Spontaneous Rxns

How do we determine whether a reaction is spontaneous?

$\Delta H < 0$ if entropy doesn't exist
$\Delta S > 0$ for isolated systems (no energy transfer)

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

The overall criterion for a spontaneous reaction is:

$\Delta A < 0$ for constant volume conditions
$\Delta G < 0$ for constant pressure conditions

Helmholtz energy

Gibbs energy

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

Spontaneous Rxn at constant V and T

From 2nd Law:

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

At constant V:

$$\delta w = -PdV = 0$$

From 1st Law:

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

So …

$$dU \overset{\text{irreversible}}{\underset{\text{reversible}}{\leq}} TdS$$

At constant V

Or…

$$d(U - TS) \leq 0$$

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

$$A = U - TS$$

For a reaction to be spontaneous:

$$dA < 0$$

(What about equilibrium?)

Helmholtz Energy and Work

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

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

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

$$\boxed{\Delta A = w_{rev}}$$

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

A&G-4

From 2nd Law:

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

From 1st Law:

$$\delta w = -PdV \qquad dU = \delta q + \delta w$$

So …

$$dU \overset{\text{irreversible}}{\underset{\text{reversible}}{\leq}} TdS - PdV$$

At constant P

Or…

$$d(U - TS + PV) \leq 0$$

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

$$G = U - TS + PV$$

$$G = H - TS$$

For a reaction to be spontaneous:

$$dG < 0$$

(What about equilibrium?)

Gibbs Energy and Work

$$G = U - TS + PV$$

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

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

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

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

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

$$\boxed{dG = \delta w_{nonPV}}$$ **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.

Summary of Helmholtz and Gibbs Energy

Ways to Define Helmholtz Energy

$$A = U - TS$$

$$dA = dU - TdS$$

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

Ways to Define Gibbs Energy

$$G = H - TS$$

$$dG = dH - TdS$$

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

Isothermal

The Gibbs and Helmholtz energy are related by PV:

$$G = A + PV$$

Maxwell Relations

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).

$$dA = dU - TdS - SdT$$ **(general)**

For reversible process: $dU = TdS - PdV$

$$dA = -PdV - SdT$$

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

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

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

The Cross Derivative

Recall: For state functions (i.e., exact differentials), cross derivative 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?

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

So…

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

One of <u>many</u> Maxwell relations

The use of a Maxwell relation

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

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:

$$P = nRT/V$$

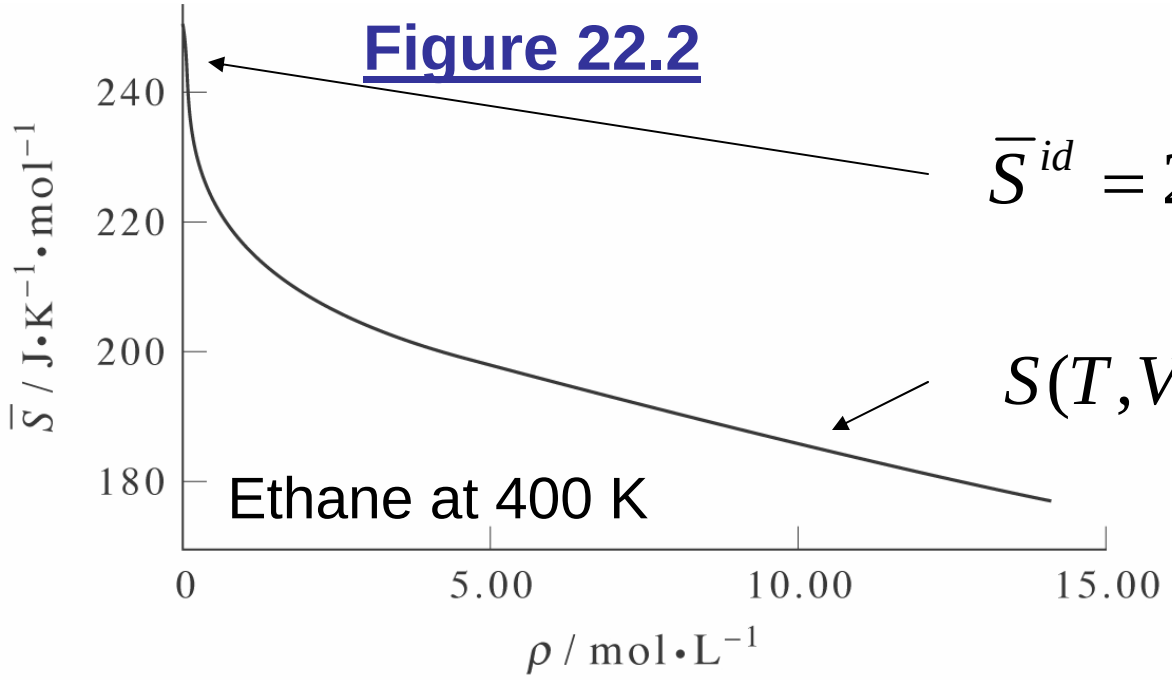
$$\Delta S = \int_{V_1}^{V_2} \frac{nR}{V} dV = nR \ln \frac{V_2}{V_1}$$

