Chem 340 - Lecture Notes 4 – Fall 2013 – State function manipulations

Properties of State Functions
State variables are interrelated by equation of state, so they are not independent, express relationship mathematically as a partial derivative, and only need two of T,V, P

Example: Consider ideal gas: PV = nRT so P = f(V,T) = nRT/V, let n=1
Can now do derivatives: \( (\partial P/\partial V)_T = -RT/V^2 \) and: \( (\partial P/\partial T)_P = R/V \)
Full differential show variation with respect to one variable at a time, sum for both:

\[ dP = \left( \frac{\partial P}{\partial T} \right)_V dT + \left( \frac{\partial P}{\partial V} \right)_T dV \]

shows total change in P if have some change in V and in T

Example, on hill and want to know how far down (dz) you will go if move some amount in x and another in y. contour map can tell, or if knew function could compute dz, from dz/dx for motion in x and dz/dy from dz/dy for motion in y total change in z is just sum: dz = (dz/dx)dx + (dz/dy)dy
Note: for dz, small change (big ones need higher derivative)

Can of course keep going with 2\(^{nd}\) and 3\(^{rd}\) derivatives or mixed ones

\[ \left( \frac{\partial}{\partial T} \left( \frac{\partial P}{\partial V} \right) \right)_V = \frac{\partial^2 P}{\partial T \partial V} = \left( \frac{\partial}{\partial V} \left( \frac{RT}{V^2} \right) \right)_T = \left( \frac{\partial}{\partial V} \left( \frac{R}{V} \right) \right)_T = \frac{R}{V^2} \]

For state functions the order of taking the derivative is not important, or

\[ \left( \frac{\partial}{\partial T} \left( \frac{\partial f(V,T)}{\partial V} \right) \right)_V = \left( \frac{\partial}{\partial V} \left( \frac{\partial f(V,T)}{\partial T} \right) \right)_V \]

The corollary works, reversed derivative equal \( \rightarrow \) determine if property is state function as above, state function has an exact differential: \( \Delta f = \int df = f_i - f_f \) good examples are \( \Delta U \) and \( \Delta H \), but, q and w are not state functions
Some handy calculus things:
If \( z = f(x,y) \) can rearrange to \( x = g(y,x) \) or \( y = h(x,z) \) [e.g. \( P=nRT/V, V=nRT/P, T=PV/nR \)]

\[
\left( \frac{\partial x}{\partial y} \right)_z = \frac{1}{\left( \frac{\partial y}{\partial x} \right)_z} \quad \left( \frac{\partial x}{\partial y} \right)_z \left( \frac{\partial y}{\partial z} \right)_x \left( \frac{\partial z}{\partial x} \right)_y = -1
\]

Inversion: cyclic rule:

So we can evaluate \( (\partial P/\partial V)_T \) or \( (\partial P/\partial T)_V \) for real system, use cyclic rule and inverse:

\[
\left( \frac{\partial P}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_P \left( \frac{\partial T}{\partial P} \right)_V = -1
\]

divide both sides by \( (\partial T/\partial P)_V \) get

\[ 1/(\partial T/\partial P)_V = (\partial P/\partial T)_V \]

similarly

\[ (\partial P/\partial V)_T = 1/(\partial V/\partial P)_T \]

so get ratio of two volume changes

cancel \( (\partial V/\partial T)_P = \beta V \)
const. \( \beta, \kappa \) norm to \( V \)

\[
\beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \quad \text{and} \quad \kappa = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T
\]

Where: \( \beta = \) volumetric thermal expansion coefficient (Atkins \( \rightarrow \alpha \))
and \( \kappa = \) isothermal compressibility

Point: We can measure both of these properties and solve relationships, for any system

Sign chosen so \( \kappa \) is positive (i.e. as \( P \) inc., expect \( V \) dec., \( (\partial V/\partial P)_T \) negative)

