H Diffusion through Pd and Pd-Alloy Membranes: Role of Non-ideality due to the Thermodynamic Factor

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- H_2 and its isotopes are the only gases which dissolve to any extent in Pd and its alloys. The H_2 molecules must first undergo dissociative chemisorption which requires clean surfaces, free from poisons such as S, CO. This can be a problem when purifying H_2 from industrial gas streams. In our experiments with pure H_2, this is not a problem and bulk diffusion is the slow step. After chemisorption, the H atoms enter into the octahedral interstices and diffuse interstitially through the metal lattices.

- The high mobility of H(D,T) in Pd and its alloys provides a means to purify H_2 and its isotopes by selective permeation through the Pd or Pd-alloy membranes.

Research on Non-Ideality in Pd-H and Pd-M-H Systems

Wicke and his students in Münster studied the diffusion of H in Pd and Pd-Ag alloys (298-373 K) in the 1960s using mainly electrochemical breakthrough techniques, i.e., time for a conc. perturbation on the upstream side of a membrane to appear on the downstream side. This can be used to obtain D_H at nearly constant H content. They were the first to systematically employ the thermodynamic factor to explain the dependence of D_H (Fick's diff. const) on the H content.

More recently (1989), Salomons in the Netherlands measured the dependence of D_H and E_D on the H content for Pd-, $Pd_{0.81}Cu_{0.19}$- and $Pd_{0.91}Y_{0.09}$-H alloys (400-600 K). He did not investigate the effect of alloy concentration on the dependence of D_H or E_D on H content.

Other Metal-H Systems

Non-ideality from the thermodynamic factor has been investigated in other metal-H systems, e.g., Nb-H, Ta-H and V-H, using mainly non-permeation techniques, e.g., NMR, quasi-elastic neutron scatt. and the Gorsky effect. The first two determine D_H^* (conc.indep. D) directly whereas the Gorsky effect measures D_H (Fick's). D_H can be determined from D_H^* for the two former techniques if the thermodynamic factor is known, e.g., from isotherms, and for the Gorsky technique, D_H^* can be obtained from D_H using the thermodynamic factor.

The conc.dep D_H is more important than D_H^* for practical H_2 separation and for H storage. Permeation through membranes is the important factor for H_2 separation/purification which depends on D_H and Δc_H.

Metal-H systems are best suited for studying the role of non-ideality because the solute concentration (H) can be varied over a wide range for some alloys and μ_H of the dissolved H is easy to determine from p_{H2}.

Why is this non-ideality relevant to H diffusion through membranes?

The conc.-dependent D_H can vary markedly with H conc. For example, Küssner (1967) found for H in $Pd_{0.77}Ag_{0.23}$ that $D_H(=D_H*)=3.5\times10^{-7}$ cm^2/s at H/metal($=r$)$\approx$0, $D_H=0.6\times10^{-7}$ cm^2/s at r=0.16 and $D_H=7.3\times10^{-7}$ cm^2/s at r=0.355 (303 K), i.e., a change in D_H of a factor of $\approx$12$\times$.

At the critical point in M-H systems, e.g., $r\approx0.27$, 563K, 19 bar for Pd-H, $D_H\rightarrow0$ because the thermodynamic factor $\rightarrow$0; this is called *critical slowing-down*.

This is an extreme example of the role of the thermodynamic factor.
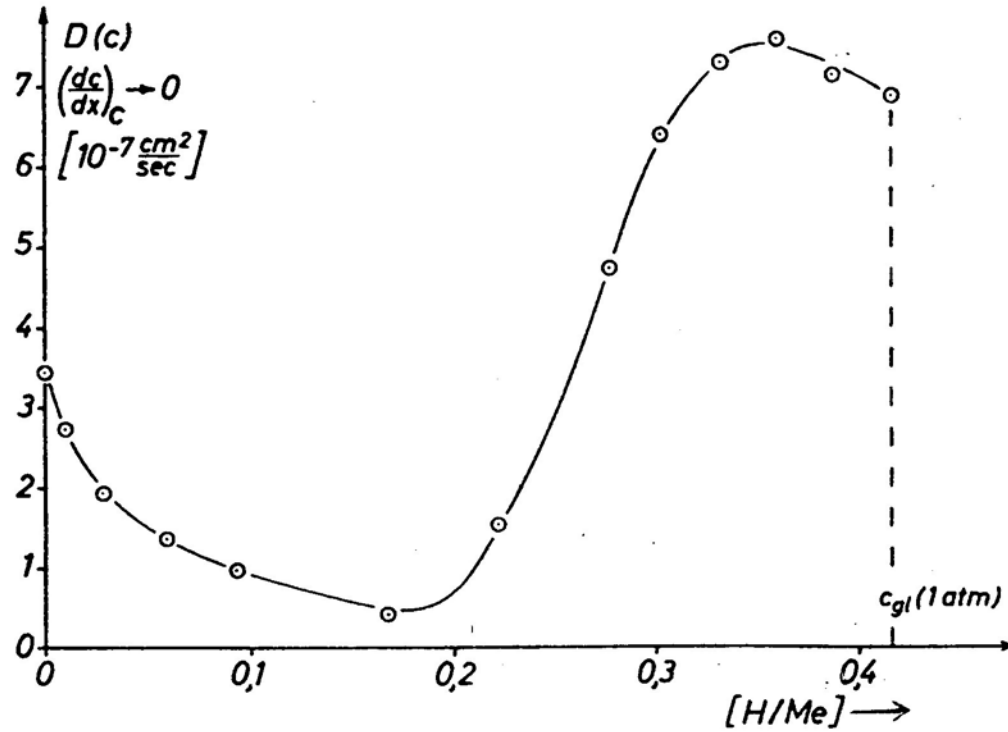
Concentration dependence of
the diffusion coefficient of H in Pd/Ag
(77/23) at 30 °C (*Küssner*)

$Pd_{0.77}Ag_{0.23}$

- $Pd_{0.77}Ag_{0.23}$ is the most commonly used membrane for H_2 purification because of its large H permeability over the range of interest for H_2 purification, ≈523 to ≈800 K.

For this alloy, $c_{H,up}$ is larger at comparable $p_{H2,up}$ than for Pd in the T-range of interest for H_2 purification while D_H is nearly the same and therefore J is larger than for Pd and for most other Pd-alloys.

- The H concentration in $Pd_{0.77}Ag_{0.23}$ can be varied continuously, i.e., a second, hydride phase does not appear as it does for Pd-H below 290°C and this is an advantage because the phase change causes plastic distortion and membrane cracking.

Simplified Diagram of Membrane Experiments

(in our experiments the thicknesses, d, are, d≈60 to 300 μm)

p_{up}

$p_{down}=0$

$\leftarrow d \rightarrow$
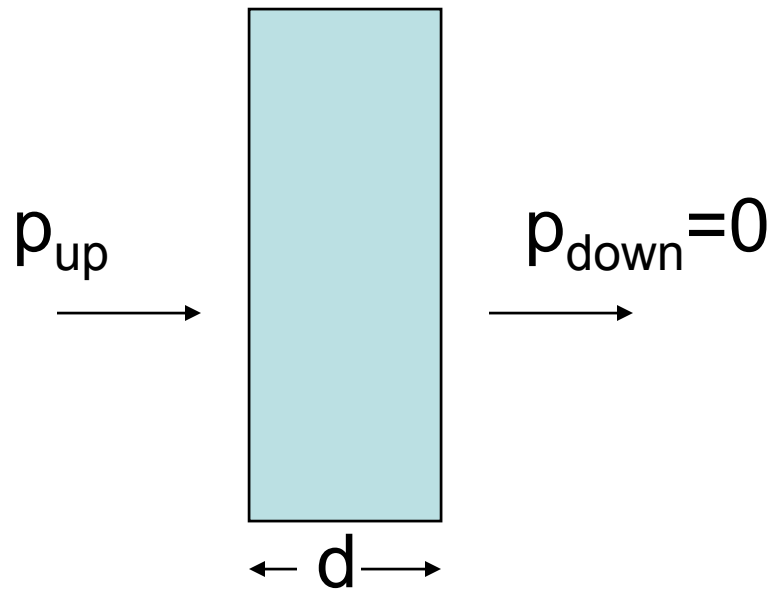
$J = -D_H(dc_H/dx)$ is Fick's 1st law for one-dim. diffusion where D_H may depend on H content.

