Helmholtz Energy

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

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

when $dV = 0$ $\delta w = 0$

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

$$dU \leq TdS$$

Thus, $dU - TdS \leq 0$

At constant T, V

$$\underbrace{d(U - TS)}_{\uparrow A} \leq 0$$

$A \longrightarrow$ Helmholtz Energy

$dA \leq 0$ 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

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

$\Delta A \leq 0$ (at constant T, V)

$\Delta A < 0$ for an irreversible, spontaneous change

$\Delta A = 0$ 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

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

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

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

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

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

In both cases, in the presence of irreversibility

$$w > w_{rev}$$

Gibbs Free Energy

Most reactions occur at constant P rather than constant V.

Again, from the Clausius inequality

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

at constant pressure $\quad \delta w = -PdV$

$$dU \leqslant TdS - PdV$$

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

at constant T, P

$$\underbrace{d(U - TS + PV)}_{G = U - TS + PV = H - TS = A + PV} \leq 0$$

Gibbs free energy

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

$$G = U - TS + PV$$

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

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

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

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

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

$\delta w_{non\ PV}$ → work that is not Pressure–Volume work

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

For a reversible process at constant T, P

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

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

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

$w_{non\ PV}$ → 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

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

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

implies

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

Thus,

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

For an ideal gas

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

$$= \frac{nR}{V}$$

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

Another example, consider

$$A = U - TS$$

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

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

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

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

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:

$$C_p - C_V = \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P$$

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

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

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,

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

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

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

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

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

P, V dependence of A, G

$dA = -PdV - SdT = -PdV$ (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

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

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

$dG = -SdT + VdP$

Remembering,

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

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

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

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

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

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

Again, remembering

$dG = dH - TdS$ at constant P, T

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

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

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

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

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

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

$dA = 0$ at constant T, V

$dA < 0$ for a spontaneous process

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

Maxwell Relations

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

$dG = 0$ at constant T, P

$dG < 0$ for a spontaneous process

Taking the above example.

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

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

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

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

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

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

Maxwell relations

The Gibbs–Helmholtz Equation

$$G = H - TS$$

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

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

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

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

$$= -\frac{H}{T^2}$$

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,

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

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 an ideal gas,

$$PV = nRT$$

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

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

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

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

$$= nR\ln\frac{P_1}{P_2}$$

$\Delta S > 0$ 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 $b = 0.04267$ L mol^{-1}, calculate ΔS. Compare your answer with the value for an ideal gas.

From Problem 3, for 1 mole

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

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

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

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

The Van der Waals gas gains slightly more entropy ($0.14\ \text{J K}^{-1}$, 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)

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

(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 $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$ at 298.15 K, $\Delta_r H^\circ = -91.8$ kJ mol^{-1} and $\Delta_r G^\circ = -32.8$ 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 mol^{-1} and K,

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

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

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

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

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

$$T = \frac{\Delta H\, T_1}{\Delta H - \Delta G(T_1)}$$

$$= \frac{(-91.8)(298.15\ \text{K})}{-91.8 - (-32.8)}$$

$$= 464\ \text{K}$$

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