Back to start, total derivative, \( dP \): integrate:

\[
dP = \frac{\beta}{\kappa} dT - \frac{1}{\kappa V} dV \quad \Delta P = \int_{T_i}^{T_f} \frac{\beta}{\kappa} dT - \int_{V_i}^{V_f} \frac{1}{\kappa V} dV \approx \frac{\beta}{\kappa} (T_f - T_i) - \frac{1}{\kappa} \ln \frac{V_f}{V_i}
\]

Example: temperature in experiment has risen so ethanol thermometer is at the top of capillary, filled. If you increase another 10°C, how much will pressure increase?

\[
\Delta P = \int (\beta_{el}/\kappa) dT - \int (1/\kappa V) dV \sim \beta_{el} \Delta T/\kappa - (1/\kappa) \ln(V_f/V_i) \quad V_f = V_i(1 + \beta_{gl} \Delta T) \quad \ln(1-x) \sim x, \quad x<<1
\]

\[
\Delta P = \beta_{el} \Delta T/\kappa - (1/\kappa) \ln(V_f/V_i) = \ln(1+\beta_{gl} \Delta T) \sim \beta_{gl} \Delta T
\]

\[
\Delta P = (\Delta T/\kappa) \left( \beta_{el}-\beta_{gl} \right) \quad \beta_{gl} = 2.0 \times 10^{-5} \, \text{oC}^{-1} \quad \beta_{el} = 11.2 \times 10^{-4} \, \text{oC}^{-1} \quad \kappa = 11.0 \times 10^{-5} \, \text{bar}^{-1}
\]

\[
\Delta P = (10 \, ^oC /11.0 \times 10^{-5} \, \text{bar}^{-1}) (11.2-0.2) \times 10^{-4} \, \text{oC}^{-1} = 100 \, \text{bar} \quad \text{(goodbye thermometer!)}
\]
κ and β (α-Atkins) values for selected solids and liquids:

### Table 3.1 Volumetric Thermal Expansion Coefficient for Solids and Liquids at 298 K

<table>
<thead>
<tr>
<th>Element</th>
<th>10^6 β/(K⁻¹)</th>
<th>Element or Compound</th>
<th>10^4 β/(K⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag(s)</td>
<td>57.6</td>
<td>Hg(l)</td>
<td>1.81</td>
</tr>
<tr>
<td>Al(s)</td>
<td>69.3</td>
<td>CCl₄(l)</td>
<td>11.4</td>
</tr>
<tr>
<td>Au(s)</td>
<td>42.6</td>
<td>CH₃COCH₃(l)</td>
<td>14.6</td>
</tr>
<tr>
<td>Cu(s)</td>
<td>49.5</td>
<td>CH₃OH(l)</td>
<td>14.9</td>
</tr>
<tr>
<td>Fe(s)</td>
<td>36.9</td>
<td>C₂H₅OH(l)</td>
<td>11.2</td>
</tr>
<tr>
<td>Mg(s)</td>
<td>78.3</td>
<td>C₆H₅CH₃(l)</td>
<td>10.5</td>
</tr>
<tr>
<td>Si(s)</td>
<td>7.5</td>
<td>C₆H₆(l)</td>
<td>11.4</td>
</tr>
<tr>
<td>W(s)</td>
<td>13.8</td>
<td>H₂O(l)</td>
<td>2.04</td>
</tr>
<tr>
<td>Zn(s)</td>
<td>90.6</td>
<td>H₂O(s)</td>
<td>1.66</td>
</tr>
</tbody>
</table>


Liquid β (α) values generally much larger than for solids, see example above.