The general (one-dimensional) diffusion eqn. is:

$J = -D^*_H(c_H/RT)(d\mu_H/dx)$, where D^*_H is independent of c_H

For M-H systems, $\mu_H(g) = \frac{1}{2}\mu_{H2}° + RT\ln p^{1/2}$ and at equil., $\mu_H(g) = \mu_H(metal) = \mu_H$

$(d\mu_H/dx) = (d\mu_H/dc_H)(dc_H/dx)$, then
$(d\mu_H/dx) = RT(d\ln p^{1/2}/dc_H)(dc_H/dx)$, subst. into above diff. eqn.,
gives $J = -D^*_H(c_H/RT) \, RT(d\ln p^{1/2}/dc_H)(dc_H/dx)$ or
$J = -D^*_H(d\ln p^{1/2}/d\ln c_H)(dc_H/dx)$

If this is compared to Fick's 1st law, $J \approx -D_H(dc_H/dx)$, it follows that

$D_H = D^*_H(d\ln p^{1/2}/d\ln c_H)_T$

$(d\ln p^{1/2}/d\ln c_H)_T$ is referred to as the thermodynamic factor and is 1.0 for an ideal solution, e.g., when H/M→0. It permits D_H^* to be determined from D_H at a given c_H.

Instead of c_H, *r*=H-to-metal, atom ratio, is usually used for M-H isotherms. The thermodynamic factor $(d\ln p^{1/2}/d\ln c_H)_T$ will be the same, $(d\ln p^{1/2}/d\ln c_H)=$

$(d\ln p^{1/2}/d\ln r)=f(r)$

We have measured isotherms to obtain f(*r*) to determine D_H^* from D_H.

The slopes of these $\ln p^{1/2}$ *versus* $\ln r$ isotherms for the $Pd_{0.77}Ag_{0.23}$ alloy give f(r) at each r; the dashed line is *for* ideal behavior.
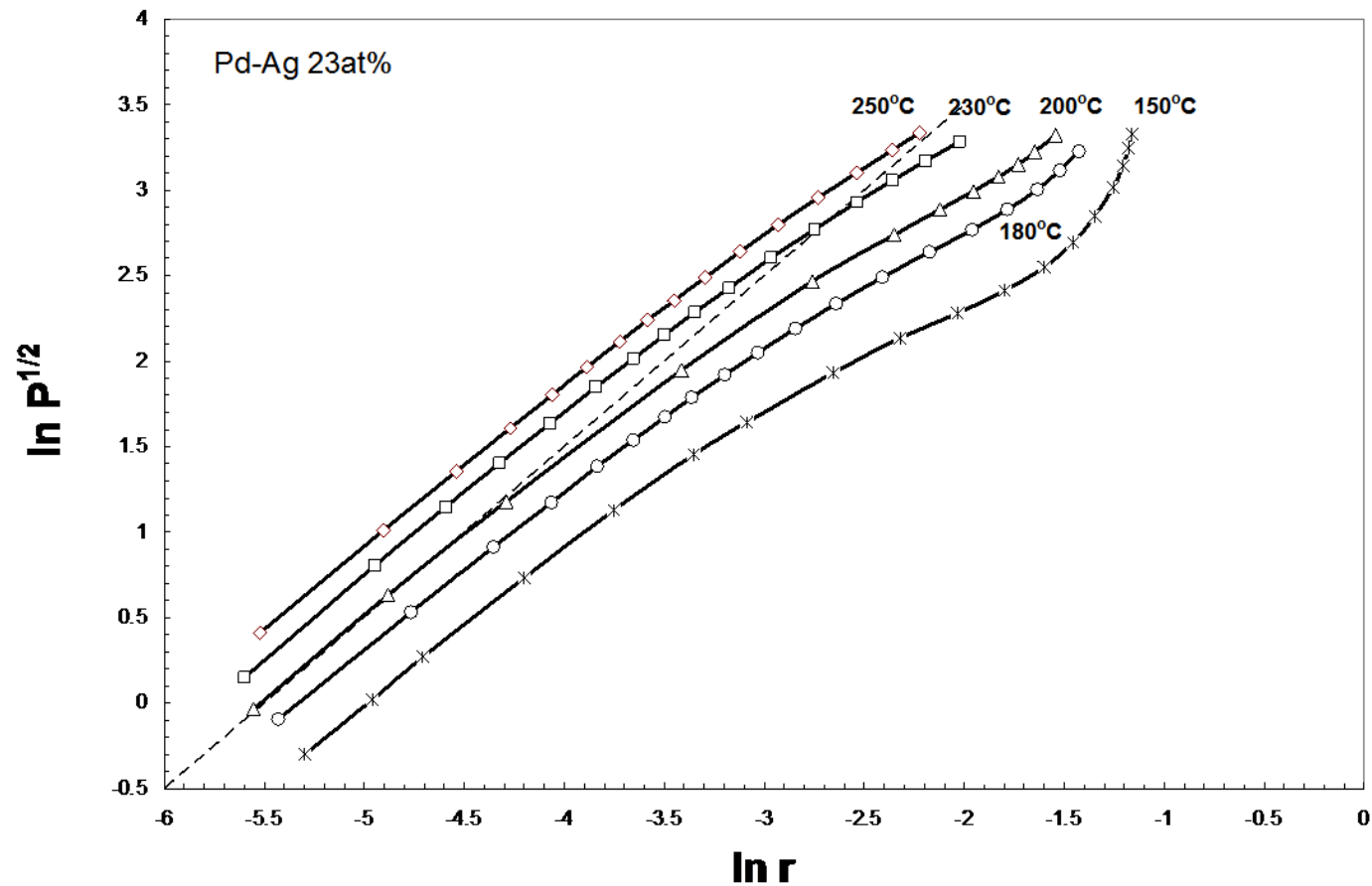
f(r) against r for the $Pd_{0.77}Ag_{0.23}$ Alloy (423 K) (from the slopes of the $lnp^{1/2}$-r isotherms)
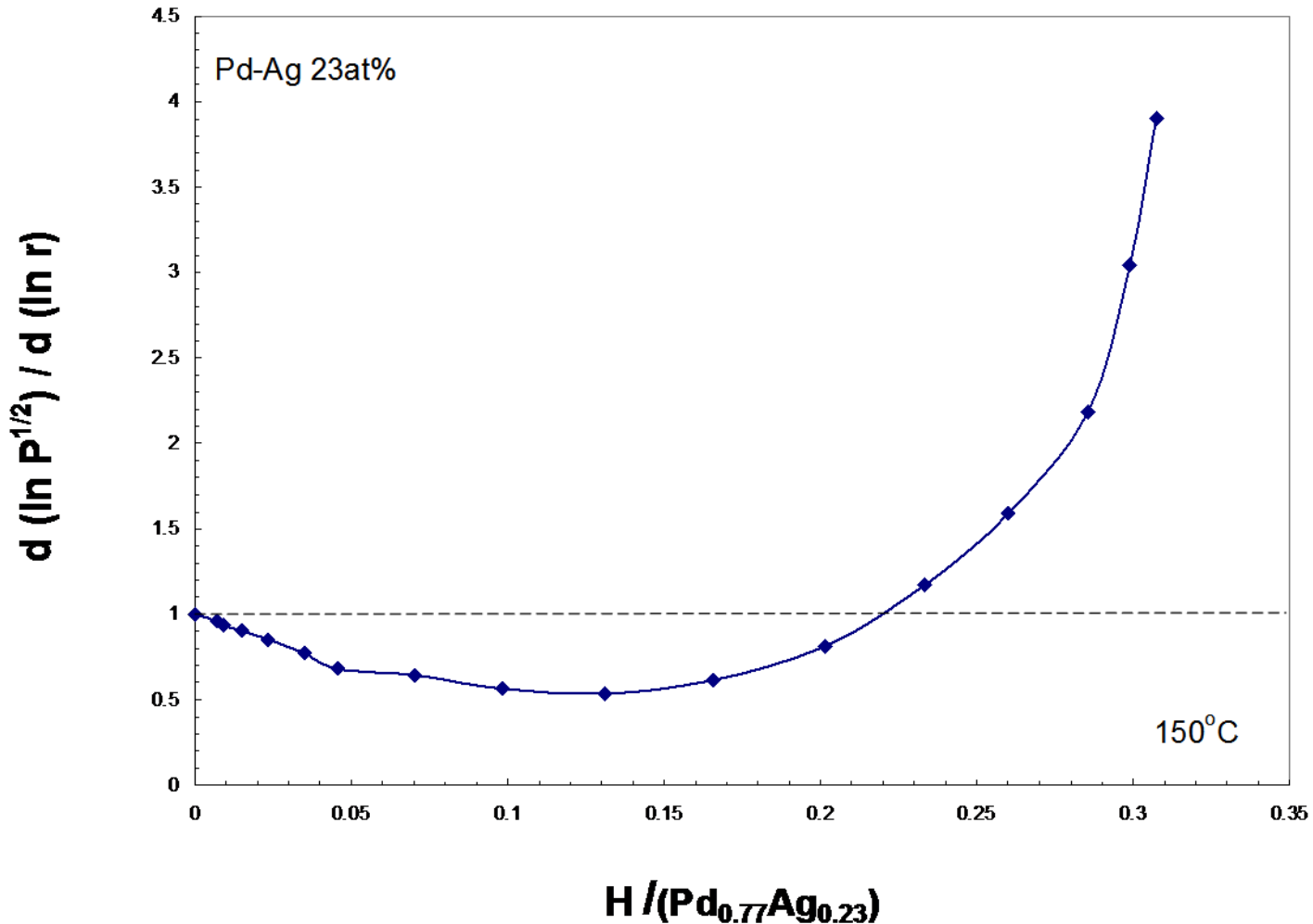
Using f(r) values from an isotherm (303K) measured in our laboratory and D_H* from Küssner's results we have calculated D_H values. (His data can be considered to be at nearly constant values of r).