Use S ideal as a reference point

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

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

Figure 22.2



$$\bar{S}^{id} = 246.45 \text{ J·mol}^{-1}\text{·K}^{-1}$$

$$S(T,V_2) = S^{id} + \int_{V^{id}}^{V_2} \left(\frac{\partial P}{\partial T}\right)_V dV$$

$$\rho = 1/\bar{V}$$

Natural independent variables for U

$$dU = TdS - PdV$$

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

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

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.

Differential Summary… what to remember

A&G-12

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

$$dU = TdS - PdV$$

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

Natural independent variables

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

Maxwell Relations (Summary)

Function	Differential Equation	Maxwell Relations
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?

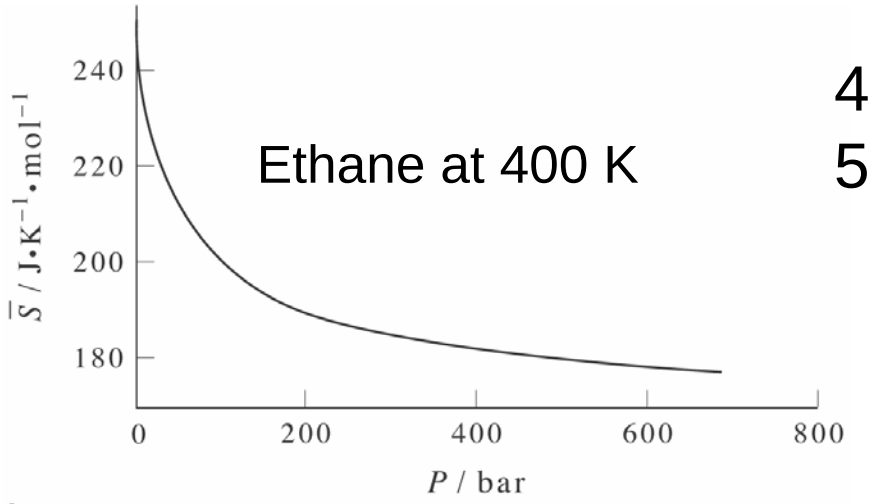
Another use of a Maxwell Relation

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: $\Delta S = \int_{P_1}^{P_2} \left(\frac{\partial V}{\partial T}\right)_P dP$



Ethane at 400 K

Figure 22-4

4. Use S^{id} as reference.
5. Label graph as in A&G-10.

V dependence of U

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:

$$\left(\frac{\partial A}{\partial V}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T - T\left(\frac{\partial S}{\partial V}\right)_T \quad \text{isothermal}$$

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

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

What do you expect for ideal gas?

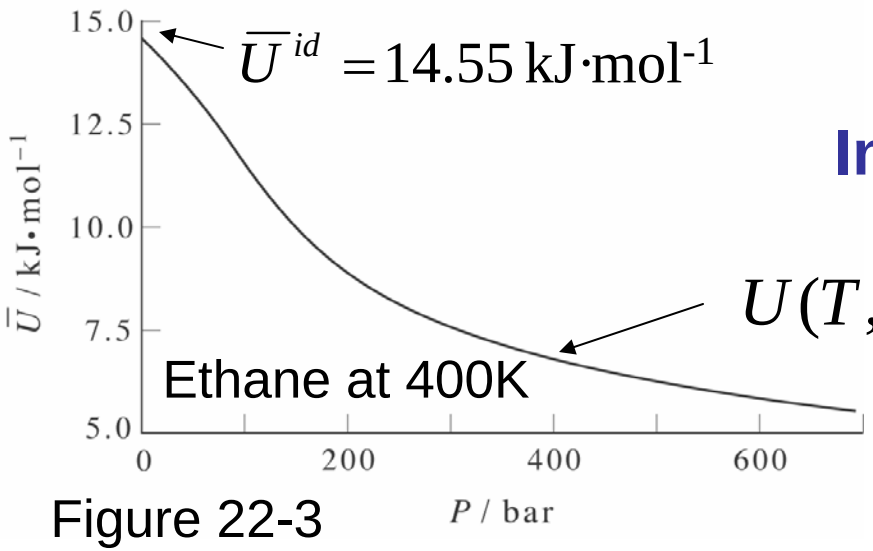


Figure 22-3

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!

