THERMODYNAMICS STUDY GUIDE

CHAPTER 1 THE PROPERTIES OF GASES

Perfect Gas

Exercise: At 100°C and 16.0 KPa, the mass density of Phosphorous vapour is 0.6388 Kg m^{-3} .

What is the molecular formula of phosphorous under these conditions?

T=100°C = 373.15K

P=16.0kPa= 16 x 10^3 Pa

D=m/V

$$D=\frac{m}{V}$$

$$PV=nRT$$

$$P(\frac{m}{D})=nRT$$

$$M=\frac{RTD}{P}=\frac{(0.08206)(373.15)(0.6388)}{0.137}$$

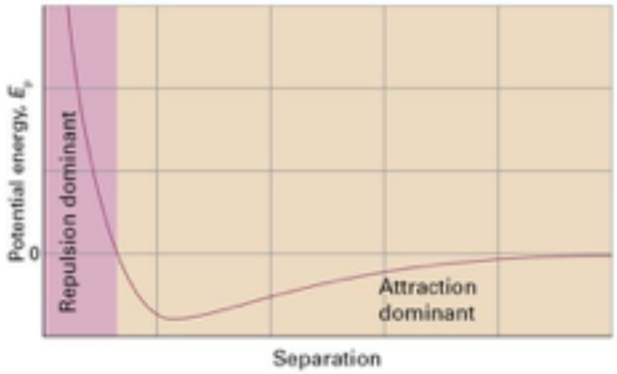
$$m=124.53g/mol$$

$$n=124.53g/30.974g/mol$$

$$=4.02$$

$$\therefore P_4$$

- When we consider molecules to be so far apart the interactions are zero.



Ideal Gas:

Definition: When we consider the interactions between molecules to be the same

Real Gas:

Definition: When these approximations break down.

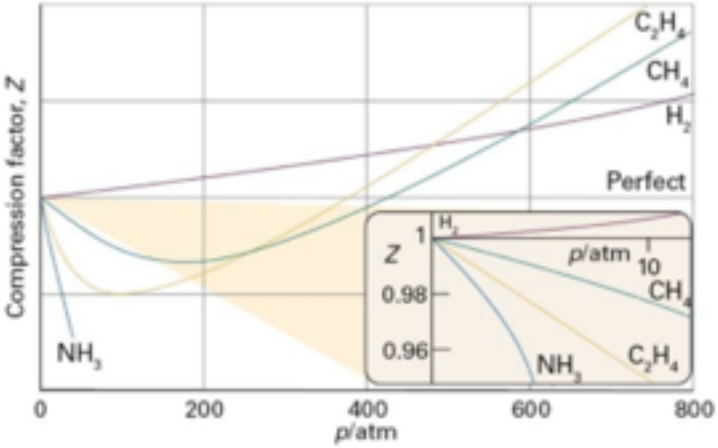
- It is an advantage to compress the real gas because the attraction is smaller.
- Minimum energy for attraction is different depending on dipole interactions.
- It is hard to compress when pressure is high because of repulsive molecular interactions.
  - Therefore it is easier to compress with assistant from attraction molecular interactions.
- Since liquid has much more compressed volume in comparison to gas, the pressure hits equilibrium.

- The perfect gas does now liquidity. The real gas does to avoid additional pressure being exerted.

$$V = \frac{nRT}{P} \qquad V = ZV^{o} \qquad Z = \frac{V_m}{V^{o}_{m}} \qquad PV_m = RTZ$$

Where Vm is the actual molar volume (V/n) at temperature and pressure, and Vm° is the volume of one mole of perfect gas (=RT/p)

- For the perfect gas, Z=1 under all conditions.
  - Thus, deviation of Z from 1 is a measure of departure from perfect behaviour.
- At low pressures Z < 1
- At high pressures, repulsions are greater, Z > 1



Mathematically Z can be replaced with a series (viral equation of state):

$$pV_m = RT(1 + \frac{B}{V_m} + \frac{C}{V_m^{\,2}} + \ldots)$$

Where the viral coefficients, B, C, D etc. depend on the temperature. They are determined from measurements of its compression factor for a gas.