Kussner Data Pd$_{0.77}$Ag$_{0.23}$
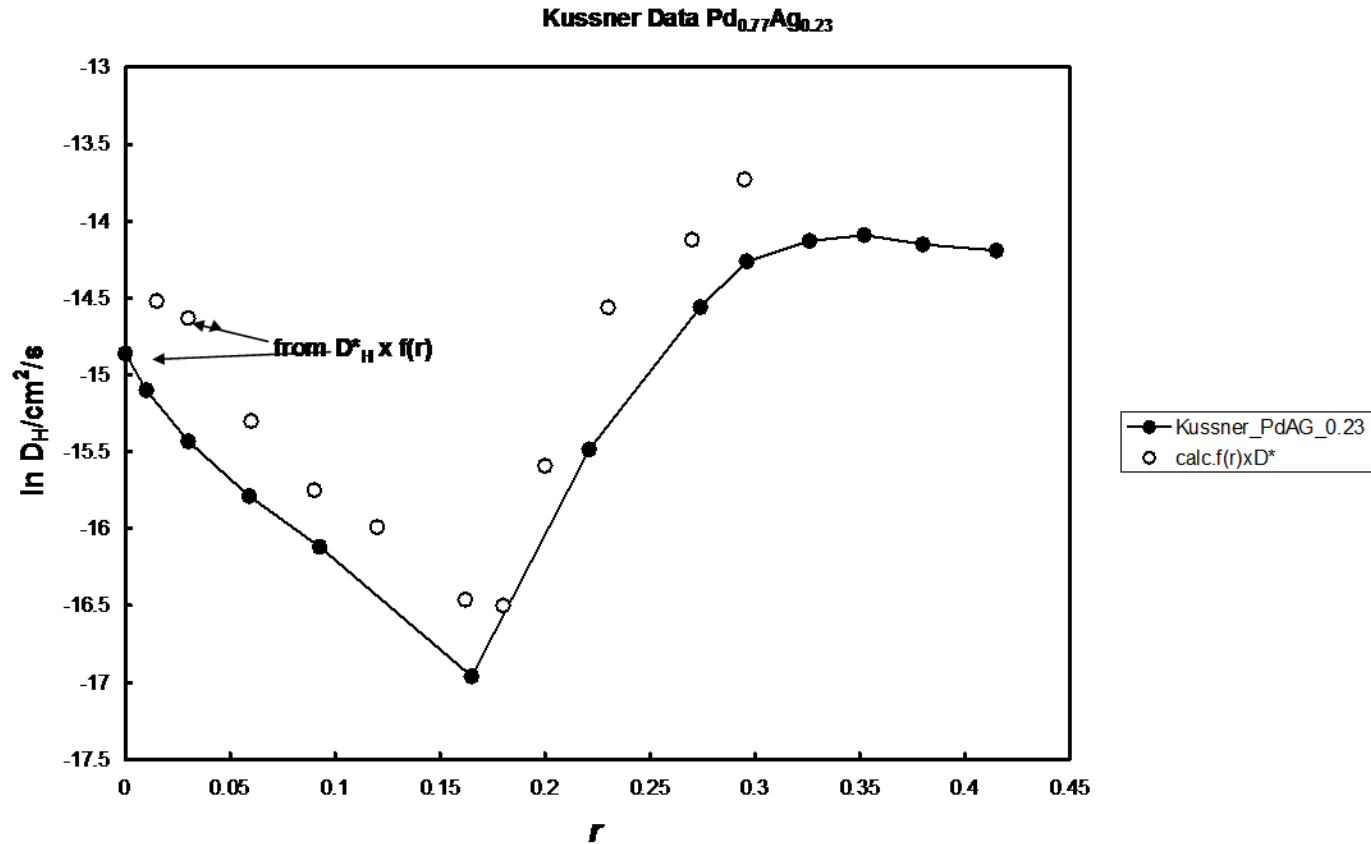
For Practical Conditions of H$_2$ Separation
$$c_{H,up} >> c_{H,down} \approx 0$$

For these boundary conditions, Fick's 1st law,
$J = -D_H(dc_H/dx)$, becomes $J = -D_H c_{H,up}/d$ when $c_{H,down}=0$
and d is the membrane thickness.
In our work the D_H are determined from this equation
because of the boundary conditions $c_{H,up} >> c_{H,down} \approx 0$.

Practical Conditions for H_2 Separation (cont.)

When $c_{H,up} >> c_{H,down} \approx 0$, f($r$) will vary with distance traveled through the membrane because c_H varies with the distance through the membrane.