P dependence of H

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

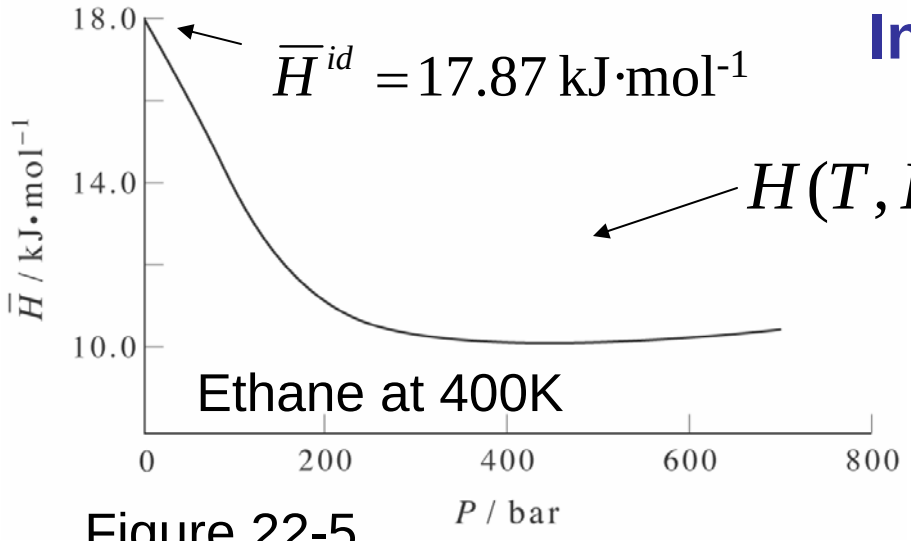


Figure 22-5

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!

T dependence of G: Method 1

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…

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

T dependence of G: Method 2

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,

$$G(T) - H(0) = \underline{H(T) - H(0)} - TS(T)$$

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

From FL-30

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

From TL-5

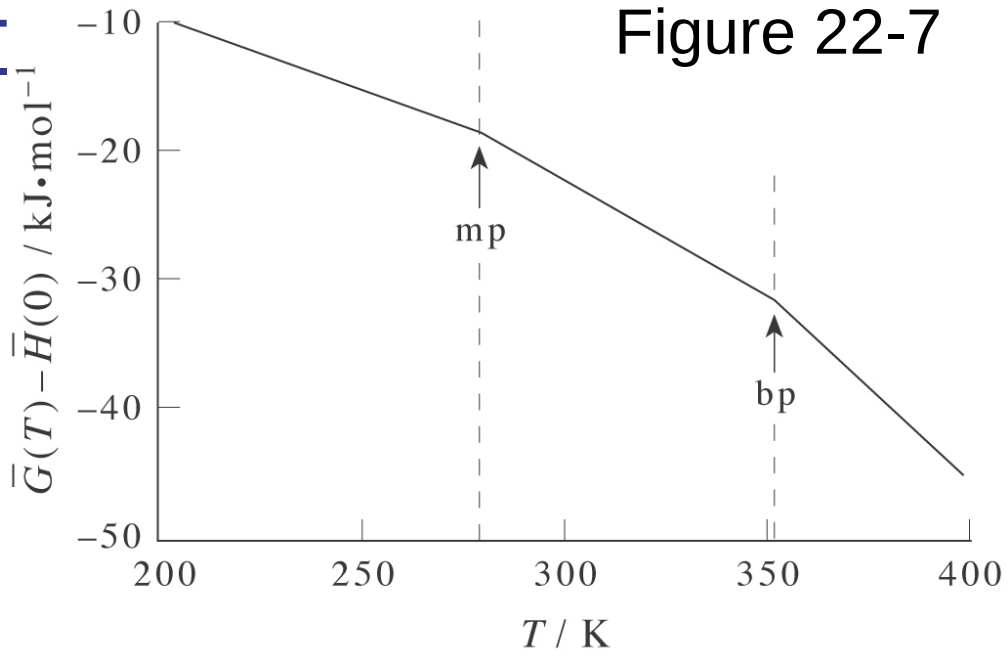
T dependence of G: Graphically

G decreases with increasing T

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

(S is positive so slope is negative)

Figure 22-7



Phase transitions

Continuous function…

Discontinuous slope…

P dependence of G

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: $\Delta \overline{G} = RT \int_{P_1}^{P_2} \frac{1}{P} dP = RT \ln \frac{P_2}{P_1}$

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

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?

What did we learn?

- 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.