Dew Point:

Definition: where liquid starts to appear.

Bubble Point:

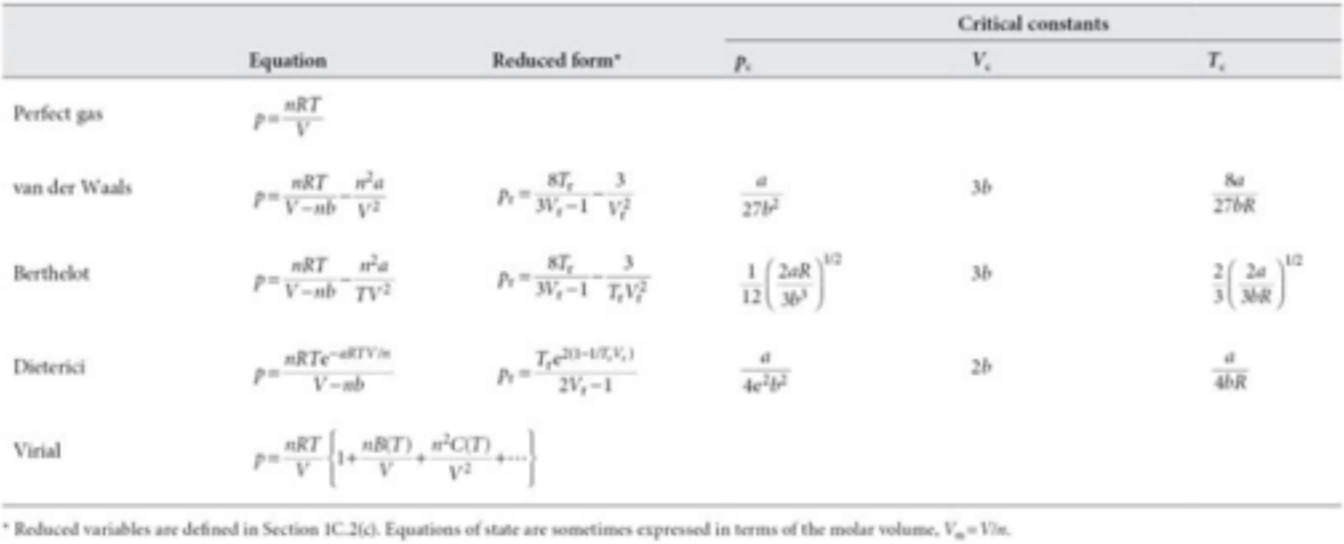
Definition: Where liquid starts to transform into gas.

- We readily see liquidification when starting at a low temperature.

Critical Point:

Definition: inflection point. Here we do not see liquidification. Vc, Pc, Tc are all critical variables.

Table 1C.4 Selected equations of state



	Equation	Reduced form*	Critical constants		
			p_c	V_c	T_c
Perfect gas	$p=\frac{nRT}{V}$				
van der Waals	$p=\frac{nRT}{V-nb}-\frac{n^2a}{V^2}$	$p_r=\frac{8T_r}{3V_r-1}-\frac{3}{V_r^2}$	$\frac{a}{27b^2}$	$3b$	$\frac{8a}{27bR}$
Berthelot	$p=\frac{nRT}{V-nb}-\frac{n^2a}{TV^2}$	$p_r=\frac{8T_r}{3V_r-1}-\frac{3}{T_rV_r^2}$	$\frac{1}{12}\left(\frac{2aR}{3b^3}\right)^{1/2}$	$3b$	$\frac{2}{3}\left(\frac{2a}{3bR}\right)^{1/2}$
Dieterici	$p=\frac{nRTe^{-an/RTV}}{V-nb}$	$p_r=\frac{T_re^{2(1-1/T_rV_r)}}{2V_r-1}$	$\frac{a}{4e^2b^2}$	$2b$	$\frac{a}{4bR}$
Virial	$p=\frac{nRT}{V}\left\{1+\frac{nB(T)}{V}+\frac{n^2C(T)}{V^2}+\cdots\right\}$				

* Reduced variables are defined in Section 1C.2(c). Equations of state are sometimes expressed in terms of the molar volume, $V_m=V/n$.