An equation which allows for this variation of f(r) is:

$$D_H = D_H*(\int f(r)dr)/r_{up} = D_H*F(r)/r_{up}$$

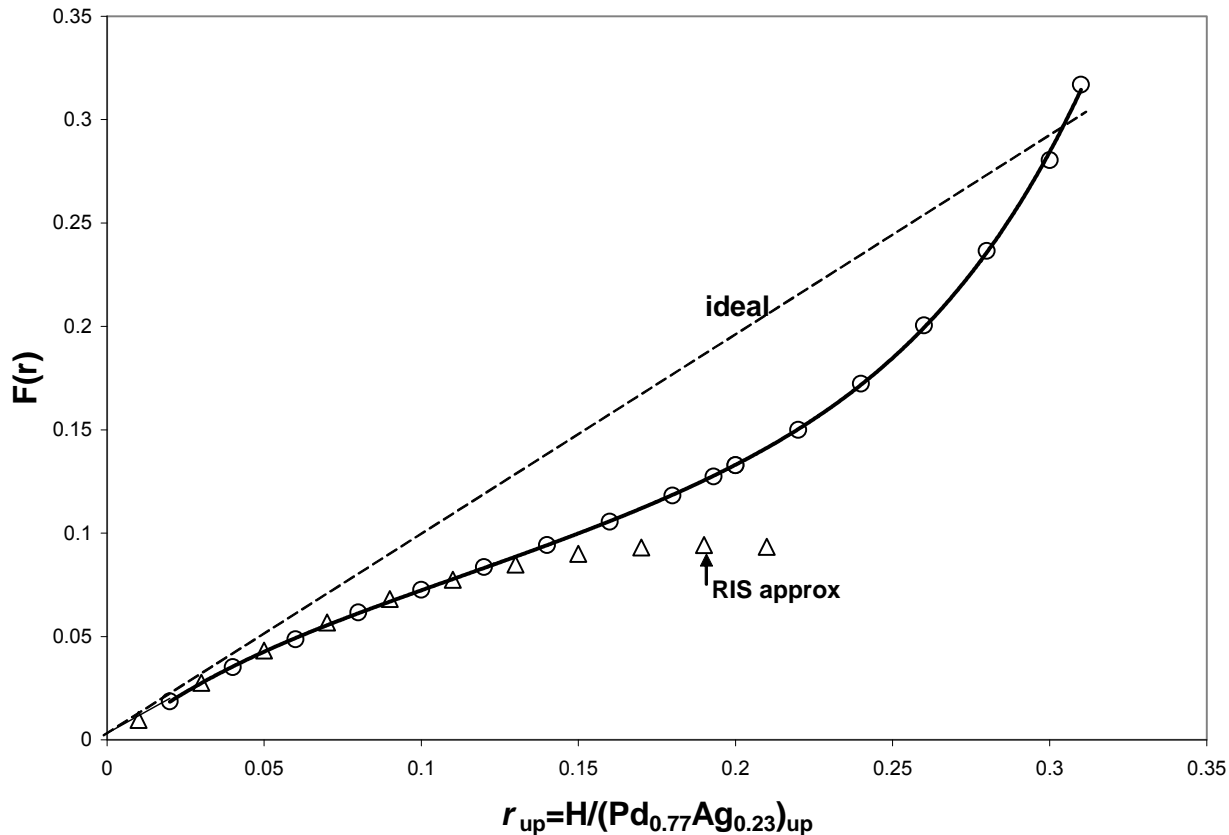where $(\int f(r)dr)/r_{up}$ is the mean value of f(r) over the membrane and D_H is that measured using

$$J = -D_H c_{H,up}/d \quad \text{where } c_{H,down} \approx 0.$$

The integration is from 0 to r_{up}. In the ideal case, f(r)=1.0 and $D_H = D_H*$

F(r) vs r from integration of f(r) vs r, shown above for Pd$_{0.77}$Ag$_{0.23}$ at 423K, i.e., F(r)=∫f(r)dr, where D$_H$=D$_H$*F(r)/r_{up}
(---, ideal, Δ, RIS approximation)

The Regular Interstitial Solution (RIS) is a useful Approx. for M-H Systems at low r

$\mu_H = \mu_H^{\circ} + RT\ln[r/(1-r)] + \mu_H^E(r)$ where E indicates an excess or non-ideal term.

The RIS approx. assumes that $\mu_H^E(r) = g_1\ r$, *i.e.*, g_1 is the 1st order coefficient of an expansion of μ_H^E in r and therefore.

$\mu_H \approx \mu_H + RT\ln[r/(1-r)] + g_1\ r$ and $g_1 = h_1 - Ts_1$.

Since $\mu_H(g) = \frac{1}{2}\mu_{H2}^{\circ} + RT\ln p^{1/2} = \mu_H(metal)$,

$RT\ln p^{1/2} = \Delta\mu_H + RT\ln[r/(1-r)] + (g_1\ r)$.

For the present boundary conditions the RIS model gives

$f(r) = (d\ln p^{1/2}/d\ln r) \approx (1-r)^{-1} + g_1 r/2RT$ and $(\int f(r)dr)/r_{up} = F(r)/r_{up} \approx [1 + g_1 r_{up}/2RT]$, $D_H = D_H^* \ F(r)/r_{up} \approx D_H^*[1 + g_1 r_{up}/2RT]$ or for small r using $\ln(1+x) \approx x$

$\ln D_H \approx \ln D_H^* + g_1 r_{up}/2RT$

At small r, expressions for E_D and $D_H°$ as a function of r can also be obtained from the RIS model and $D_H=D_H°\exp(-E_D/RT)$

If ln $D_H \approx$ ln D_H*+ $g_1 r_{up}/2RT$ is differentiated with respect to 1/T at constant r_{up}, d lnD_H/d(1/T)$\approx$d ln D_H*/d(1/T)+ [d(g_1/T)/d(1/T)](r_{up}/2R) or $-E_D/R=-E_D$*/R+[d(g_1/T)/d(1/T)](r_{up}/2R). Since $g_1=h_1-Ts_1$, d(g_1/T)/d(1/T)=h_1, $E_D \approx E_D$*$-h_1 r_{up}/2$.

It follows from the above that

ln $D_H° \approx$ ln $D_H°$*$- s_1 r_{up}/2R$

Summary of Relations between Diffusion and Thermodynamic Parameters from the RIS Approx for small *r*

$$\ln D_H = \ln D_H^* + g_1 r_{up}/2RT$$

$$E_D = E_D^* - h_1 r_{up}/2$$

$$\ln D_H^\circ = \ln D_H^{\circ *} - s_1 r_{up}/2R$$

$$(g_1 = h_1 - Ts_1)$$

(for conditions of constant *r*, $r_{up}/2 = r$ in these eqns.)

These excess parameters can also be determined from thermodynamics. For instance, slopes of plots of $\ln p^{1/2}(1-r)/r$ against *r* at constant T give g_1 at small *r*.

