Lecture 12: Perfect Differentials

If A is a state function, then dA is said to be a perfect differential. A necessary and sufficient condition for a function of two variables $A(x,y)$ to have a perfect differential is that

$$\frac{\partial^2 A}{\partial x \partial y} = \frac{\partial^2 A}{\partial y \partial x}$$

$$dA = \left(\frac{\partial A}{\partial x}\right)_y dx + \left(\frac{\partial A}{\partial y}\right)_x dy = f(x,y)dx + g(x,y)dy$$

The necessary and sufficient condition is

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

Example: $A = x^2 \sin(xy)$

$$dA = \{2x\, \sin(xy) + x^2 y \cos(xy)\}dx + x^3 \cos(xy)dy$$

$$\partial f/\partial y = 3x^2 \cos(xy) - x^3 y \sin(xy) = \partial g/\partial x$$

Thermodynamic Perfect Differentials

$$dU = TdS - PdV$$

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

$$dH = TdS + VdP$$

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

These are examples of the Maxwell Relations, which are summarized in the Maxwell Square.

Goal of Thermodynamic Manipulations: to express any quantity in terms of V, T, P, S, n, α, κ_T, and C_V.

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

Thermal expansion

Ideal gas: $\alpha = \frac{1}{V}\frac{nR}{P} = \frac{1}{T}$

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

Isothermal compressibility

Ideal gas: $\kappa_T = -\frac{1}{V}\left(\frac{-nRT}{P^2}\right) = \frac{1}{P}$

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

Heat Capacity, constant V

Ideal gas: $C_V = 3/2nR$

Lecture 13: Thermodynamic Calculations

Partial derivatives of implicit functions

Consider a function A(x,y,z)

$$dA = \left(\frac{\partial A}{\partial x}\right)_{y,z} dx + \left(\frac{\partial A}{\partial y}\right)_{x,z} dy + \left(\frac{\partial A}{\partial z}\right)_{x,y} dz$$

x, y, and z are said to be implicit functions of each other; i.e., z = z(x,y).

In addition, x, y, z, may be functions of some other variable, t.

Examples: A = U, H, A, G
x, y, z, t = P, V, T, S.

Properties of implicit functions

$$\left(\frac{\partial x}{\partial y}\right)_{A,z} = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_{A,z}}$$

$$\left(\frac{\partial x}{\partial y}\right)_{A,z} = -\frac{\left(\frac{\partial A}{\partial y}\right)_{x,z}}{\left(\frac{\partial A}{\partial x}\right)_{y,z}}$$

$$\left(\frac{\partial x}{\partial y}\right)_{A,z} = \frac{\left(\frac{\partial x}{\partial t}\right)_{A,z}}{\left(\frac{\partial y}{\partial t}\right)_{A,z}}$$

Origin of the minus sign:

$$dA = \left(\frac{\partial A}{\partial x}\right)_{y,z} dx + \left(\frac{\partial A}{\partial y}\right)_{x,z} dy + \left(\frac{\partial A}{\partial z}\right)_{x,y} dz$$

Set dA=0:

$$0 = \left(\frac{\partial A}{\partial x}\right)_{y,z} dx + \left(\frac{\partial A}{\partial y}\right)_{x,z} dy + \left(\frac{\partial A}{\partial z}\right)_{x,y} dz$$

Set dz=0 and divide through by dx:

$$0 = \left(\frac{\partial A}{\partial x}\right)_{y,z} + \left(\frac{\partial A}{\partial y}\right)_{x,z} \left(\frac{\partial y}{\partial x}\right)_{A,z}$$

$$\left(\frac{\partial y}{\partial x}\right)_{A,z} = -\frac{\left(\partial A/\partial x\right)_{y,z}}{\left(\partial A/\partial y\right)_{x,z}}$$

Manipulations of the Maxwell Square

$$\left(\frac{\partial X}{\partial Y}\right)_{Z} = \frac{1}{\left(\frac{\partial Y}{\partial X}\right)_{Z}}$$

$$\left(\frac{\partial X}{\partial Y}\right)_Z = -\frac{\left(\frac{\partial Z}{\partial Y}\right)_X}{\left(\frac{\partial Z}{\partial X}\right)_Y}$$

$$\left(\frac{\partial X}{\partial Y}\right)_Z = \frac{\left(\frac{\partial X}{\partial W}\right)_Z}{\left(\frac{\partial Y}{\partial W}\right)_Z}$$

Example 1. Internal Pressure

$$\pi_T = \left(\frac{\partial U}{\partial V}\right)_T$$

dU = TdS – PdV

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

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

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

$$= \frac{T\alpha}{\kappa_T} - P$$

Ideal gas: π_T = TP/T – P =0

Example 2. The Joule-Thompson Coefficient

A pump drives a high pressure gas through a porous plug. The work done **on** the gas on the high pressure side is P_iV_i. The work done **by** the gas on the low pressure side is P_fV_f.

Conservation of energy gives

$$U_f = U_i + P_iV_i - P_fV_f$$

$$U_f + P_fV_f = U_i + P_iV_i$$

$$H_f = H_i$$

$$dT = \left(\frac{\partial T}{\partial P}\right)_H dP = \mu dP$$

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H = -\frac{\left(\frac{\partial H}{\partial P}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_P} = -\frac{\mu_T}{C_P}$$

$$dH = TdS + VdP$$

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

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

$$= -\alpha VT + V$$

$$= V(1 - \alpha T)$$

$$\alpha T_{inv} = 1$$

Ideal gas: $\mu_T = (1 - (1/T)T) = 0$

Application to a real gas:

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

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

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT$$

$$\left[\left(P + \frac{a}{V_m^2}\right) - 2(V_m - b)\frac{a}{V_m^3}\right] dV_m = RdT$$

$$\alpha = \frac{1}{V_m}\left(\frac{\partial V_m}{\partial T}\right)_P$$

$$\alpha = \frac{1}{\dfrac{TV_m}{V_m - b} - \dfrac{2a(V_m - b)}{RV_m^2}}$$

We can simplify this result by taking a series expansion:

Let $\varepsilon_1 = b/V_m$ and $\varepsilon_2 = a/V_m^2$

$$\alpha = \left[\frac{T}{1-\varepsilon_1} - \frac{2V_m}{R}(1-\varepsilon_1)\varepsilon_2\right]^{-1}$$

$$\approx \frac{1}{T}\left[\frac{1}{1-\varepsilon_1} - \frac{2V_m}{RT}\varepsilon_2\right]^{-1}$$

$$\approx \frac{1}{T}\left[1 + \varepsilon_1 - \frac{2V_m}{RT}\varepsilon_2\right]^{-1}$$

$$\approx \frac{1}{T}\left[1-\varepsilon_1+\frac{2V_m}{RT}\varepsilon_2\right]$$

$$\approx \frac{1}{T}\left[1-\frac{b}{V_m}+\frac{2a}{RTV_m}\right]$$

Substituting V_m =RT/P,

$$\alpha \approx \frac{1}{T}\left[1 \ -\frac{bP}{RT}+\frac{2aP}{R^2T^2}\right]$$

$$T_{inv} = 1/\alpha \Rightarrow \ \frac{bP}{RT_{inv}}=\frac{2aP}{R^2T^2}$$

$$\therefore T_{inv} \approx 2a/bR$$

For example, $T_{inv}(H_2) \approx 227$ K
$T_{inv}(CO_2) \approx 2079$ K

We can also determine the Joule-Thompson coefficient:

$$\mu = -\frac{\mu_T}{C_P} = \frac{V}{C_P}(\alpha T - 1)$$

$$\approx \frac{V}{C_P}\left[1 \ -\frac{bP}{RT}+\frac{2aP}{R^2T^2}-1\right]$$

$$= \frac{PV}{C_P RT}\left(\frac{2a}{RT}-b\right) \approx \frac{1}{C_{P.m}}\left(\frac{2a}{RT}-b\right)$$

Application to the virial equation:

$$PV_m = RT\left(1+\frac{B(T)}{V_m}+\frac{C(T)}{V_m^2}\right)$$

$$PdV_m = -RT\left(\frac{B}{V_m^2}+\frac{2C}{V_m^3}\right)dV_m + R\left(1+\frac{B}{V_m}+\frac{C}{V_m^2}\right)dT + \left(\frac{RT}{V_m}\frac{dB}{dT}+\frac{RT}{V_m^2}\frac{dC}{dT}\right)dT$$

$$\left[P + RT\left(\frac{B}{V_m^2} + \frac{2C}{V_m^3}\right)\right]dV = \left[R\left(1 + \frac{B}{V_m} + \frac{C}{V_m^2}\right) + \frac{RT}{V_m}\left(\frac{dB}{dT} + \frac{1}{V_m}\frac{dC}{dT}\right)\right]dT$$

$$\frac{1}{V_m}\left(\frac{\partial V_m}{\partial T}\right)_P = \frac{\frac{1}{T}\left[\frac{RT}{V_m}\left(1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \frac{T}{V_m}\frac{dB}{dT} + \frac{T}{V_m^2}\frac{dC}{dT}\right)\right]}{P + RT\left(\frac{B}{V_m^2} + \frac{2C}{V_m^3}\right)}$$

$$\alpha = \frac{1}{T}\frac{RT}{PV_m}\frac{\left[\left(1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \frac{T}{V_m}\frac{dB}{dT} + \frac{T}{V_m^2}\frac{dC}{dT}\right)\right]}{1 + \frac{RT}{PV_m}\left(\frac{B}{V_m} + \frac{2C}{V_m^2}\right)}$$

$$\alpha \approx \frac{1}{T}\left(1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \frac{T}{V_m}\frac{dB}{dT} + \frac{T}{V_m^2}\frac{dC}{dT}\right)\left(1 - \frac{B}{V_m} - \frac{2C}{V_m^2}\right)$$

Example 3. $C_P - C_V$

$dH = dq_{P,rev} + VdP$

$= C_P dT + VdP$

$= TdS + VdP$

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

S = S(T,P)

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

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

$$= \frac{C_P dT}{T} - V\alpha dP$$

$$TdS = C_P dT - TV\alpha dP$$

$$T\left(\frac{\partial S}{\partial T}\right)_V = C_P - TV\alpha\left(\frac{\partial P}{\partial T}\right)_V$$

$$C_V = C_P + TV\alpha \frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T}$$

$$C_V = C_P - \frac{TV\alpha^2}{\kappa_T}$$

Lecture 15: Introduction to the Second Law

Significance of the First Law

Implications:

1. Allows us to calculate the energy change for any process (Thermochemistry)
2. Allows us to calculate q and w for a given path
3. Rules out perpetual motion machines of the fisrst kind

Limitations:

1. Tells us nothing about the feasibility of a process. $\Delta U<0$ and $\Delta H<0$ are not valid indicators.
2. Tells us nothing about equilibrium
3. Does not treat q or w as state variables
4. Says nothing about perpetual motion of the second kind ($q\rightarrow w$ machines)

The heart of the problem is our understanding of q.
Heat is a chaotic form of energy, and is not 100% useable.

1. We would like to have a measure of chaos.

2. We would like to have a measure of the usefulness of heat.

The quantity of interest is the entropy, S.

1. S is a state variable. It is the extensive counterpart to T that appears in the Euler relation.
2. S has an absolute value, S=0 for perfect order.
3. An incremental change of heat, dq, leads to more disorder at low T than at high T. Transfer of dq from a hot body to a cold body leads to more useful work at high T than at low T. Hence, we expect that S, as measure of disorder and as a measure of the usefulness of heat, varies inversely with T.

Lecture 16. Entropy

We would like to discover what it would take to make dq a perfect differential. We will use an ideal gas to test out ideas.

Let's start with a problem that we already understand.
Let's demonstrate that dV is a perfect differential.

$$V = V(T,P) = nRT/P$$

$$dV = f(T,P)dT + g(T,P)dP$$

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

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

$$\left(\frac{\partial f}{\partial P}\right)_T = -\frac{nR}{P^2} = \left(\frac{\partial g}{\partial T}\right)_P$$

Q.E.D. (but hardly surprising)
Now let's examine dw_{rev}.

$$dw_{rev} = -PdV = -nRdT + \frac{nRT}{P}dP$$

$$f(T,V) = -nR$$

g(T,V) = nRT/P

$$\left(\frac{\partial f}{\partial P}\right)_T = 0$$

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

∴ dw_{rev} is not a perfect differential.
Now let's examine dq_{rev}. For an ideal gas:

$$dq_{rev} = dU - dw_{rev} = C_V dT + nRdT - \frac{nRT}{P}dP$$

$f(T,V) = C_V + nR$

g(T,V) = −nRT/P

$$\left(\frac{\partial f}{\partial P}\right)_T = 0$$

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

∴ dq_{rev} is not a perfect differential.

What will it take to make dq_{rev} exact?