CHAPTER 2 THE FIRST LAW

Internal Energy

- The internal energy of an isolated system is constant
  - Adiabatic container provides an isolated system.
  - No exchange of energy or matter.
- Closed systems use diathermic containers which allows energy exchanges only.
- The first law states any change in external energy is the result of work done and or heat transferred to the system.

$$\Delta U = q + w$$

Heat vs. Work

- Both are a manifestation of energy transferred
  - Heat (q): system stimulates "random" thermal, motion in surroundings. q represents the energy transferred as heat to a system
  - Work (w): system stimulates "organized" motion in the surroundings

- There is no negative or positive affiliation with either of these words.
- In an adiabatic container q=0.

Isolated system:

- Internal energy has increased
- Temperature then must've increased due to adiabatic container

$$
\begin{aligned}
&W = force \times dis\tan ce \\
&= F \times \Delta Z \\
&\mathrm{P} = \frac{F(force)}{A(area)} \\
&\therefore F = P \times A \\
&W = P \times A \times \Delta Z \\
&Note: A\Delta Z = \Delta volume \\
&W = P\Delta V
\end{aligned}
$$

Expansion Work against Constant External Pressure:

For an infinitesimal change of volume:

$$\Delta w = -p_{ex}\Delta V$$

Note: the negative sign makes the work positive when the system is being compressed. Gives direction of work.

For a finite interval:

$$\Delta w = -\int_{Vi}^{Vf} p_{ex}\, dV$$

Pressure is a constant in the integral, and work is negative in terms of direction.

Reversible Expansion Work:

- The system is calibrated over time, slowly. The system therefore has time to equilibrate and keep its pressure equal to the external pressure.

$$
\begin{aligned}
&\Delta w = -P_{ex}\Delta V \\
&= -p\Delta V
\end{aligned}
\qquad
w = -\int_{Vi}^{Vf} P\, dV
$$

The pressure depends on V, and is not a constant as were expanding. It therefore CANNOT be taken out of the integral.

Isothermal Reversible Expansion Work (Diathermic container):

- Since its a perfect gas, we know how the pressure varies with volume.

$$\begin{aligned} w &= -\int_{Vi}^{Vf} P\,dV \\ &= -\int_{Vi}^{Vf} \frac{nRT}{V} dV = -nRT\ln\left(\frac{V_f}{V_i}\right) \end{aligned}$$

Note: Reversible work= maximum work.

Internal Energy (U) and Heating at Constant Volume:

Heat transfer at a constant volume:

$$\Delta U = q_v$$

Note we do not write the integral over dq as delta q because q, unlike U is not a state function.

- If we measure the temperature change, we can calculate the heat capacity at constant volume:

$$C_v = \left(\frac{dU}{dT}\right)_v$$

Derivative along an isochore, constant volume and constant moles. This also infers that the slope is constant

- Cv: is the heat capacity

Enthalpy (H) and Heating at Constant Pressure:

$$H = U + PV$$

- Heat transfer at constant pressure
- At constant pressure

$$\begin{aligned} &H = U + PV \\ &\Delta H = \Delta U + pdV = \Delta q \\ &\Delta H = q_p \end{aligned}$$

- At constant pressure, heat transfer directly translates into a change in enthalpy.