(It's unusual to be able to derive the same quantities from both experimental kinetic and thermodynamic data)

Plots of RTln D_H(473 K) and E_D versus *r* for the $Pd_{0.90}Ag_{0.10}$ Alloy (Wang, Flanagan, Shanahan, J. Phys. Chem.,**112** (2008) 1135)
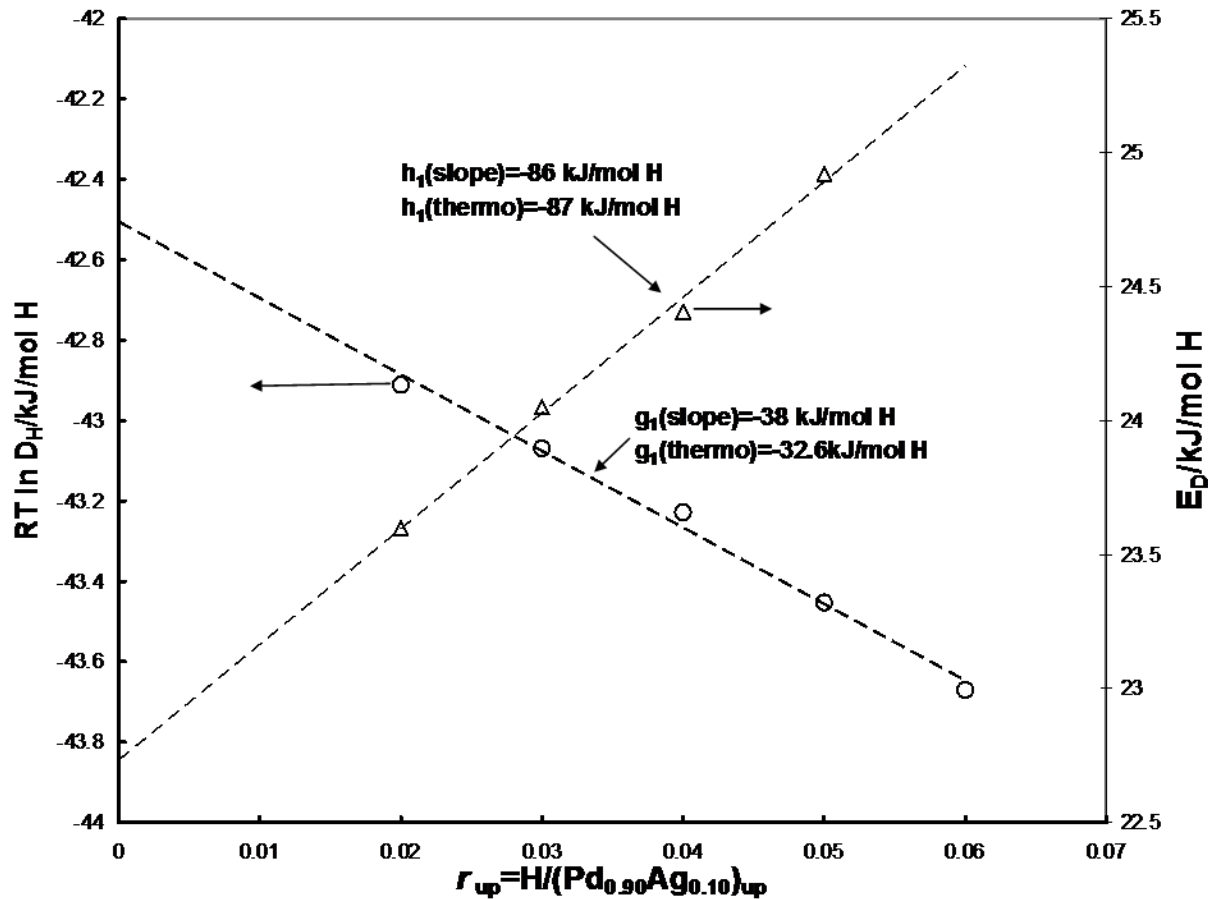
# Effect of H content on E_D for $Pd_{0.77}Ag_{0.23}$ and $Pd_{0.5}Ag_{0.5}$ Alloy