

From what we know now (i.e, ΔH and ΔS)...

How do we determine whether a reaction is spontaneous?

But ΔH and ΔS are not enough... There is competition between lowering energy and raising entropy!

The overall criterion for a spontaneous reaction is:

So what are ΔG and ΔA and how do we determine them?



Spontaneous Rxn at constant V and T

A&G-2

From 2nd Law:

$$dS \geq$$

At constant V:

$$\delta w =$$

From 1st Law:

$$dU =$$

So ...

At constant V

Or...

Define a new state function,
the Helmholtz energy, A:

$$A = U - TS$$

For a reaction to be spontaneous:



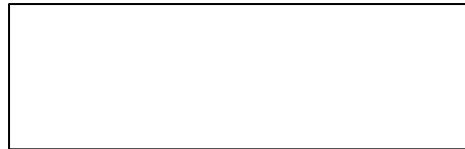
(What about equilibrium?)



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

A is a state function so we can choose a path to use to evaluate.
If a reversible path is chosen, we know: $\Delta S = q_{rev} / T$

$$\Delta A = \Delta U - q_{rev}$$



**Isothermal,
reversible**

If $\Delta A < 0$, w_{rev} is the max work that can be obtained.

If $\Delta A > 0$, w_{rev} is the min work that must be provided to drive rxn.



Spontaneous Rxn at constant P and T

From 2nd Law:

$$dS \geq$$

If only PV work...

$$\delta w =$$

From 1st Law:

$$dU =$$

So ...

At constant P

Or...

Define a new state function,
the Gibbs energy, G:

$$G = U - TS + PV$$

$$G = H - TS$$

For a reaction to be spontaneous:



(What about equilibrium?)



$$G = U - TS + PV$$

Differentiate:

Sub: $dU = TdS + \delta w_{rev} \longrightarrow dG = \delta w_{rev} - SdT + PdV + VdP$

Sub: $\delta w_{rev} = \delta w_{PV} + \delta w_{nonPV} = -PdV + \delta w_{nonPV}$

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

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



Reversible, constant T and P

If $\Delta G < 0$, max non-PV work that can be obtained.

If $\Delta G > 0$, min non-PV work that must be provided to drive rxn.



Ways to Define Helmholtz Energy

$$A = U - TS$$

$$dA = dU - TdS \swarrow$$

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

Ways to Define Gibbs Energy

$$G = H - TS$$

$$\nearrow dG = dH - TdS$$

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

The Gibbs and Helmholtz energy are related by PV:

$$G = A + PV$$



Hermann von Helmholtz



Josiah Willard Gibbs



These relations relate thermodynamic properties that can't be measured (i.e., S, H, U, etc) to thermodynamic properties that can be measured (i.e., P, T, V, etc).

$$dA = dU - TdS - SdT \quad \text{(general)}$$

For reversible process: $dU = TdS - PdV$

$$dA = -PdV - SdT$$

Compare to
formal total
derivative of
 $A(V,T)$



Recall: For state functions (i.e., exact differentials), cross derivatives are equal (Math Ch H).

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

What are the cross derivatives?

So...

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

**One of many
Maxwell relations**



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

Can we measure all of the thermodynamic properties in this equation?

We can use this Maxwell relation to determine how S changes with V .

Integrate at constant T ...

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

If you know the EOS, you can determine ΔS . Take the ideal gas EOS:

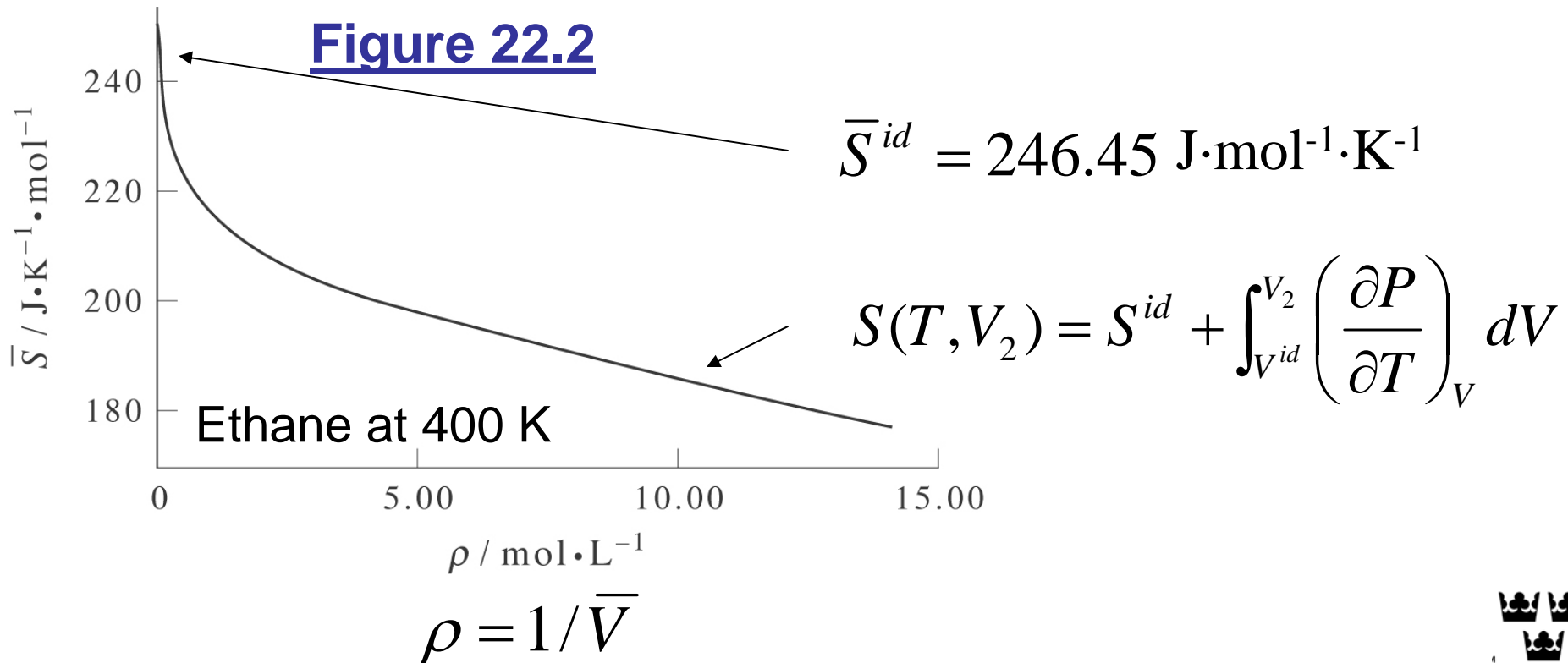
$$P = nRT / V$$

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



If you let V_1 become very large, the gas behaves ideally...

$$\Delta S = S(T, V_2) - S^{id} = \int_{V^{id}}^{V_2} \left(\frac{\partial P}{\partial T} \right)_V dV \quad (\text{constant } T)$$



$$dU = TdS - PdV$$

If we consider S and V as independent variables of U , the coefficients of ΔS and ΔV are **simple** thermodynamic functions.

$$dU = \left(\frac{\partial U}{\partial S} \right)_V dS + \left(\frac{\partial U}{\partial V} \right)_S dV \quad \left(\frac{\partial U}{\partial S} \right)_V = T \quad \left(\frac{\partial U}{\partial V} \right)_S = -P$$

Compare with V and T as independent variables:

$$dU = \left[T \left(\frac{\partial P}{\partial T} \right)_V - P \right] dV + C_V dT$$

The differential form suggests that S and V are the natural independent variables of U .



You'll need to know the 1st and 2nd laws of thermodynamics:

$$dU = TdS - PdV$$

Also, you should know the definitions of the other state functions:

$$dH = d(U + PV) \quad dA = d(U - TS) \quad dG = d(U + PV - TS)$$

From these you can derive:

1. Add $d(PV)$ to both sides:

$$d(U + PV) = TdS - PdV + VdP + PdV$$

2. Subtract $d(TS)$ to both sides:

$$d(U - TS) = TdS - PdV - TdS - SdT$$

3. Add $d(PV)$ and subtract $d(TS)$

to both sides:

$$d(U + PV - TS) = TdS - PdV + VdP + PdV - TdS - SdT$$

What are natural independent variables?