We can "fix up" g(T,P) by dividing it by T.

Define: $dS = dq_{rev}/T$

$$dS = \frac{C_V + nR}{T}dT - \frac{nR}{P}dP$$

$$dS = C_P\frac{dT}{T} - nR\frac{dP}{P} \qquad (1)$$

$$\left(\frac{\partial f}{\partial P}\right)_T = 0 = \left(\frac{\partial g}{\partial T}\right)_P$$

∴ dS is a perfect differential.

We can write this result equivalently as

dU = TdS − PdV

For an ideal gas,

$$dS = C_V \frac{dT}{T} + \frac{PdV}{T} = C_V \frac{dT}{T} + \frac{nRdV}{V} \qquad (2)$$

ΔS is independent of path.

From Eq. (1): $\Delta S = \int_{T_1}^{T_2} C_P(T)\frac{dT}{T} - nR\int_{P_1}^{P_2}\frac{dP}{P}$

$$= \int_{T_1}^{T_2} C_P(T)\frac{dT}{T} - nR\ln\left(\frac{P_2}{P_1}\right)$$

From eq. (2): $\Delta S = \int_{T_1}^{T_2} C_V(T)\frac{dT}{T} + nR\int_{V_1}^{V_2}\frac{dV}{V}$

$$= \int_{T_1}^{T_2} C_P(T)\frac{dT}{T} + nR\ln\left(\frac{V_2}{V_1}\right)$$

Contributions result from increases in both temperature and volume

Lecture 17. Calculating the Entropy

Summary of results from the previous lecture, for an ideal gas:

1. Constant pressure (reversible):

$$\Delta S = \int_{T_1}^{T_2} C_P(T)\frac{dT}{T} = C_P \ln\frac{T_2}{T_1}$$

The second equality assumes a constant heat capacity.

2. Constant volume (reversible):

$$\Delta S = \int_{T_1}^{T_2} C_V(T)\frac{dT}{T} = C_V \ln\frac{T_2}{T_1}$$

3. Constant temperature (reversible):

$$\Delta S = nR\ln\frac{V_2}{V_1} = -nR\ln\frac{P_2}{P_1}$$

4. Adiabatic process:

$$\Delta S_{ad,\,rev} = 0$$

$\Delta S_{ad,\,irrev}$ depends on the process

5. Phase transition:

$$\Delta S_{trans} = \Delta H_{trans}/T_{trans}$$

Troutons' Rule: $\Delta S_{vap,m} \approx 85\ \text{J mol}^{-1}\ \text{K}^{-1}$

$$\Rightarrow \Delta H_{vap,m} \approx 85\ T_{b.p.}\text{J mol}^{-1}$$

Example: Heating of I_2 at constant pressure, revisited

$$C_{p,m} = a + bT + c/T^2$$

$$\Delta S = a\ln\left(\frac{T_2}{T_1}\right) + b(T_2 - T_1) - \frac{c}{2}\left(\frac{1}{T_2^2} - \frac{1}{T_1^2}\right)$$

Phase	a	b	c
solid	40.12	0.04979	0
liquid	80.33	0	0
vapor	37.40[a]	0.00059	−0.71e+5

[a]Note: C_P at 300 K is 4.42R

Melting point = 386.8 K
Boiling point = 458.4 K

$\Delta H_{fus,m}$ = 15.52 kJ mol^{-1} ⇒ $\Delta S_{fus,m}$ = 40.12 J mol^{-1} K^{-1}

$\Delta H_{vap,m}$ = 41.80 kJ mol^{-1} ⇒ $\Delta S_{vap,m}$ = 91.18 J mol^{-1} K^{-1}
(Trouton's rule predicts 85 J mol^{-1} K^{-1})

Calculate the entropy change accompanying the heating of one mole of I_2 from 100 to 500 K at 1 atm.

$$\begin{aligned}\Delta S &= 40.12 \ln(386.8/100) \\ &+ 0.04979\,(386.8-100) + 40.12 \\ &+ 80.33 \ln(458.4/386.8) + 91.18 \\ &+ 37.40 \ln(500/458.4) \\ &+ 0.00059(500-458.4) \\ &- 0.5\times 0.71\times 10^{5}(500^{-2}-458.4^{-2}) \\ &= 216.21 \text{ J mol}^{-1}\text{ K}^{-1}\end{aligned}$$

Note: Table 2.6 gives $\Delta S_{f,m}$ = 116.135 J mol^{-1} K^{-1} at 298 K.

Third Law of Thermodyanamics

If the entropy of every element in its most stable state at T=0 is taken as zero, then every substance has a positive entropy which at T=0 may become zero, and which does become zero for all perfect crystalline substances, including compounds.

Law of Dulong and Petit: C_V = 3R for all atomic crystals.

Data taken from Atkins Table 2.2 and McQuarie:

Metal	C_V/R	Θ_D (K)
Al	2.48	396
Cu	2.72	313
Pb	2.66	88

This "law" clearly violates the Third Law, because, if C_V is a constant, $\int_{T_1}^{T_2} C_V \frac{dT}{T}$ is ill-behaved as $T_1 \to 0$.

Experimentally it is observed that

$$\lim_{T\to 0} C_V = 0$$

This discovery was crucial in the foundation of quantum mechanics.

Debye Heat Capacity:

The Debye theory treats a crystal as having a continuous distribution of frequencies, ν, with a maximum cutoff frequency, ν_D. This model predicts that C_V is given by

$$C_V = \left[9R\left(\frac{T}{\Theta_D}\right)^3\right]\int_0^{\Theta_D/T}\frac{x^4e^x}{\left(e^x-1\right)^2}dx$$

where x = hν/kT and the Debye temperature is given by

$$\Theta_D = \frac{h\nu_D}{k}$$

Limiting behavior:

$$\lim_{T\to\infty} C_V = 3R$$

$$\lim_{T\to 0} C_V = \frac{12\pi^4 R}{5}\left(\frac{T}{\Theta_D}\right)^3$$

This is the famous T^3 temperature law for the heat capacity and entropy.

Lecture 18: The Second Law: Examples

How to deal with irreversible processes:

Two moles of an ideal atomic gas occupy a volume of 25 Liters at a temperature of 300K. Calculate the entropy change of the system and its surroundings in each of the following isothermal processes.

A. Suppose that one wall of the vessel is actually a piston that is held in place by a pin. The pressure behind the piston is 10 atm. The pin is removed and the piston is allowed to push on the gas irreversibly until it comes to rest on its own.