Membranes (Wang, Flanagan, Shanahan, J. Phys. Chem.,**112** (2008) 1135)
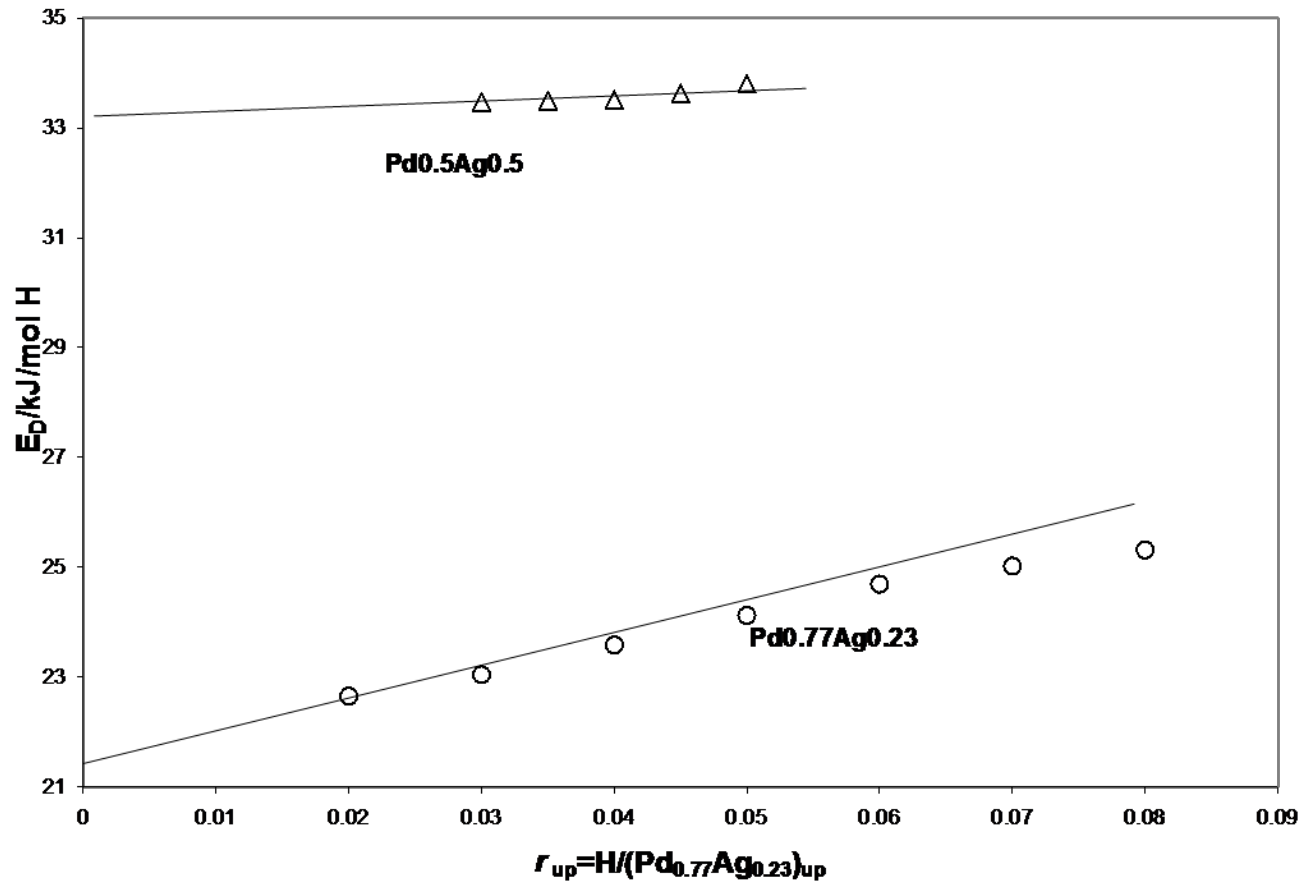
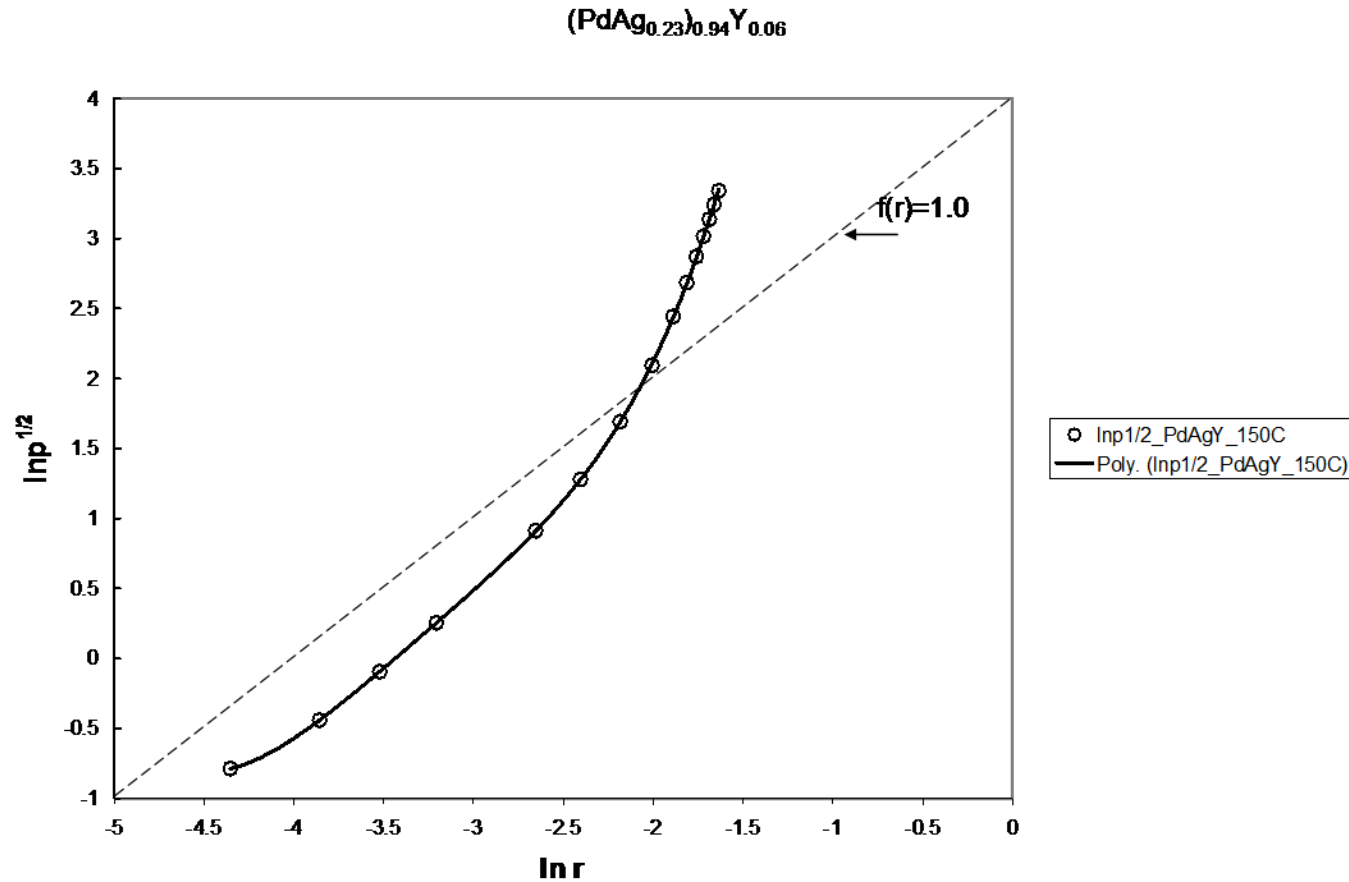# Increases shown for $D_H°$ and E_D with *r* for the $Pd_{0.77}Ag_{0.23}$ Alloy $(D_H=D_H°exp(−E_D/RT))$
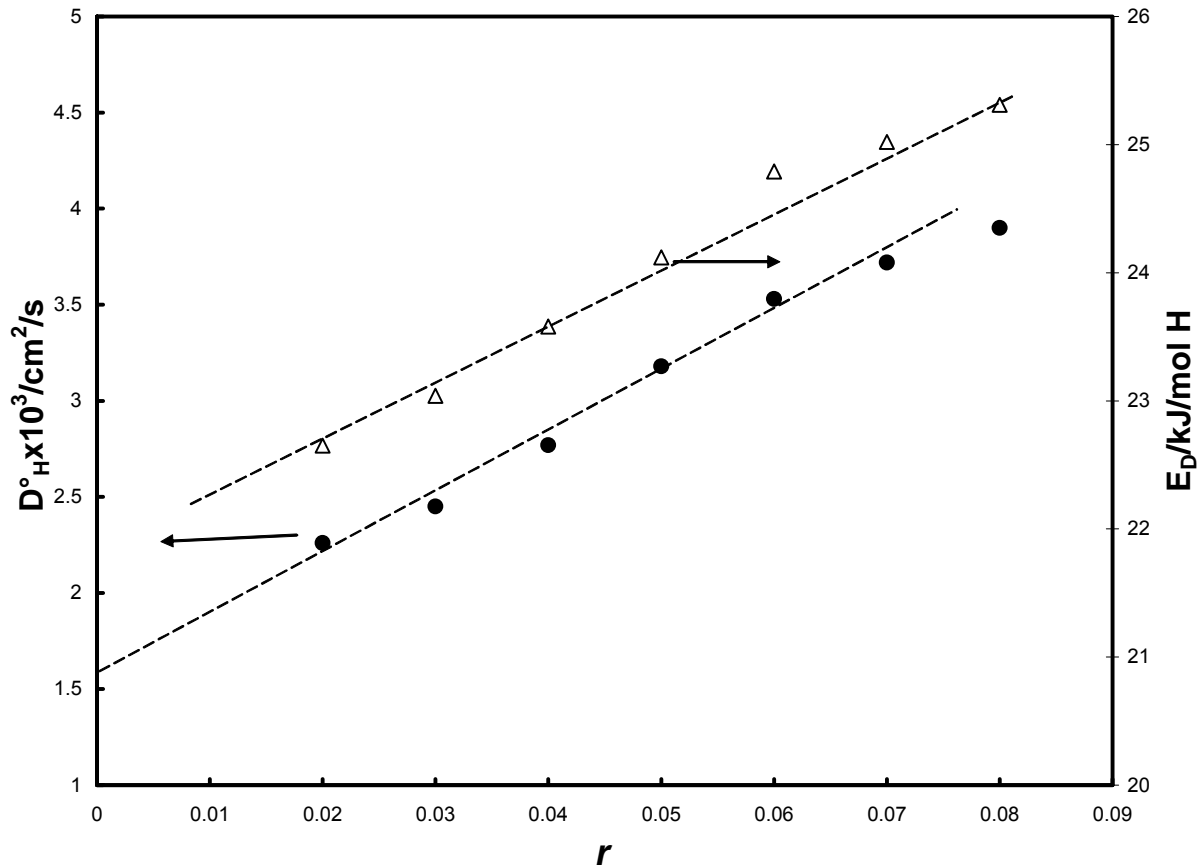
H_2 Isotherms for $(Pd_{0.77}Ag_{0.23})_{0.94}Y_{0.06}$. (Pd-Y alloys have