Note: water will be different close to 273 K, max density ~4°C

### Table 3.2 Isothermal Compressibility at 298 K

<table>
<thead>
<tr>
<th>Substance</th>
<th>10⁶ κ/bar⁻¹</th>
<th>Substance</th>
<th>10⁶ κ/bar⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>AI(s)</td>
<td>1.33</td>
<td>Br₂(l)</td>
<td>64</td>
</tr>
<tr>
<td>SiO₂(s)</td>
<td>2.57</td>
<td>C₂H₅OH(l)</td>
<td>110</td>
</tr>
<tr>
<td>Ni(s)</td>
<td>0.513</td>
<td>C₆H₅OH(l)</td>
<td>61</td>
</tr>
<tr>
<td>TiO₂(s)</td>
<td>0.56</td>
<td>C₆H₆(l)</td>
<td>94</td>
</tr>
<tr>
<td>Na(s)</td>
<td>13.4</td>
<td>CCl₄(l)</td>
<td>103</td>
</tr>
<tr>
<td>Cu(s)</td>
<td>0.702</td>
<td>CH₃COCH₃(l)</td>
<td>125</td>
</tr>
<tr>
<td>C(graphite)</td>
<td>0.156</td>
<td>CH₃OH(l)</td>
<td>120</td>
</tr>
<tr>
<td>Mn(s)</td>
<td>0.716</td>
<td>CS₂(l)</td>
<td>92.7</td>
</tr>
<tr>
<td>Co(s)</td>
<td>0.525</td>
<td>H₂O(l)</td>
<td>45.9</td>
</tr>
<tr>
<td>Au(s)</td>
<td>0.563</td>
<td>Hg(l)</td>
<td>3.91</td>
</tr>
<tr>
<td>Pb(s)</td>
<td>2.37</td>
<td>SiCl₄(l)</td>
<td>165</td>
</tr>
<tr>
<td>Fe(s)</td>
<td>0.56</td>
<td>TiCl₄(l)</td>
<td>89</td>
</tr>
<tr>
<td>Ge(s)</td>
<td>1.38</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Now look at how $U$ varies with $V$ and $T$, since state function can do same things

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

but $\Delta U = q + w$ and differential: $dU = dq + dw$

So

$$dU = dq - P_{\text{external}} dV = \left( \frac{\partial U}{\partial T} \right)_V dT + \left( \frac{\partial U}{\partial V} \right)_T dV$$

If $dV = 0$, so like state fct, if $V$ const $\implies$ path

Already discuss $C_V$: positive, extensive, $C_{V_m} = C_V/n$ intensive, vary with substance and $T$

**Microscopic picture:** due to the variation in accessible energy states, so more degrees of freedom (rotations, vibrations) for polyatomics as opposed to atoms

$$\Delta U = \int_{T_1}^{T_2} C_V dT$$

or

$$\int \left[ dq_V = \int \frac{\partial U}{\partial T} \right]_V dT \text{ or } q_V = \Delta U$$

$dq$ is inexact but if path defined has unique value, here constant $V$, so $q_V$ eval, $C_V$ fixed

that was one part of complete differential, what about: $(\partial U/\partial V)_T = \pi_T$ - internal pressure

Can show that put it into

$$dU = dq = \int \frac{\partial P}{\partial T} dV$$

Ideal gas, $\pi_T = 0$, no interaction

work out: $T[\frac{\partial (nRT/V)}{\partial T}]_V - P = T(nR/V) - P = P - P = 0$

so ideal gas $dU = C_V dT$ (but do not need const $V$!)

Each part of $dU$ above is experimentally observable

Alternatively: If have a process can break up into simpler steps and evaluate state functions, sum for state change:

e.g. const $T$

$$dU = dU_T = [T(\partial P/\partial T)_V - P]$$

const $V$

$$dU = dU_V = C_V dT$$

total is sum, path independent (do red or blue path)
Comparing dependence of $U$ on $T$ and $V$

Ideal gas, $U = U(T)$, but real gas interaction $\rightarrow U(T,V)$

**Joule experiment** – expand gas into a vacuum,
heat from system to bath should be $(\partial U/\partial V)$

since vacuum: $p_{ext} = 0$, $w = 0$, so $dU = dq = dU_V + dU_T$

Joule result - no change in $T$, so assume $dT_{sys} = dT_{sur} = 0$ or $dq = 0 \rightarrow (\partial U/\partial V) dV = 0$ since $dV \neq 0 \rightarrow (\partial U/\partial V)_T = 0$