B. Suppose that the gas is compressed reversibly to the same final volume as in the previous question.

Let's treat the reversible case first.

$$dq_{rev} = -dw_{rev} = PdV = nRT\ dV/V$$

$$dS = dq_{rev}/T = nR\ dV/V$$

$$\Delta S = nR \ln (V_2/V_1)$$

$$T = 300\text{ K},\ V_1 = 25\text{ L},\ P_2 = 10\text{ atm},\ V_2 = nRT/P_2 = 4.92\text{ L}$$

$$\Delta S = -1.62R$$

$$dq_{rev,surr} = -\ dq_{rev,sys} \Rightarrow \Delta S_{surr} = -\Delta S_{sys}$$

Now let's treat the irreversible case.

Because S is a state variable, ΔS_{sys} has the same value as in the reversible case, so long as the final state is the same. But ΔS_{surr} is different.

Suppose the outside world has a constant pressure. Then ΔH_{surr} equals the heat loss of the system, regardless if the process is reversible or not. That is:

$\Delta S_{surr} = -q_{rev}/T_{surr} = \Delta H_{surr}/T_{surr} = -q_{irrev}/T_{surr}$

Note: 1) The minus sign comes from the fact that heat leaves the system and enters the surroundings.
2) This principle works because the surrounding heat bath is so large that its temperature does not change when q is added or removed.

$$q_{irrev} = -w_{irrev} = P_{ex}\Delta V$$

$$\Delta S_{surr} = -P_{ex}\Delta V/T = 8.156R$$

$$\Delta S_{tot} = \Delta S_{sys} + \Delta S_{surr} = 6.54\ R$$

The total entropy change for a spontaneous process is greater than zero.

Let's consider next the equivalent adiabatic processes.

For the reversible case, $\Delta S_{sys} = \Delta S_{surr} = 0$

For the irreversible case, $\Delta S_{surr} = 0$ because no heat enters the surroundings. But for ΔS_{sys} we must find an equivalent reversible path.

$$-P_{ex}\ (V_2 - V_1) = C_V\ (T_2 - T_1)$$

$$P_{ex}V_2 = P_2V_2 = nRT_2$$

$$P_2V_1 + C_VT_1 = C_VT_2 + nRT_2 = 5/2\ nRT_2$$

$$P_2V_1 + C_VT_1 = 29{,}072\text{ J}$$

$$T_2 = 1399\text{ K},\ V_2 = 4.591\text{ L}$$

$$\Delta S_{sys} = C_V \ln (T_2/T_1) + nR\ l\mathit{n}\ (V_2/V_1)$$

$= 3/2\ R \ln (4.6633) + R \ln (0.1836)$

$= 0.615\ R = \Delta S_{tot}$

S_{tot} Again, $\Delta S_{tot} > 0$ for an irreversible process.
The bottom line in these examples:

1. Because ΔS is a state quantity, ΔS_{sys} is the same for reversible and irreversible processes, provided that the final state is the same for both cases. If it is not (as in the adiabatic example above), then for the irreversible process it is necessary to construct a reversible path and calculate ΔS_{sys} along that path.
$\Delta S_{sys}=0$ for reversible adiabatic processes but not for irreversible ones.

2. ΔS_{surr} is given by $-q/T_{surr}$, both for reversible and irreversible processes. It follows that $\Delta S_{surr}=0$ for all adiabatic processes.
Another example: An ice cube falls into the ocean and melts. Calculate ΔS_{sys}, ΔS_{surr}, and ΔS_{tot}

Assume one mole of ice:
$T_{ice} = 273.2$ K, $T_{ocean} = 283.2$ K.

What is $\Delta H_{fus}(H_2O, 283.2\ K)$? Construct a cycle:

$$\begin{array}{ccc} & 1 & \\ H_2O(\text{solid, } 283.2\ K) & \rightarrow & H_2O(\text{liq, } 283.2\ K) \\ \downarrow 2 & & \uparrow 4 \\ H_2O(\text{solid, } 273.2\ K) & \rightarrow & H_2O(\text{liq, } 273.2\ K) \\ & 3 & \end{array}$$

$\Delta H_1 = \Delta H_2 + \Delta H_3 + \Delta H_4$

$\Delta H_2 = C_P(H_2O, \text{solid})$[1] x $(273-283) = -378$ J/mol

$\Delta H_3 = \Delta H_{fus}(H_2O, 273.2\ K) = 6{,}008$ J/mol

$\Delta H_4 = C_P(H_2O, \text{liq})$ x $(283-273) = 335.6$ J/mol

$\therefore \Delta H_4 = \Delta H_{fus}(H_2O, 283.2\ K) = 5966$ J/mol

Now let's calculate the entropy changes.

$\Delta S_{ice} = \Delta S_2 + \Delta S_3 + \Delta S_4$

[1] Estimated to be 37.8 J/mol, from CRC handbook

$\Delta S_2 = C_P(H_2O, \text{solid}) \ln (273.2/283.2)$
$= -1.36 \text{ J mol}^{-1}\text{K}^{-1}$

$\Delta S_3 = \Delta H_{fus}(H_2O, 273.2 \text{ K})/273.2$
$= 22.0 \text{ J mol}^{-1}\text{K}^{-1}$ (This agrees with Table 4.1)

$\Delta S_4 = C_P(H_2O, \text{liq}) \ln (283.2/273.2) = 2.71 \text{ J mol}^{-1}\text{K}^{-1}$

$\therefore \Delta S_{ice} = 23.35 \text{ J mol}^{-1}\text{K}^{-1}$

What is the entropy change of the ocean?

$\Delta S_{ocean} = -\Delta H_{fus}(H_2O, 283.2 \text{ K})/283.2$
$= -21.07 \text{ J mol}^{-1}\text{K}^{-1}$

$\Delta S_{total} = = 2.28 \text{ J mol}^{-1}\text{K}^{-1}$

Again, we find that the total entropy increases for a spontaneous (irreversible) process.

Another example: Thermal equilibration of two objects.

Suppose we have two identical copper blocks, one heated to 500 K and the other at 300 K. Suppose they are brought into contact and allowed to reach a common final temperature, T.

1. Irreversible heat transfer:

$$C_P(500 - T) = C_P(T - 300)$$

$$\therefore T = 400$$

$$\Delta S = C_P \ln(T/500) + C_P \ln(T/300)$$

$$= C_P \ln\left(\frac{400^2}{300 \cdot 500}\right) = 0.0645 C_P$$

Again, we find that the total entropy increases for a spontaneous (irreversible) process.