Constant Volume	**Constant Pressure**
C_v=(dU/dT)	C_P=(dH/dT)
We use Cv to calculate the change in internal energy from a change in temperature	We use Cp to calculate the change in enthalpy from a change in temperature
dU=C_v	dH=C_p
If Cv is independent of T, ΔU=C	If Cp is independent of T, ΔH=C

Heat Capacity of a Perfect Gas:

Enthalpy:

$$H = U + nRT$$

Heat Capacity: Cp:

$$C_p = (\frac{dU}{dT})_p + nR$$

$$\therefore C_{p,m} = C_{v,m} + R$$

Internal energy depends on temperature only for a perfect gas, thus,

$$(\frac{dU}{dT})_v + nR$$

- Any change in molar enthalpy, Cp,m is dependent
- If you need a change in molar enthalpy between T1 and T2, integrate:

$$\int_{T_1}^{T_2} (a + bT + \frac{c}{T^2}) dT$$

Reversible Adiabatic Changes:

- Heat transfer at a constant volume:
  - $q_v > 0$, U increasing
- Heat = 0, as we compress internal energy of the system increases
  - q=0, w > 0, U increasing

Representing in an equation(s):

$$\int_{T_i}^{T_f} C_v \frac{dT}{T} = \int_{V_i}^{V_f} nR\frac{dV}{V}$$

$$c = \frac{C_v}{nR}$$

$$-pdV = \frac{nRT}{V}dV$$

$$T_f = T_i(\frac{V_i}{V_f})^{1/c}$$

- On an adiabat, for a perfect gas:
  - VT^c= Constant
  - PV^r= Constant

Exercise: One mole of gas at 100K is compressed isothermally from an initial volume of 20dm^3 to a final volume of 5 dm^3. Calculate work done using real equation of state.

$$w = -\int p\,dV_m$$

$$pV_m = RT$$

$$-RT\ln\frac{V_f}{V_i} = RT\ln\frac{V_i}{V_f} = 8.3145(100)\ln\frac{20}{5} = 1153Jmol^{-1}$$

$$(p + \frac{a}{V_m^2})V_m = RT$$

$$w = -(RT\int_{V_i}^{V_f}\frac{dV_m}{V_m} - a\int_{V_i}^{V_f}\frac{dV_m}{V^2m})$$

$$= -[RT\ln\frac{V_f}{V_i} + a(-\frac{1}{V_f} + \frac{1}{V_i})]$$

$$= RT\ln\frac{V_i}{V_f} + a(-\frac{1}{V_f} + \frac{1}{V_i})$$

$$w = 1153Jmol^{-1} - 0.384(\frac{1}{0.02} - \frac{1}{0.005}) = 1.21kJ \times mol^{-1}$$

Standard Enthalpy Changes:

$$\Delta H^{\theta}$$

- For precesses in which the initial and final substances are in their standard states
  - That means in pure form and at pressure = 1 bar

Note: 1 bar =100kPa, 1 atm = 101.325 kPa

- Enthalpy is a state function, this means it only depends on the current state and not the path it took to get there, the enthalpy will always be the same.
- In general,

$$\Delta_r H^\theta = \sum_{products} \nu H_m{}^\theta - \sum_{react(s)} \nu H_m^\theta$$

Where ν is the stoichiometric coefficient.

- Formation of a compound from its elements in its reference state— most stable form
- We can build any reaction by destroying reactants into their elements and building up/forming any chemical reactant from it.

Hess's Law

- The standard enthalpy of a overall reaction is the sum of the standard enthalpies of the individual reactions into which a reaction may be divided.

CHAPTER 3 THE SECOND AND THIRD LAWS

Kelvin:

Definition: There is no process, where heat energy can be completely changed to work.

Clausius:

Definition: There is no process where energy (as heat) from a cold source is transferred to a hot sink.

Second Law:

The entropy (disorder) of an isolated system increases in the course of a spontaneous change.