Joule experiment not sensitive enough, but observation does fit ideal behavior (above), later with Thomson they got more sensitive $(\partial U/\partial V)_T \neq 0$ but very small

**Example**: For van der Waals gas: $P = RT/(V_m-b) - a/V_m^2$ calculate

And determine $\Delta U_{Tm} = \int (\partial U/\partial V)_T dV_m$ from $V_m^i$ to $V_m^f$

a. $\pi_T = T(\partial U/\partial V)_V - P = T[R/(V_m-b)] - P = RT/(V_m-b) - [RT/(V_m-b) - a/V_m^2] = a/V_m^2$

b. $\Delta U_{Tm} = \int (\partial U/\partial V)_T dV_m = \int a/V_m^2 dV_m = -a(1/V^i - 1/V^f) \rightarrow$ expansion, $1/V^i > 1/V^f$, $\Delta U_{Tm} (+)$

So change in $U$ depends on $a$, the interaction term in van der Waals model

Relative size of $dU_T = (\partial U/\partial V)_T$ and $dU_V = (\partial U/\partial T)_V$

**Example**: expand $N_2$ from $(T=200K, P=5.0$ bar$)$ to $(T=400 K, P=20$ bar$)$,

$a = 0.137$ Pa$^m$m$^6$mol$^{-2}$, $b = 3.87x10^{-5}$m$^3$mol$^{-1}$, $C_v = (22.5 - 1.2x10^{-2}T + 2.4x10^{-5}T^2)$JK$^{-1}$mol$^{-1}$

solution can be done by breaking into const $V$ step and const $T$ step, find:

$\Delta U_T = -132$ Jmol$^{-1}$ and $\Delta U_V = 4.17$ kJmol$^{-1}$ $\rightarrow$ $dU_T = (\partial U/\partial V)_T$ much smaller (~3%)

Good approximation for gasses assume: $\Delta U \sim \Delta U(T)$ or $\Delta U_T = \int (\partial U/\partial V)_T dV \sim 0$

Solids and liquids, moderate conditions, $V_m = 1/\rho \sim$ const, or $dV_m \sim 0$

So $\Delta U_{Tm} = \int (\partial U/\partial V)_T dV \sim (\partial U/\partial V)_T dV$ much independent of $(\partial U/\partial V)_T$

Result means in most cases: $\Delta U = U_f(T,V) - U_i(T,V) = \int C_v dT$ (but not only const.$V$)

Note: assumes no phase changes, no chemical reactions (these come later!)

**Enthalpy and constant Pressure processes**

Let $P = P_{ext}$ (const) : $dU = dq_P - P dV$ integrate $U_f^i - U_i^f = q_P - P(V_f^i - V_i^f)$

$(U_f^i - PV_f^i) - (U_i^f - PV_i^f) = q_P$ so if $H = U + PV$ then $\Delta H = q_P \rightarrow$ independent

$\rightarrow$ any process, const $P$, closed system, only $P$-$V$ work

**Fusion and vaporization**, need heat to overcome molecular interaction, form new phase

$\Delta H = q_P > 0$, $\Delta U_{vap} = \Delta H_{vap} - P \Delta V_{vap} > 0$ ---- $\Delta V_{vap} >> 0$, so $\Delta U_{vap} < \Delta H_{vap}$

By contrast, $\Delta V_{fus}$ small, so $\Delta U_{fus} \sim \Delta H_{fus}$
like before:  
\[ dH = \left( \frac{\partial H}{\partial T} \right)_P dT + \left( \frac{\partial H}{\partial P} \right)_T dP \]  
for const P, dP = 0,
so we again get heat capacity at const P:  
\[ C_P = \left( \frac{\partial H}{\partial T} \right)_P \]
extensive, so use \( C_{Pm} \), \( H \) state variable, so evaluate by  
\[ \Delta H_P = \int C_P dT \]
relationship works for all systems, if there is no reaction or phase change