a larger H_2 solubilities than Pd or Pd-Ag alloys over the T range of interest and have been suggested and employed as purification membranes by I. R. Harris et al.)
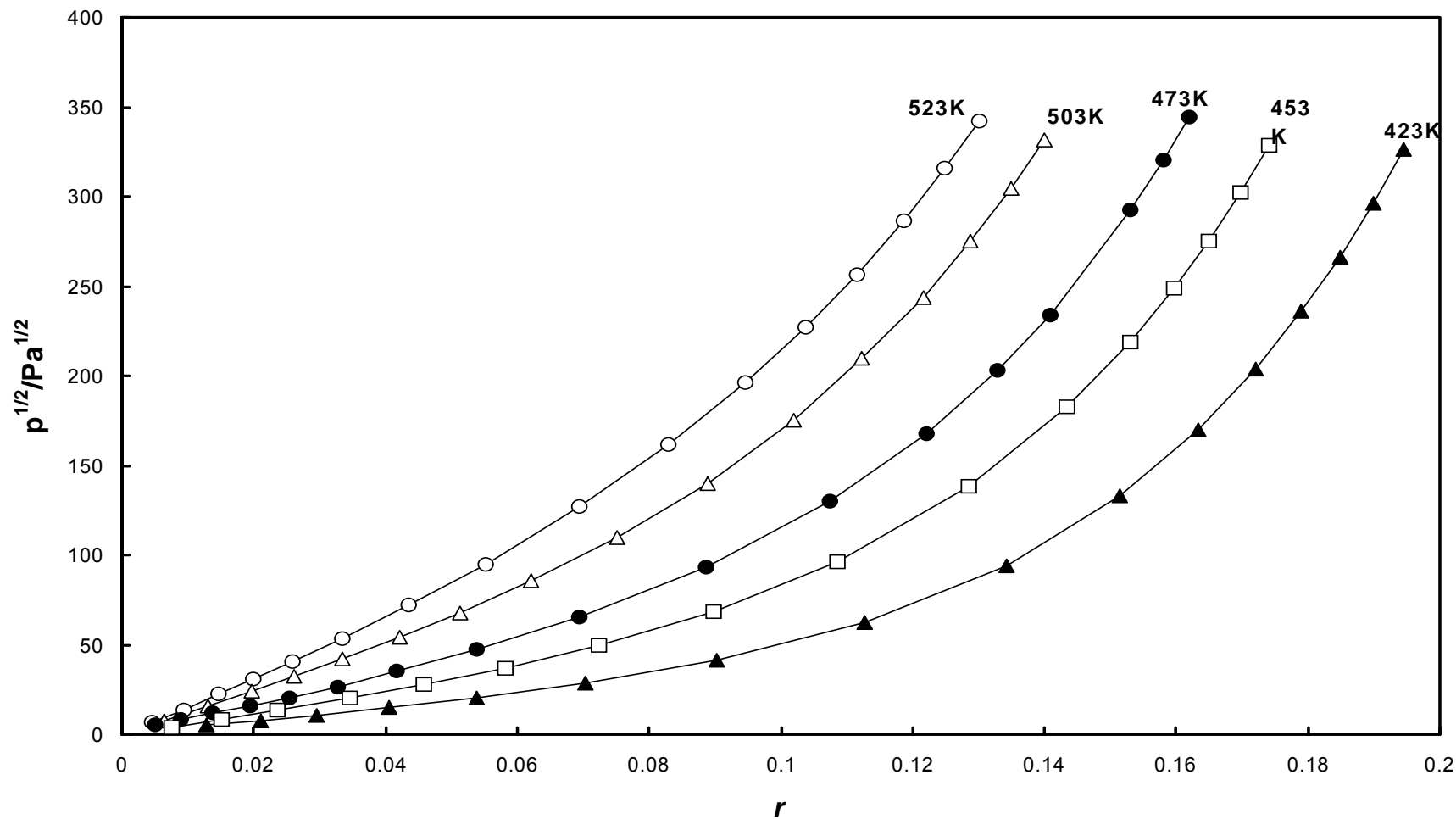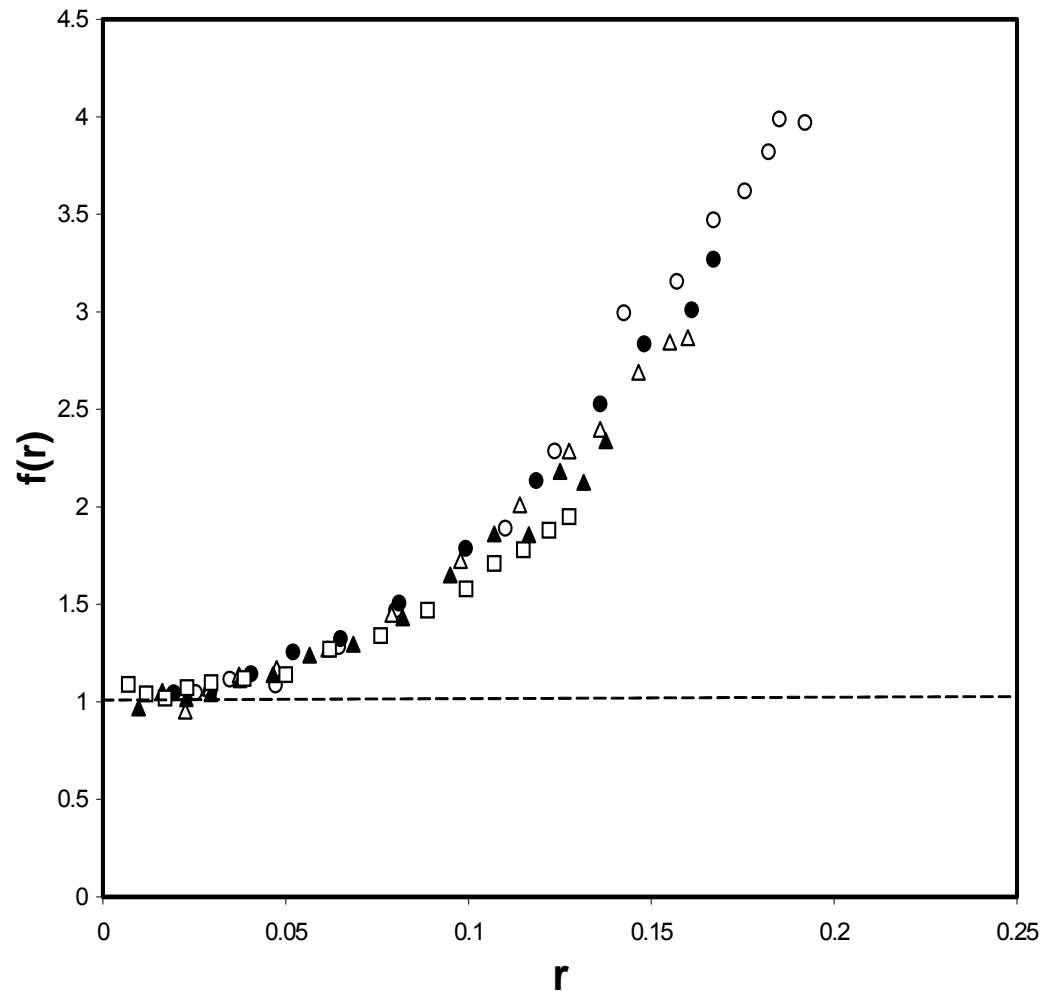
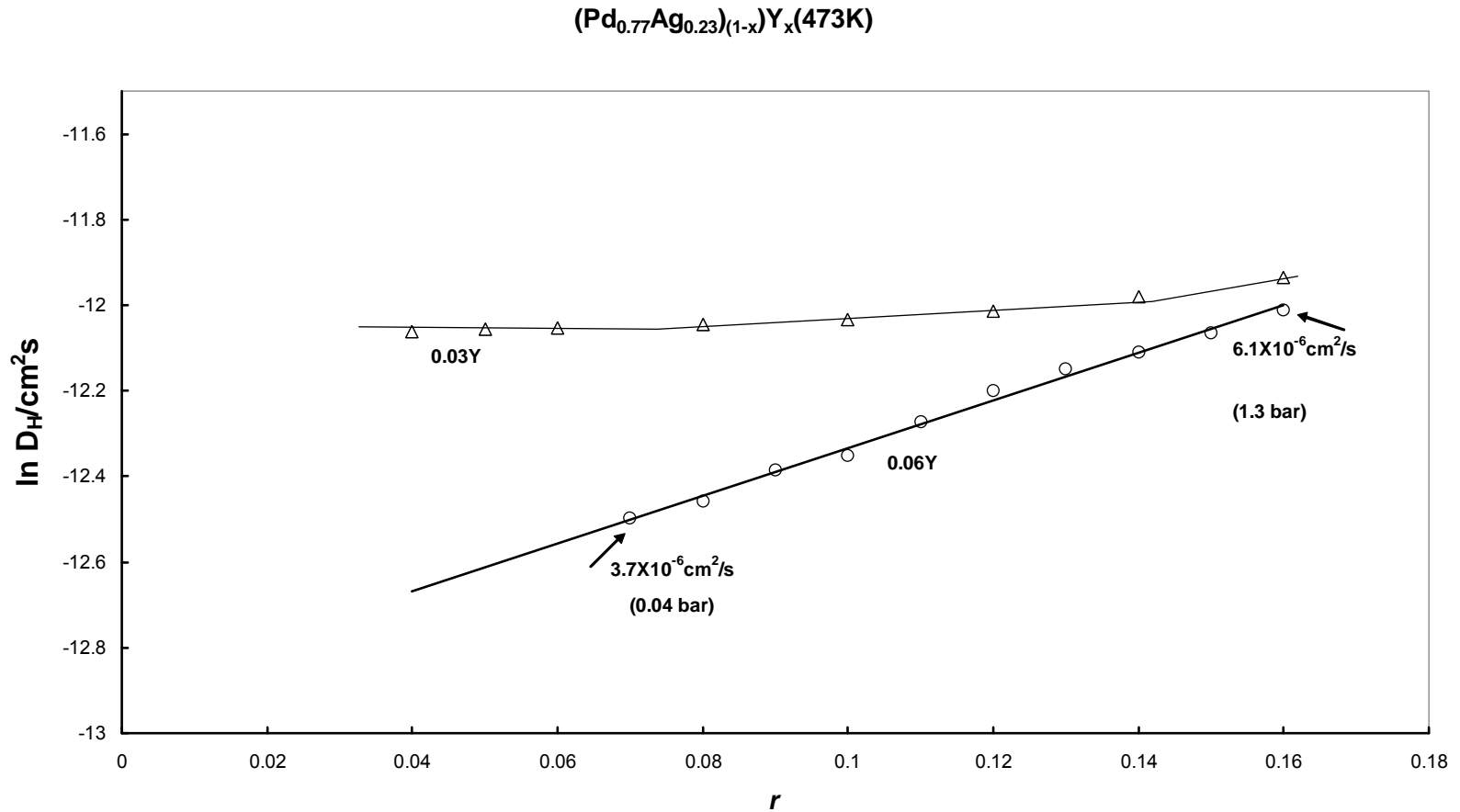# The slopes give f(*r*) for the $(Pd_{0.77}Ag_{0.23})_{0.94}Y_{0.06}$ Alloy at 423K