<u>Function</u>	<u>Differential Equation</u>	<u>Independent Variables</u>
U	$dU = TdS - PdV$	S and V
S	$dS = \frac{1}{T}dU + \frac{P}{T}dV$	U and V
H	$dH = TdS + VdP$	S and P
A	$dA = -SdT - PdV$	T and V
G	$dG = -SdT + VdP$	T and P



<u>Function</u>	<u>Differential Equation</u>	<u>Maxwell Relations</u>
U	$dU = TdS - PdV$	$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$
H	$dH = TdS + VdP$	$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$
A	$dA = -SdT - PdV$	$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$
G	$dG = -SdT + VdP$	$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$

Can you derive these Maxwell relations?



Starting from the differential equation for the Gibbs energy, find an expression for the P dependence of S (See A&G-9 and 10)...

1. Compare $dG = -SdT + VdP$ to total formal derivative.
2. Find the cross derivatives and set equal to each other.

This gives the Maxwell relation:

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

3. Integrate at constant T to find: $\Delta S = \int_{P_1}^{P_2} \left(\frac{\partial V}{\partial T}\right)_P dP$

4. Use S^{id} as reference.

5. Label graph as in A&G-10.

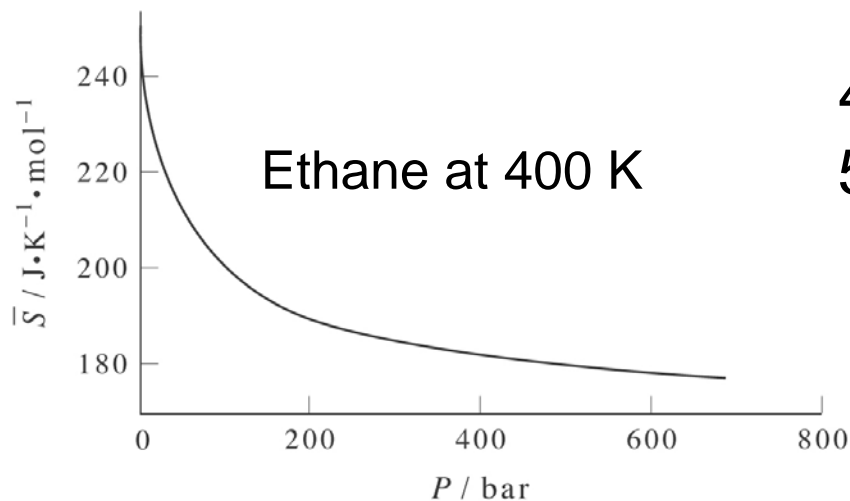


Figure 22-4

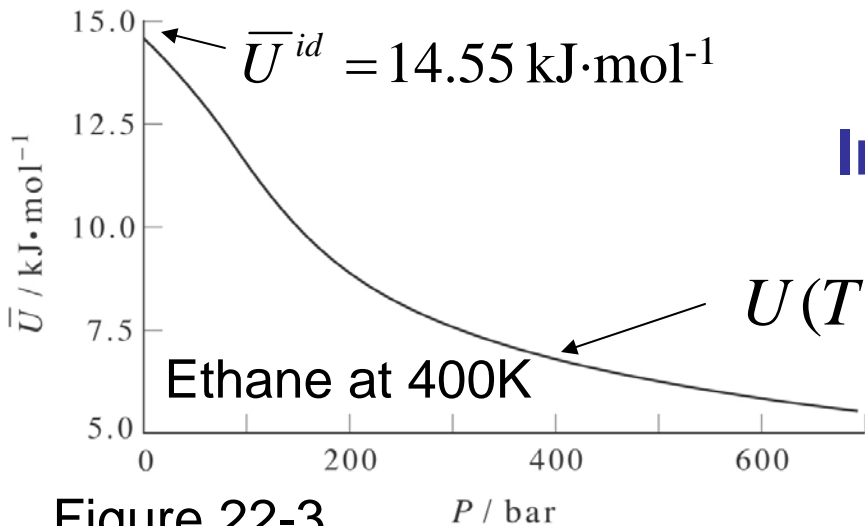


From Maxwell relations on A&G-14, we can relate S to PVT data. What if we want to know how other thermodynamic properties vary as a function of P, V, or T?