$$\Delta S_{total} > 0$$

$$dS = \frac{dq_{rev}}{T} = \frac{\Delta heat}{temperature}$$

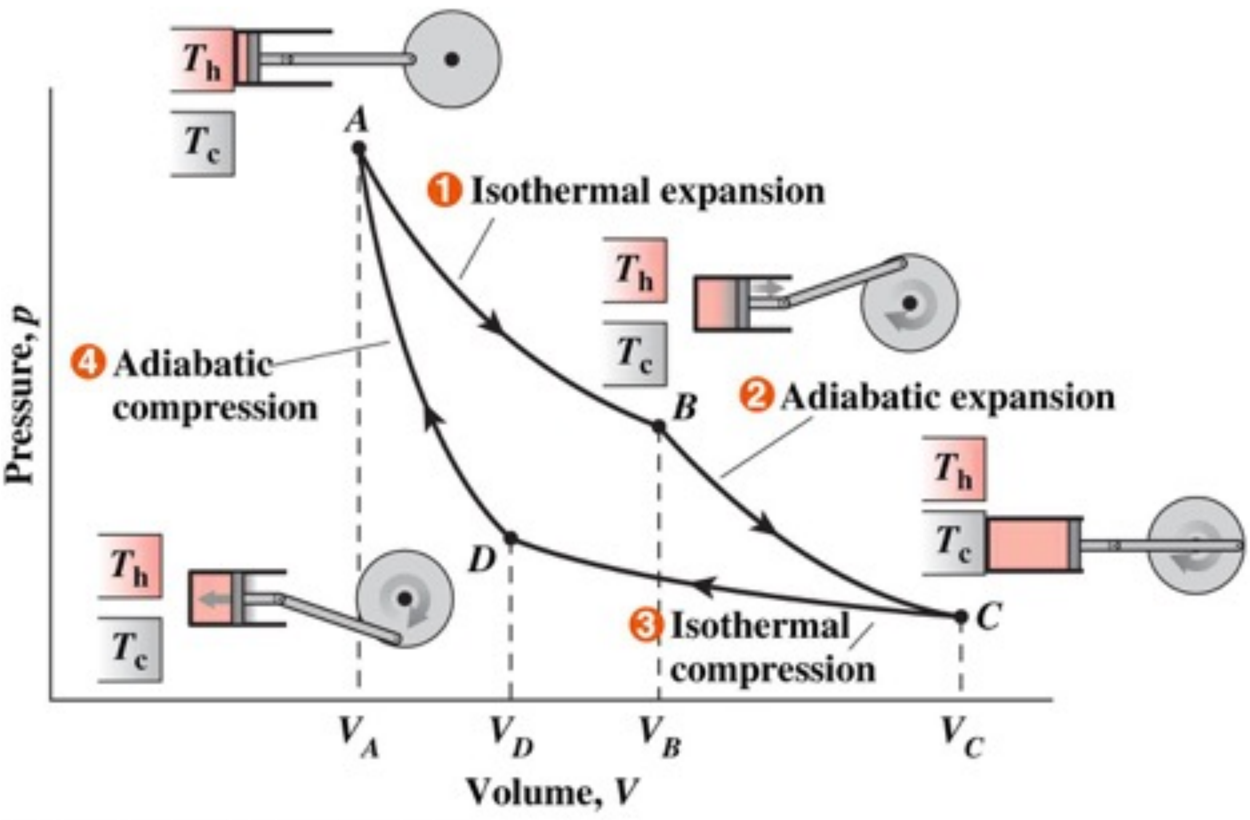
$$\Delta S = \int_i^f \frac{dq_{rev}}{T}$$

- Total entropy increases greater than zero
- Entropy is a measure of dispersal of energy not entropy. The system can occupy more states as entropy increases. STATE FUNCTION.

- We must prove that a closed path can be integrated to zero:

$$\Delta S = \oint \frac{dq_{rev}}{T_{surr}} = 0$$

The Carnot Cycle:



Copyright © 2007 Pearson Education, Inc., publishing as Pearson Addison-Wesley

- The Carnot cycle is a special closed path, along a hot isotherm, an adiabat, a cold isotherm and another adiabat.

$$\Delta S_1 = \frac{q_h}{T_h} \qquad \Delta S_2 = 0 \qquad \Delta S_3 = \frac{q_c}{T_c} \qquad \Delta S_4 = 0$$

1. Reversible isothermal expansion
   - As we expand the pressure will drop
   - q_h is the energy supplied to the system
2. Reversible adiabatic expansion

  - No energy leaving the system as heat

3. Reversible isothermal compression
   - At Tc energy is released to the cold sink as heat
4. Reversible adiabatic compression
   - No energy entering the system