2. Reversible heat transfer. (Suppose the copper blocks are used as the heat source and sink for a reversible engine.)

$$\Delta S = C_P \ln(T/500) + C_P \ln(T/300) = 0$$

Solve for T:

$$\ln(T/500) = -\ln(T/300) = \ln(300/T)$$

$T^2 = 300x500$

$T = 387$ K

The geometric mean is less than the arithmetic mean.

Work extracted = $(400 - 387)C_P$
It is instructional to examine this problem in the limit of very large heat sources. See accompanying diagrams.

Irreversible transfer of heat q from a hot reservoir at T_{hot} to a cold reservoir at T_{cold} via a thin wire:

$$\Delta S_{hot} = -q/T_{hot}$$

$$\Delta S_{cold} = q/T_{cold}$$

$$\Delta S_{total} = q[1/T_{cold} -/T_{hot}] > 0$$

Reversible transfer of heat q from a hot reservoir at T_{hot} to a cold reservoir at T_{cold} via a gas and a piston:

1. Transfer of q from T_{hot} to the gas by an isothermal expansion:

$$\Delta S_{hot} = -q/T_{hot} = -\Delta S_{gas}$$

2. Adiabatic expansion of the gas, cooling it to T_{cold}

$$\Delta S_{gas} = 0$$

Transfer of q from the gas to T_{cold} to by an isothermal compression:

$$\Delta S_{cold} = q/T_{hot} = -\Delta S_{gas}$$

Lecture 19: Formulations of the Second Law

1. Entropy formulation: The entropy of an isolated system increases in the course of a spontaneous change: $\Delta S_{tot} > 0$.

2. Kelvin-Planck statement: It is impossible for a system to undergo a cyclic process for which the only effects are the flow of heat into the system from a heat reservoir (a "reversible heat source") and the performance of an equivalent amount of work by the system on its surroundings (a "reversible work source").

3. Clausius statement: It is impossible for a system to undergo a cyclic process for which the only effects are the flow of heat into the system from a cold reservoir and flow of an equal amount of heat out of the system into a hot reservoir.

Theorems

1. $\Delta S_{tot} = 0$ for a reversible process. Decompose the path into an adiabatic and an isothermal component. $\Delta S_{sys} \equiv \Delta S = 0$ along the adiabatic path and $\Delta S = q/T$ along the isothermal path. $\Delta S_{surr} = 0$ along the adiabatic path and $\Delta S_{sys} = -q/T$ along the isothermal path. $\therefore \Delta S_{tot} = \Delta S + \Delta S_{surr} = 0$.

2. Clausius inequality:

$$dS \geq dq/T$$

Proof:

$$dS_{tot} \geq 0$$

$$dS + dS_{surr} \geq 0$$

$$dS_{surr} = -dq/T$$

$$\therefore dS \geq dq/T$$

$$\Delta S_{cyc} \geq \oint dq/T$$

But $\Delta S_{cyc} = 0$ because S is a state variable.

$$\therefore \oint dq/T \leq 0$$

It follows from the Clausius inequality that the entropy change along an irreversible path is positive (something we already knew.)

Let A→B be an irreversible and isolated process.

$\therefore q_{A\to B}=0.$

Let B→A be a reversible process that completes the cycle.

The Clausius inequality $\Rightarrow \int_B^A \frac{dq}{T} < 0$

But q along path B→A is a reversible.

$\therefore \Delta S(B\to A) < 0$

$\therefore \Delta S(A\to B) > 0$

Q.E.D

3. The entropic formulation and Kelvin's formulation are equivalent. To be proven later.

4. All reversible engines have the same efficiency,

$$\varepsilon = \frac{|work|}{q_{absorbed}} = \frac{q_{hot} + q_{cold}}{q_{hot}} = \frac{q_{hot} - |q_{cold}|}{q_{hot}} = 1 - \frac{|q_{cold}|}{q_{hot}}$$

Proof: Suppose engine 1 absorbs $q_{1,hot}$ and produces $q_{1,cold}$ and w_1. Similarly, engine 2 has parameters $q_{2,hot}$, $q_{2,cold}$, and w_2. Suppose that $\epsilon_2 > \epsilon_1$. Run engine 2 in reverse (i.e., as a refrigerator), such that its input is $-q_{1,cold}$ and w_2. Its greater efficiency implies that less work, $w_2 < -w_1$, is needed to remove $q_{1,cold}$ and less heat, $q_{2,hot}$, is generated. (See accompanying figure). Net result:

$q_{1,hot} - |q_{2,hot}|$ is converted into $|w_1| - w_2$.

This violates the Kelvin formulation.

5. The Kelvin and Clausius formulations are equivalent.

Proof that Kelvin ⇒ Clausius:

Suppose this statement is false. Set up a conventional engine that converts $q_{hot} \rightarrow q_{cold} + w$. Then hook up an anti-Clausius refrigerator to our engine and transfer q_{cold} back into the hot reservoir. Net result: $q_{hot} - |q_{cold}|$ is converted into $|w|$, in contradiction to the Kelvin formulation.

Proof that Clausius ⇒ Kelvin:

Suppose this statement is false. Set up a conventional refrigerator to convert $q_{hot} \leftarrow q_{cold} + w$. Then hook up an anti-Kelvin refrigerator to our refrigerator and convert to generate the work needed to run it by direct transfer out of the hot reservoir. Net result: $|q_{cold}|$ is converted into $q_{hot} - |w|$, in contradiction to the Clausius formulation.

6. The efficiency of a reversible engine is given by

$$\varepsilon_{engine} = \frac{|w|}{q_{hot}} = 1 - \frac{T_{cold}}{T_{hot}}$$

Proof: Use a Carnot Cycle

$$\Delta S = C_V \ln\frac{T_1}{T_2} + nR\ln\frac{V_2}{V_1}$$

Path 1: $\Delta S_{A\to B} = C_V \ln\frac{T_{hot}}{T_{hot}} + nR\ln\frac{V_B}{V_A} = nR\ln\frac{V_B}{V_A}$

Recall: $q_1 = nRT_{hot}\ln\left(\frac{V_B}{V_A}\right)$

Path 2: $\Delta S_{B\to C} = C_V \ln\frac{T_{cold}}{T_{hot}} + nR\ln\frac{V_C}{V_B}$

$$\frac{\Delta S_{B\to C}}{nR} = \frac{C_V}{nR}\ln\frac{T_{cold}}{T_{hot}} + \ln\frac{V_C}{V_B}$$

$$= \ln\left[\left(\frac{T_{cold}}{T_{hot}}\right)^{\frac{C_V}{nR}}\frac{V_C}{V_B}\right] = 0$$

This result is expected because $dq_{rev} = 0$ along an adiabat.