Differentiate $A = U - TS$ wrt V: $\left(\frac{\partial A}{\partial V}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T - T\left(\frac{\partial S}{\partial V}\right)_T$ isothermal

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

What do you expect for ideal gas?



Integrate from V^{id} to V:

$$U(T, V) = U^{id} + \int_{V^{id}}^V \left[T\left(\frac{\partial P}{\partial T}\right)_V - P \right] dV$$

U from PVT!



Figure 22-3

P / bar

Show:

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

Differentiate $G = H - TS$ wrt P and constant T ;

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

Integrate from P^{id} to P :

$$H(T, P) = H^{id} + \int_{P^{id}}^P \left[-T \left(\frac{\partial V}{\partial T} \right)_P + V \right] dP$$

H from PVT!

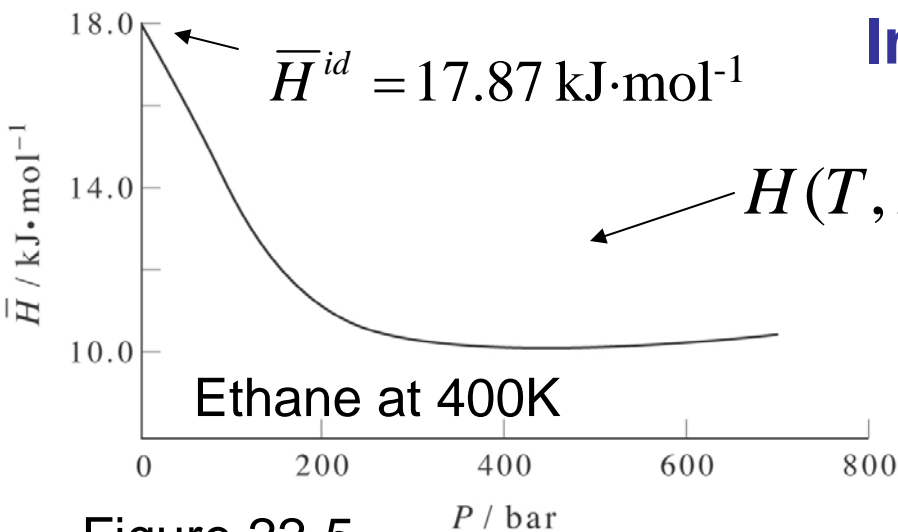


Figure 22-5



Expressions derived on pages 902-903

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

Gibbs-Helmholtz Equation

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

Will be important for equilibrium constants

Integrate both sides and assume ΔH is temp independent...

$$\frac{\Delta G_2}{T_2} - \frac{\Delta G_1}{T_1} = \Delta H \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$



We already know how to find $H(T)$ and $S(T)$ individually
 can could find $G(T)$ from:

$$G(T) = H(T) - TS(T)$$

Using $H(0)$ as the reference for energy,

$$G(T) - H(0) = \underbrace{H(T) - H(0)}_{\nearrow} - T \underbrace{S(T)}_{\nwarrow}$$

$$\begin{aligned} H(T) - H(0) &= \int_0^{T_{fus}} C_P^s(T) dT + \Delta_{fus} H \\ &+ \int_{T_{fus}}^{T_{vap}} C_P^l(T) dT + \Delta_{vap} H \\ &+ \int_{T_{vap}}^T C_P^g(T) dT \end{aligned}$$

