem 3, for 1 mole

$$\Delta S = R \ln \frac{V_2 - b}{V_1 - b}$$

$$\begin{aligned}\Delta S &= (8.314 \text{ J K}^{-1}) \ln \frac{10.00 - 0.04267}{2.00 - 0.04267} \\ &= (8.314 \text{ J K}^{-1}) \ln (5.087) \\ &= 13.52 \text{ J K}^{-1}\end{aligned}$$

For an ideal gas ($b = 0$),

$$\begin{aligned}\Delta S_{\text{ideal}} &= (8.314 \text{ J K}^{-1}) \ln \frac{10.00}{2.00} \\ &= 13.38 \text{ J K}^{-1}\end{aligned}$$

The Van der Waals gas gains slightly more entropy (0.14 J K^{-1} , about 1%): the molecules' own volume b makes the fractional gain in free volume larger. Note that ΔS does not depend on a .

Problem 6

For liquid water at 25°C , $\alpha = 2.57 \times 10^{-4} \text{ K}^{-1}$, $\kappa = 4.52 \times 10^{-10} \text{ Pa}^{-1}$ and the molar volume is $V_m = 18.07 \text{ cm}^3 \text{ mol}^{-1}$.

(a) Calculate $C_{p,m} - C_{v,m}$. (b) Show that the same formula gives R for an ideal gas.

(a)

$$\begin{aligned}C_{p,m} - C_{v,m} &= \frac{\alpha^2 T V_m}{\kappa} \\ &= \frac{(2.57 \times 10^{-4} \text{ K}^{-1})^2 (298.15 \text{ K})(1.807 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1})}{4.52 \times 10^{-10} \text{ Pa}^{-1}} \\ &= 0.787 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

(using $1 \text{ Pa m}^3 = 1 \text{ J}$)

With $C_{p,m} = 75.3 \text{ J K}^{-1} \text{ mol}^{-1}$, $C_{v,m} = 74.5 \text{ J K}^{-1} \text{ mol}^{-1}$: for a liquid the two heat capacities differ by only about 1%.

(b) For an ideal gas, $V = nRT/P$

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = \frac{1}{V} \frac{nR}{P} = \frac{1}{T}$$

$$\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = \frac{1}{V} \frac{nRT}{P^2} = \frac{1}{P}$$

$$C_{p,m} - C_{v,m} = \frac{(1/T)^2 TV_m}{1/P} = \frac{PV_m}{T} = R$$

Problem 7

For the reaction $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ at 298.15 K, $\Delta_r H^\circ = -91.8 \text{ kJ mol}^{-1}$ and $\Delta_r G^\circ = -32.8 \text{ kJ mol}^{-1}$. Assuming $\Delta_r H^\circ$ does not depend on temperature, use the Gibbs-Helmholtz equation to (a) estimate $\Delta_r G^\circ$ at 500 K and (b) find the temperature above which the reaction is no longer spontaneous under standard conditions.

$$\left(\frac{\partial(\Delta G/T)}{\partial T} \right)_P = -\frac{\Delta H}{T^2}$$

Integrating from T_1 to T_2 with ΔH constant,

$$\frac{\Delta G(T_2)}{T_2} - \frac{\Delta G(T_1)}{T_1} = \Delta H \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

(a) In $J \text{ mol}^{-1}$ and K,

$$\begin{aligned} \frac{\Delta G(500 \text{ K})}{500 \text{ K}} &= \frac{-32.8 \times 10^3}{298.15} + (-91.8 \times 10^3) \left(\frac{1}{500} - \frac{1}{298.15} \right) \\ &= -110.01 + 124.30 \\ &= 14.29 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

$$\Delta G(500 \text{ K}) = (500 \text{ K})(14.29 \text{ J K}^{-1} \text{ mol}^{-1}) = +7.14 \text{ kJ mol}^{-1}$$

The reaction is spontaneous under standard conditions at 298 K but not at 500 K.

(b) Setting $\Delta G(T) = 0$,

$$0 = \frac{\Delta G(T_1)}{T_1} + \Delta H \left(\frac{1}{T} - \frac{1}{T_1} \right)$$

$$\begin{aligned}
 T &= \frac{\Delta H T_1}{\Delta H - \Delta G(T_1)} \\
 &= \frac{(-91.8)(298.15 \text{ K})}{-91.8 - (-32.8)} \\
 &= 464 \text{ K}
 \end{aligned}$$

Above about 464 K, $\Delta_r G^\circ > 0$. Heating favours the reactants because $\Delta_r S^\circ$ is negative: $\Delta_r S^\circ = (\Delta_r H^\circ - \Delta_r G^\circ)/T = -198 \text{ J K}^{-1} \text{ mol}^{-1}$.