Path 3: $\Delta S_{C\to D} = C_V \ln\frac{T_{cold}}{T_{cold}} + nR\ln\frac{V_D}{V_C} = -nR\ln\frac{V_B}{V_A}$

Recall: $q_3 = nRT_{cold}\ln\left(\frac{V_D}{V_C}\right)$

Path 4: $\Delta S_{D\to A} = 0$

For the entire cycle: $\Delta S=0$

Heat budget: $\frac{q_{hot}}{q_{cold}} = -\frac{T_{hot}}{T_{cold}}$

Work done in one cycle: $w = -(q_{hot} + q_{cold})$

Engine efficiency: $\varepsilon = \frac{|w|}{q_{hot}} = \frac{q_{hot} + q_{cold}}{q_{hot}} = 1 - \frac{T_{cold}}{T_{hot}}$

Actually, we don't need to use the Carnot cycle (or any specified system) to prove this result. It all comes directly from the First and Second Laws.

Note: In this and the subsequent discussion, we label heat and work leaving a heat or work source with a minus sign and the heat or work entering those sources with a plus sign. The focus is on the sources because we are interested in calculating the efficiency of work or heat production.

Here, it follows that for a cycle

$$q_{hot} = q_{cold} + w \Rightarrow q_{hot} + q_{old} + w = 0.$$

This equality will always hold for a cycle.

Lecture 20: Consequences of the Second Law

7. Derivation of the Clausius inequality using a Carnot Cycle:

Suppose a cycle contains an irreversible part. Construct a Carnot engine that includes that path. It's efficiency will be less than ideal.

$$\frac{q_{hot}^{irr} + q_{cold}^{irr}}{q_{hot}^{irr}} < \frac{T_{hot} - T_{cold}}{T_{hot}}$$

$$\frac{q_{cold}^{irr}}{q_{hot}^{irr}} < \frac{-T_{cold}}{T_{hot}}$$

$$\frac{q_{cold}^{irr}}{T_{cold}} + \frac{q_{hot}^{irr}}{T_{hot}} < 0$$

$$\oint \frac{dq_{irr}}{T} < 0$$

Use of the Clausius inequality to derive the Kelvin formulation of the Second Law

Suppose the Kelvin formulation were false.
Use an engine operating at temperature T_0 to withdraw heat q and convert it into work w.

With respect to the engine, q > 0 and w < 0. (This follows because $\Delta U = q + w = 0$ for a cycle.)

q > 0 and T_0 constant ⇒ $\oint \frac{dq}{T_0} > 0$

But this contradicts the Clausius inequality
⇒ the Kelvin formulation must be true.

We can use the same argument to prove the converse.

Suppose that $\Delta S_{tot} < 0$ ⇒ the process is spontaneous. Then the Clausius inequality becomes

$$\oint \frac{dq}{T} > 0$$

For an engine connected to an isothermal bath at $T=T_0$, it follows that q > 0 and w < 0. This is contrary to the Kelvin formulation, proving the theorem.

Lecture 21: Thermodynamic Engines

Note: In each of the following examples, you need to refer to the diagrams presented in class.

1. Reversible engines:

First Law: $-dq_{hot} = dq_{cold} + dw$

Second Law: $\frac{dq_{hot}}{T_{hot}} + \frac{dq_{cold}}{T_{cold}} = 0$

$$dq_{cold} = -\frac{T_{cold}}{T_{hot}} dq_{hot}$$

$$dq_{hot} = \frac{T_{cold}}{T_{hot}} dq_{hot} - dw$$

$$dq_{hot}\left[1 - \frac{T_{cold}}{T_{hot}}\right] = -dw$$

$$\varepsilon_{engine} = -\frac{dw}{dq_{hot}} = 1 - \frac{T_{cold}}{T_{hot}}$$

$$\lim_{T_{cold} \to 0} \varepsilon_{engine} = 1$$

2. Reversible heat pumps:

First Law: $dq_{hot} = -dq_{cold} - dw$

Second Law: $\frac{dq_{hot}}{T_{hot}} + \frac{dq_{cold}}{T_{cold}} = 0$

$$dq_{cold} = -\frac{T_{cold}}{T_{hot}} dq_{hot}$$

$$dq_{hot} = \frac{T_{cold}}{T_{hot}} dq_{hot} - dw$$

$$dq_{hot}\left[1 - \frac{T_{cold}}{T_{hot}}\right] = -dw$$

$$\varepsilon_{heat\_pump} = -\frac{dq_{hot}}{dw} = \frac{T_{hot}}{T_{hot} - T_{cold}}$$

$$\lim_{T_{cold} \to T_{hot}} \varepsilon_{heat\_pump} = \infty$$

3. Reversible refrigerators:

First Law: $dq_{hot} = -dq_{cold} - dw$

Second Law: $$\frac{dq_{hot}}{T_{hot}} + \frac{dq_{cold}}{T_{cold}} = 0$$

$$dq_{hot} = -\frac{T_{hot}}{T_{cold}} dq_{cold}$$

$$dq_{cold} \frac{T_{hot}}{T_{cold}} = dq_{cold} + dw$$

$$dq_{cold}\left(\frac{T_{hot}}{T_{cold}} - 1\right) = dw$$

$$\varepsilon_{refrigerator} = \frac{dq_{cold}}{dw} = \frac{T_{cold}}{T_{hot} - T_{cold}}$$

$$\lim_{T_{hot} \to T_{cold}} \varepsilon_{refrigerator} = \infty$$

Lecture 22: Microscopic Basis of The Second and Third Laws

S is a measure of the number of microscopic states W that are consistent with an observed macroscopic state (i.e., for a given U, V, n_1, n_2,…).