- Steps 1 and 3 are the only two steps with an entropy change, therefore to have the system have a net entropy of zero they much cancel themselves.
  - 1=(-3)
- For a perfect gas we also want q_c+q_h=0

$$q_c = nRT_c \ln \frac{V_a}{V_b} \qquad \frac{q_h}{q_c} = \frac{nRT_h \ln {}^{V_b}\!/_{V_a}}{-nRT_c \ln {}^{V_b}\!/_{V_a}}$$

this leaves us with,

$$\frac{q_h}{q_c} = \frac{T_h}{-T_c}$$

$$\oint ds = \frac{q_c}{T_c} + \frac{q_h}{T_h} = 0$$

- The Carnot cycle proves entropy to be a state function.

Statistical Definition of Entropy:

$$S = K \ln W$$

$$K = 1.38065 \times 10^{-23} J/K$$

Where K is the Boltzmann constant and W is the number of micro states of energy.

- To calculate W(U) we nee dot use the statistical definition of entropy.

Clausius Inequality:

- For a reversible change:

$$dS = \frac{dq_{rev}}{T}$$

- In general a classic inequality proves,

$$dS \geq \frac{dq}{T}$$

- For a Clausius inequality,

$$\frac{dq_{rev}}{T} \geq \frac{dq}{T}$$

- This simply means, there is more work done for an reversible change, than irreversible.
- For a volume expansion:

$$-dw_{rev} \geq -dw$$

- For an isolated system:

$$dS \geq 0$$

This is because dq=0 for an isolated system.

Isothermal Expansion of a Perfect Gas:

- The system, whether reversible or not will be defined:

$$\Delta S = nR\ln\frac{V_f}{V_i}$$

- The surroundings is it is reversible will be defined:

$$\Delta S_{surr} = -nR\ln\frac{V_f}{V_i}$$

$$\Delta S_{total,reversible} = \Delta S + \Delta S_{surr} = 0$$
$$\Delta S_{total,irreversible} = \Delta S + \Delta S_{surr} > 0$$

Entropy Change Accompanying a Phase Transition:

- The total amount of heat (per mole) to completely evaporate from the system is defined at constant pressure as:

$$q = \Delta_{trs}H$$

- The entropy of a phase transition is defined as:

$$\Delta_{trs,endothermic} S = \frac{q}{T_{trs}} > 0$$

$$\Delta_{trs,exothermic} S = \frac{q}{T_{trs}} < 0$$

Entropy Change Accompanying Heating:

- If Cp is approximately constant, or constant, over a temperature range than,

$$\Delta S = \int_i^f \frac{dq_{rev}}{T} \qquad S(T_f) = S(T_i) + C_p \ln \frac{T_f}{T_i}$$

Third Law:

Definition: The entropy of all perfect crystalline substances is zero at T=0.

- Why?
  - Because the system only has one microstate— W=1

$$S^{\theta}(T) = 0$$

This is true for the substance in its standard state at temperature T.

Standard Reaction Entropy:

$$\Delta_r S^{\theta} = \sum_{products} \nu S_m{}^{\theta} - \sum_{react(s)} \nu S_m^{\theta}$$

- For ions we assume in aqueous conditions to have an entropy of zero at any temperature.

Heating at Constant Volume:

$$dq_v = dU$$

- Heating increases internal energy, U.
- Clausius inequality—> Condition

$$dS - \frac{dU}{T} \geq 0$$

Heating at Constant pressure:

- Heating increases enthalpy, H=U+PV
- Clausius inequality—> Condition:

$$dS - \frac{dH}{T} \geq 0$$

Constant Volume Heating—> Helmholtz Energy

- Condition for spontaneity at constant temp and volume:

$$dA_{T,V} \leq 0$$

- There is only a change in spontaneity if the Helmholtz energy decreases.

Helmholtz work:

$$dw \leq dA_{T,V} = dU - Tds$$

Where ds is the heat transfer.