Relate \( C_V \) and \( C_P \) – from \( dH = dU + d(PV) = dq_P = C_V dT + \left( \frac{\partial U}{\partial V} \right)_T dV + P dV \)
Const P:  
but \( dq_P = C_P dT \), so “divide through” by dT, combine terms in \( (\partial V/\partial T)_P \)

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

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

Use then cyclic rule
\[ (\partial V/\partial T)_V = -1/(\partial V/\partial P)_T (\partial P/\partial T)_V \]
and definitions of \( \beta \) (\( \alpha - \)Atkins) and \( \kappa \):

So \( C_P \) and \( C_V \) for any substance or phase, can be related by knowing only \( V_m, \kappa \) and \( \beta \)

Ideal gas, \( (\partial U/\partial V)_T = 0 \), and \( P(\partial V/\partial T)_T = P(nR/P) = nR \), so \( C_P - C_V = nR \)

For solids and liquids \( (\partial V/\partial T)_P = V\beta \) and is much smaller, so \( C_P \sim C_V \rightarrow \) solid and liquid heat capacities measure at const P, not easy to control V

Enthalpy with pressure at const T

Same as above for dU, full variation for d(PV):
\[ dH = dU + d(PV) = C_V dT + (\partial U/\partial V)_T dV + V dP + V dP \]

\[ dH = C_V dT + \left[ \left( \frac{\partial U}{\partial V} \right)_T + P \right] dV + V dP \]

Often \( (\partial H/\partial T)_P dT >> (\partial H/\partial P)_T dP \) so ignore P dependence, but need for refrigerator divide through above by dP , then \( (\partial H/\partial P)_T \rightarrow \) isothermal, dT = 0, 1st term \((C_V dT)_0\), 0,

\[ \left( \frac{\partial H}{\partial P} \right)_T = \left[ \left( \frac{\partial U}{\partial V} \right)_T + P \right] \left( \frac{\partial V}{\partial P} \right)_T + V \]
Rearrange using \( (\partial U/\partial V)_T = T(\partial P/\partial T)_V V - P \), so two P’s cancel in bracket, and then use cyclic rule: \( (\partial P/\partial T)_V (\partial V/\partial P)_T = -1/(\partial T/\partial V)_P = (\partial V/\partial T)_P = \beta V \)
\[ \left( \frac{\partial H}{\partial P} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial V}{\partial P} \right)_T + V = V - T \left( \frac{\partial V}{\partial T} \right)_P = V(1 - T\beta) \]

So \( P \) dependence of \( H \) is \( V \), corrected by \( \beta \) expansion coefficient, ideal is \((\partial H/\partial P)_T = 0\)

Recall ideal: \( \beta = (\partial V/\partial T)_P/V = (\partial(RT/P)/\partial T)_P = R/PV = 1/T \)

Real gases \((\partial H/\partial P)_T \neq 0\), and important for heat transfer (refrigerator – expand gas, extract heat from “system” and then recompress, dump heat to “surroundings” \( \rightarrow \) kitchen!)

Solids and liquids, \((\partial V/\partial P)_T \) very small, so \((\partial H/\partial P)_T \sim V\), and \( dH = C_PdT + VdP \)

Example: Calculate \( \Delta H \) for 124 g liquid MeOH at 1.0 bar and 298 K
change to 2.5 bar and 425 K, \( \rho = 0.79 \text{ gcm}^{-3} \) and \( C_{pm} = 81 \text{ JK}^{-1}\text{mol}^{-1} \)

Choose const \( T \) path follow with const \( V \) path, use above result for \( dH \) liquid

\[ \Delta H = nC_{pm}dT + \int VdP \sim nC_{pm}\Delta T + V\Delta P \]

\[ = 81\text{ JK}^{-1}\text{mol}^{-1}(124\text{ g}/32\text{ g/mol}^{-1})127\text{ K} + (124\text{ g}/0.79\text{ gcm}^{-3})10^{-6}\text{ m}^3\text{cm}^{-3} \times 1.5 \times 10^5\text{ Pa} \]

\[ = 39.9 \times 10^3\text{ J} + 23.5\text{ J} \sim 40\text{ kJ} \] - first term, heat capacity, dominates, \( P \) depend. small