Analogy with a pair of dice:

Macroscopic state	Microscopic state	W
2	{1,1}	1
3	{1,2},{2,1}	2
4	{1,3},{2,2},{2,1}	3
5	{1,4},{2,3},{3,2},{4,1}	4
6	{1,5},{2,4},{3,3},{4,2},{5,1}	5
7	{1,6},{2,5},{3,4}{4,3},{5,2},{6,1}	6
8	{2,6}{3,5},{4,4},{5,3},{6,2}	5

9	{3,6},{4,5},{5,4},{6,3}	4
10	{4,6},{5,5},{6,4}	3
11	{5,6},{6,5}	2
12	{6,6}	1

Molecular example: m energy levels

$$U = \sum_{i=1}^{m} N_i E_i$$

Microscopic configurations:

$$\{N_{11}, N_{21}, \ldots, N_{m1}\},$$

$$\{N_{12}, N_{22}, \ldots, N_{m2}\},$$

$$\ldots,$$

$$\{N_{1W}, N_{2W}, \ldots, N_{mW}\}$$

Boltzmann's definition of the entropy:

$$S = k \ln W$$

$$k = R/N_A = 1.381 \times 10^{-23}\ J\ K^{-1}$$

S is dimensionless if T has the units of energy.

As $T \rightarrow 0$, all molecules drop to E_1, so that

$$W=1$$

$$k \ln W = 0$$

Exception: 2 (or more) molecular orientations at the ground energy level.

Suppose there are N molecules with 2 equivalent orientations. (g=2)

$$W = 2^N$$

$$S(T=0) = k \ln\{2^N\} = kN \ln 2$$

$$= kN_A(N/N_A) \ln 2$$

$$= nR \ln 2$$

Rationalization for using a logarithm is that it makes S extensive.

Example: isothermal expansion

g ~ V/V$_0$

$$S = k \ln\left(\frac{V}{V_0}\right)^N$$

$$\Delta S = k \ln\left(\frac{V_2}{V_0}\right)^N - k \ln\left(\frac{V_1}{V_0}\right)^N$$

$$\Delta S = Nk \ln\left(\frac{V_2}{V_0}\right) - Nk \ln\left(\frac{V_1}{V_0}\right) = Nk \ln\left(\frac{V_2}{V_1}\right)$$

$$\Delta S = nR \ln\left(\frac{V_2}{V_1}\right)$$

Nernst's Heat Theorem: For any physical or chemical transformation,

$$\lim_{T \to 0} \Delta S = 0$$

$$\begin{array}{ccc} R(T) & \rightarrow & P(T) \\ \uparrow & & \downarrow \\ R(0) & \rightarrow & P(0) \end{array}$$

$$\Delta S(T) + \int_0^T (C_R - C_P) \frac{dT}{T} = 0$$

$$\Delta S(T) = \int_0^T (C_P - C_R) \frac{dT}{T}$$

Lecture 23: Thermodynamic Potentials

The fundamental relation U = U(S, V, n) contains all thermodynamic information about an equilibrium state, using only extensive quantities.

A Legendre transform replaces a variable by its derivative in a functional relation. If Y(X) is a function of X, and P=dY/dX, then ψ is a function of P, where

$$\psi(P) = Y - PX$$

In thermodynamics we use Legendre Transforms to replace extensive variables by intensive ones.

$$-P = \left(\frac{\partial U}{\partial V}\right)_S$$

$$T = \left(\frac{\partial U}{\partial S}\right)_V$$

Legendre Transforms

The conventional way to describe a curve is by a function, where for every X we specify a Y:

$$Y = Y(X)$$

But we could also map out the curve by drawing the tangent at every point and tabulating the slopes,

$$P = \frac{dY}{dX}$$

and intercepts,

$$\frac{Y - \psi}{X - 0} = P$$

$$\psi = Y - PX$$

for every point on the curve. Elimination of X and Y gives a new function,

$$\psi = \psi(P).$$

Example:

$$Y = \frac{1}{4}X^2$$

$$P = \frac{1}{2}X$$

$$\psi = Y - PX = P^2 - 2P^2 = -P^2$$

In general, the Legendre transform is given by

$$\psi = Y - PX,$$

where it is understood that X and Y are eliminated.

Legendre Transforms in Thermodynamics

Replace V by –P: H = U + PV = H(S, P, n)

Replace S by T: A = U – TS = A(T, V, n)

Replace V by –P and S by T:

$$G = U + PV - TS = H - TS = G(P, T, n)$$

Derivative Relations

$$dU = TdS - PdV$$

$$dH = dU + PdV + VdP = TdS + VdP$$

$$dA = dU - TdS - SdT = -SdT - PdV$$

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

Look at the thermodynamic square.

Two more Maxwell relations:

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

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

Macroscopic changes at constant T

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

$$\Delta G = \Delta H - T\Delta S$$

Inequalities and signposts

$$dS + dS_{surr} \geq 0$$

$$dS - dq/T \geq 0$$

$$dS \geq dq/T \quad \text{(Clausius)}$$

$$TdS \geq dq$$

$$TdS \geq dU + PdV$$

Note: This becomes an equality for a reversible process.

At constant V,

$$TdS \geq dU$$

At constant U and V,

$dS > 0 \Rightarrow$ S is at a local maximum at equilibrium

At constant S and V,

$dU < 0 \Rightarrow$ U is at a local minimum at equilibrium

Transform $V \rightarrow -P$

$$TdS \geq dq = dH - VdP$$

At constant P,

$$TdS \geq dH$$

At constant H and P,

$$dS > 0 \Rightarrow \text{S is at a local maximum at equilibrium}$$

At constant S and P,

$$dH < 0 \Rightarrow \text{H is at a local minimum at equilibrium}$$

By similar reasoning, at constant V and T,

$$dA < 0 \Rightarrow \text{A is at a local minimum at equilibrium}$$

At constant P and T,

$$dG < 0 \Rightarrow \text{G is at a local minimum at equilibrium}$$

Differential Quantities

$$dU = dq_V$$

$$dH = dq_P$$

$$dA = dw_{max,total}$$

$$dG = dw_{max,other}$$

Maximum Work

For an irreversible process,

$$TdS \geq dU + PdV = dU - dw$$

$$\therefore dw \geq dU - TdS$$

Note: The work is a maximum when it is the most negative, i.e. when w is as small as possible.

$$\therefore dw_{max} = dU - TdS = dA + SdT$$

At constant temperature,

$$dw_{max} = dA$$

$$w_{max} = \Delta A$$

We can distinguish between mechanical ("PV") work and other types of work (e.g., electrical):

$$dw = -PdV + dw_{other} \geq dU - TdS$$

$$dw_{other} \geq dU - TdS + PdV$$

$$dw_{other,max} = dU - TdS + PdV = dG + SdT - VdP$$

At constant T and P,

$$dw_{other,max} = dG$$

$$\Delta w_{other,max} = \Delta G$$

Properties of the Gibbs Free Energy

$$dG = VdP - SdT$$

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

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

1. Pressure dependence of G

$$G(P_f) - G(P_i) = \int_{P_i}^{P_f} VdP$$

Incompressible material:

$$G(P_f) - G(P_i) = V(P_f - P_i)$$

Ideal gas:

$$G(P_f) - G(P_i) = \int_{P_i}^{P_f} \frac{nRT}{P} dP = nRT \ln\left(\frac{P_f}{P_i}\right)$$

2. Temperature dependence

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

Gibbs-Helmholtz Equation:

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

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

Lecture 24: Thermodynamic Calculations, Revisited

Recipe for evaluating thermodynamic derivatives

1. If the derivative contains any potentials, bring them one by one to the numerator and eliminate them using the thermodynamic square.