Constant Pressure Heating —> Gibbs Energy

- At constant pressure and temperature a change is spontaneous only if the Gibbs energy decreases:

$$dG_{T,P} \leq 0$$

- This is called an exergonic reaction, if delta G is greater than zero it is the reverse of spontaneous and called endergonic.
- If ΔG=0 then the reaction is at equilibrium.

Non-expansion work (change in Gibbs energy):

$$dw \leq dG_{T,P} = dH - Tds$$
$$= dU + PdV - Tds$$

- Use the above equation when we transfer heat/change volume reversible
- when we transfer heat and change volume irreversibly.

Standard Gibbs Energy of Reaction:

$$\Delta_r G^\theta = \Delta_r H^\theta - T\Delta_r S^\theta$$

Maxwell Relations:

- Maxwell relations use total differentials (differentiating x while keeping y constant and then vice versa)
- Also exact differentials to test them.
- Only functions which have exact differentials are state functions
  - Thus see table 3.5, and notice state functions, Internal energy, enthalpy, Helmholtz, and Gibbs are using exact differentials also known as maxwell relations to describe their relationships.
- We can also use the definition of G to relate the maxwell relation to enthalpy.

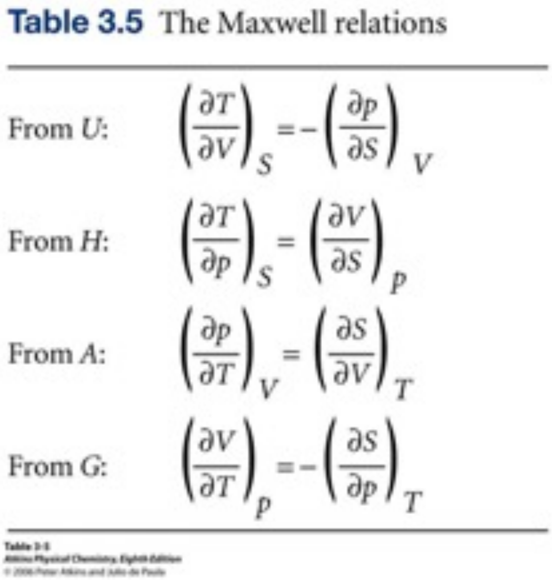


Table 3.5 The Maxwell relations

From *U*:	$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$
From *H*:	$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$
From *A*:	$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$
From *G*:	$\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T$

$$\left(\frac{dG}{dT}\right)_p = -S,$$
$$G = H - TS$$

Gibbs-Helmholtz Equation:

$$\left(\frac{d\,{}^{G}\!/_{T}}{dT}\right)_p = -\frac{H}{T^2}$$

Variation of ΔG with Temperature:

$$\left(\frac{d\,{}^{\Delta G}\!/_{T}}{dT}\right)_p = -\frac{\Delta H}{T^2}$$

Molar Gibbs Energy and Molar Volume:

$$G_m(P_f) = G_m(P_i) + \int_{Pi}^{P_f} V_m\,dP$$

PRACTICE PROBLEMS:

CHAPTER 1: THE PROPERTIES OF GASES

Exercises

1A.1 to 1A.4 (a and b) and 1A.8 to 1A.13 (a and b) 1B.1 to 1B.7 (a and b) 1C.1 to 1C.9 (a and b)

Numerical problems

1A.2, 1A.3, 1A.4, 1A.6, 1C.3, 1C.6

CHAPTER 2:THE FIRST LAW

Exercises

2A.1 to 2A.6 (a and/or b) 2B.1 to 2B.3 (a and/or b) 2C.1 to 2C.10 (a and/or b)

Numerical problems

2A.1, 2A.2, 2A.3, 2B.2, 2B.3, 2C.1, 2C.4, 2C.6, 2C.7

CHAPTER 3:THE SECOND AND THIRD LAWS

Exercises

3A.1 to 3A.12 (a and/or b), except 3A.2
3B.1 and 3B.2 (a and/or b)
3C.1 to 3C.5 (a and/or b)

Numerical problems

3A.6, 3A.7, 3A.9, 3A.11
3B.1, 3B.3, 3B.4, 3B.6