Joule Thomson Effect

Expand a gas, e.g. open an \( \text{N}_2 \) cylinder, \( \Delta P >> 0 \), see nozzle get cold (typical)

Model system: Gas transferred from high to low pressure through porous plug, isolated cylinder, piston moves to keep \( P \) values const, \( \Delta P = 0 \), \( V \) and \( T \) both changing

Changes are determined by gas property, e.g. \( \text{N}_2 \) cools as expands, \( P_1 > P_2 \) and \( T_1 < T_2 \)

\( w_{int} = w_{lt} + w_{rt} = -\int P_1dV - \int P_2dV = P_1V_1 - P_2V_2 \) (recall start \( V_1 \rightarrow 0 \) and other side \( 0 \rightarrow V_2 \))

adiabatic, \( q = 0 \), \( \Delta U = w = U_1 - U_2 = P_1V_1 - P_2V_2 \), rearrange: \( U_1 + P_1V_1 = U_2 + P_2V_2 \)

\( \rightarrow H_1 = H_2 \) isoenthalpic, here \( dP \) and \( dT \) negative, so \( (\partial T/\partial P)_H > 0 \)
Joule Thomson coefficient:

\[
\mu_{J-T} = \lim_{\Delta P \to 0} \left( \frac{\Delta T}{\Delta P} \right)_H = \left( \frac{\partial T}{\partial P} \right)_H
\]

For isenthalpic:

\[
dH = C_P dT + \left( \frac{\partial H}{\partial P} \right)_T dP = 0
\]

divide by dP, rearrange:

\[
C_P \left( \frac{\partial T}{\partial P} \right)_H + \left( \frac{\partial H}{\partial P} \right)_T = 0 \quad \text{giving} \quad \left( \frac{\partial H}{\partial P} \right)_T = -C_P \mu_{J-T}
\]

So \( \frac{\partial H}{\partial P} \)_T can be measured knowing \( C_P \) and \( \mu_{JT} \) both of which depend on material

Define: \( \mu_T = \left( \frac{\partial H}{\partial P} \right)_T - C_P \mu_{JT} \) as isothermal Joule-Thomson coefficient

As before \( \mu_{JT} = 0 \) for ideal gas, but for van der Waals, as \( P \to 0, \mu_{JT} = \frac{2a}{RT} - \frac{b}{C_P} \)

Some example values and temperature variation from Web

\[
\mu_{JT}(\frac{dH}{dP})_T/C_P
\]

Which can be shown to be:

\[
\mu_{JT} = \left( \frac{\partial T}{\partial P} \right)_H = \frac{V}{C_P} \left( \alpha T - 1 \right)
\]

where \( \alpha \) – thermal expansion

[or \( \beta = (\partial V/\partial T)_P/V \)]

Note: \( \mu_{JT} (-) \) cools on expand

Example: solve \( \mu_{JT} \) for van der Waals gas

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

evaluate \( \frac{\partial P}{\partial T} \) and \( \frac{\partial P}{\partial V} \): \( \mu_{JT} = \frac{1}{C_P} \left[ -T \left( \frac{\partial P}{\partial V} \right)_T - \bar{V} \right] \)

\[
\frac{\partial P}{\partial V} = \frac{RT}{(V-b)^2} + 2 \frac{a}{\bar{V}^3}
\]

Take limit of large molecular volume:

\[
\lim_{\bar{V} \to \infty} \mu_{JT} = \frac{1}{C_P} \lim_{\bar{V} \to \infty} \left[ -T \left( \frac{R}{(V-b)} \right)_T \right] = \frac{1}{C_P} \left[ \frac{2a}{RT} \right]
\]

Expansion tricky, find common denom.