2. If the derivative contains the entropy, bring it to the numerator. If possible, use on of the Maxwell relations to eliminate it. If this doesn't work, put a ∂T under the ∂S. The numerator will now be expressible as either C_V or C_P.

3. Bring the volume to the numerator. The remaining derivative will now be expressible in terms of α and κ_T.

4. Invoke $C_P = C_V + TV\alpha^2 / \kappa_T$

Example of step 1.

$$\left(\frac{\partial P}{\partial U}\right)_G = \left[\left(\frac{\partial U}{\partial P}\right)_G\right]^{-1}$$

$$= \left[T \left(\frac{\partial S}{\partial P} \right)_G - P \left(\frac{\partial V}{\partial P} \right)_G \right]^{-1}$$

$$= \left[\frac{-T \left(\frac{\partial G}{\partial P} \right)_S}{\left(\frac{\partial G}{\partial S} \right)_P} + \frac{P \left(\frac{\partial G}{\partial P} \right)_V}{\left(\frac{\partial G}{\partial V} \right)_P} \right]^{-1}$$

$$\left[-T \frac{-S \left(\frac{\partial T}{\partial P} \right)_S + V}{-S \left(\frac{\partial T}{\partial S} \right)_P} + P \frac{-S \left(\frac{\partial T}{\partial P} \right)_V + V}{-S \left(\frac{\partial T}{\partial V} \right)_P} \right]^{-1}$$

Example of step 2.

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

Note that at constant pressure, $dq_p = dH = TdS$
But also $dq_p = C_P dT$. $\therefore C_P dT = TdS$.

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

Another example:

$$\left(\frac{\partial S}{\partial V} \right)_P = \frac{\left(\frac{\partial S}{\partial T} \right)_P}{\left(\frac{\partial V}{\partial T} \right)_P} = \frac{C_P / T}{\alpha V}$$

Example of step 3.

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

Lecture 25: Fugacity

Chemical potential for a mixture of substances:

$$dG = -SdT + VdP + \mu_1 dn_1 + \mu_2 dn_2$$

At constant T, P, $n_1 + n_2$,

$$dG = \mu_1 dn_1 + \mu_2 dn_2 = (\mu_1 - \mu_2)\, dn_1$$

At equilibrium, $dG = 0 \Rightarrow \mu_1 = \mu_2$

In general,

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}}$$

For a pure substance, $G = nG_m \Rightarrow \mu = G_m$

In this lecture we will consider only this case. For an ideal gas,

$$G(T,P) = G(T,P^0) + nRT\ln\left(\frac{P}{P^0}\right)$$

$$\mu(T,P) = \mu(T,P^0) + RT\ln\left(\frac{P}{P^0}\right)$$

Choice of a standard state:

1. Specify T
2. For a condensed phase, $P^0 = 1$ bar.
3. For a gas, the standard state is a hypothetical state at 1 atm in which the gas behaves ideally.

Definition of the fugacity, f: For a non-ideal gas,

$$\mu(\mathrm{T},\mathrm{P}) = \mu(\mathrm{T},\mathrm{P}^0) + \mathrm{RT}\ln\left(\frac{\mathrm{f}}{\mathrm{P}^0}\right)$$

Definition of the fugacity coefficient:

$$\phi = f/P$$

$$\lim_{P \to 0} \phi = 1$$

How to calculate the fugacity: At constant T,

$$d\mu = RT\, d\ln f$$

But we also know that

$$\left(\frac{\partial \mu}{\partial P}\right)_T = \left(\frac{\partial G_m}{\partial P}\right)_T = V_m$$

$$\therefore \quad d\mu = V_m dP$$

$$\therefore \quad RT\, d\ln f = V_m dP$$

$$RTd\ln\left(\frac{f}{P}\right) = V_m dP - RTd\ln P$$

$$= \left(V_m - \frac{RT}{P}\right)dP$$

$$d\ln\left(\frac{f}{P}\right) = \left(\frac{V_m}{RT} - \frac{1}{P}\right)dP$$

$$= \left(\frac{PV_m}{RT} - \frac{1}{P} \right) \frac{dP}{P} = \left(\frac{Z-1}{P} \right) dP$$

Integrating over pressure,

$$\ln\left(\frac{f}{P}\right) - \ln\left(\frac{f}{P}\right)_{P=0} = \ln\left(\frac{f}{P}\right) = \ln\phi = \int_0^P \left(\frac{Z-1}{P'}\right) dP'$$

Interpretation: Thermodynamic path

Ideal gas @ P, T → Ideal gas @ P=0, T

→ Real gas @ P=0, T → Real gas @ P, T

Note that

$$\ln\left(\frac{f}{P}\right) = \ln f_{real} - \ln f_{ideal}$$

$$\frac{\partial \ln\left(\frac{f}{P}\right)}{\partial P} = \frac{Z-1}{P} = \frac{Z}{P} - \frac{1}{P}$$

where
$$\frac{\partial \ln\left(\frac{1}{P}\right)}{\partial P} = -\frac{1}{P}$$

and
$$\frac{\partial \ln f}{\partial P} = \frac{Z}{P}$$

Integrating along the thermodynamic path,

$$\ln f_{real}(p) - \ln f_{ideal}(P)$$

$$= \int_P^0 Z_{ideal} \frac{dP'}{P'} + 0 + \int_0^P Z_{real} \frac{dP'}{P'}$$

$$= -\int_0^P \frac{dP'}{P'} + \int_0^P Z \frac{dP'}{P'} = \int_0^P (Z - 1) \frac{dP'}{P'}$$

Example of a real gas

$$Z = 1 + B'P + C'P^2 + \ldots$$

$$\ln\left(\frac{f}{P}\right) = \int_0^P (B' + C'P')dP'$$

$$= B' + \frac{1}{2} C'P^2$$

$$f = Pe^{B'P + \frac{1}{2}C'P^2}$$