From FL-30

$$\begin{aligned} S(T) &= \int_0^{T_{fus}} \frac{C_P^s(T)}{T} dT + \frac{\Delta_{fus} H}{T} \\ &+ \int_{T_{fus}}^{T_{vap}} \frac{C_P^l(T)}{T} dT + \frac{\Delta_{vap} H}{T} \\ &+ \int_{T_{vap}}^T \frac{C_P^g(T)}{T} dT \end{aligned}$$

From TL-5



G decreases with increasing T

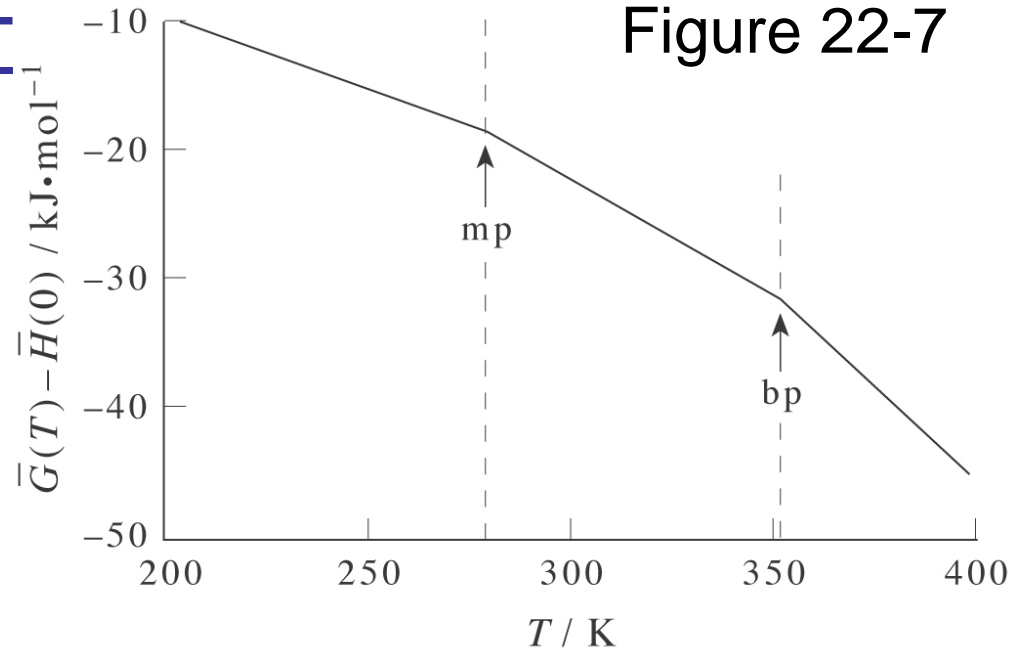
$$\left(\frac{\partial G}{\partial T}\right)_P = -S \quad (\text{S is positive so slope is negative})$$

Phase transitions

Continuous function... phases are in equilibrium and have same G

$$\Delta_{trs} G = 0$$

Discontinuous slope... $S(\text{gas}) > S(\text{liquid}) > S(\text{solid})$




We have: $\left(\frac{\partial G}{\partial P}\right)_T = V$ (~A&G-15)

Integrating at constant T: $\Delta G = \int_{P_1}^{P_2} V dP$

Per mole of ideal gas: $\Delta \bar{G} = RT \int_{P_1}^{P_2} \frac{1}{P} dP = RT \ln \frac{P_2}{P_1}$

Let $P_1 = 1$ bar: $\bar{G}(T, P) = G^\circ(T) + RT \ln \frac{P_2}{1\text{bar}}$



The standard molar Gibbs energy. Only depends on T.
(Standard conditions: one mole of ideal gas at 1 bar.)

G increases with the ln of P. Is this due to H or S?



- There is a balance between lowering the energy and increasing the entropy for a spontaneous process at constant T .
- The Helmholtz and Gibbs energies provide us with thermodynamic state functions representing this balance.
- Helmholtz and Gibbs energies predict the direction of spontaneity and indicate the condition of equilibrium.
- Maxwell relations allow us to determine thermodynamic state functions (S or G) from PVT data or equations of state.
- We can translate tabulated values of G at a given (standard) P and T to *any* P and T .