$(PdAg_{0.23})_{0.94}Y_{0.06}$

Plots of f(*r*) against *r* for $(Pd_{0.77}Ag_{0.23})_{0.94}Y_{0.06}$

(○,423K;●,453K;△,473K;▲,503K;□,523K)

In D_H as function of H content for the $(Pd_{0.77}Ag_{0.23})_{0.97}Y_{0.03}$ and $(Pd_{0.77}Ag_{0.23})_{0.97}Y_{0.06}$ Alloys (473 K). D_H increases with *r* for the latter!

$(Pd_{0.77}Ag_{0.23})_{(1-x)}Y_x$(473K)

E_D as a function of H content for $(Pd_{0.77}Ag_{0.23})_{0.97}Y_{0.03}$ and $(Pd_{0.77}Ag_{0.23})_{0.94}Y_{0.06}$ alloys. E_D decreases with r for the latter alloy.
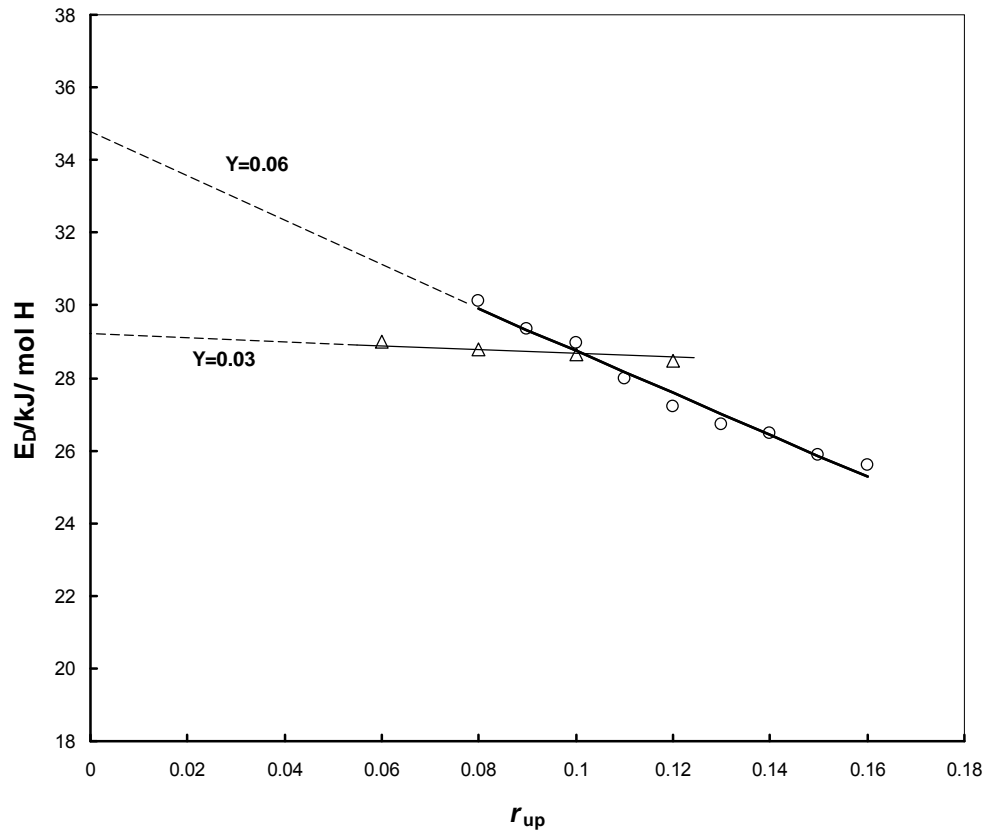
Conclusions

When p_{up} is relatively high, i.e., conditions needed to maximize H_2 separation, f(r) may differ from 1.0 even at elevated T and this has often been ignored. For example, Harris et al have determined D_H. with ($p_{up} - p_{down}$)=3.5 bar at 473 K for $Pd_{0.75}Ag_{0.25}$, $Pd_{0.92}Y_{0.08}$ and other alloys. These conditions will lead to f(r)≠1.0 and will have different values for the alloys and therefore it is not clear what D_H values are being compared under these conditions.

One goal will be to use non-ideality to increase the membrane permeability by increasing D_H at T and p_{H2} of interest for H_2 separation. Alloys with isotherms similar to that of the $(Pd_{0.77}Ag_{0.23})_{0.94}Y_{0.06}$ alloy at the desired temperatures are needed, i.e., those with large positive deviations from ideality yet having large solubilities.
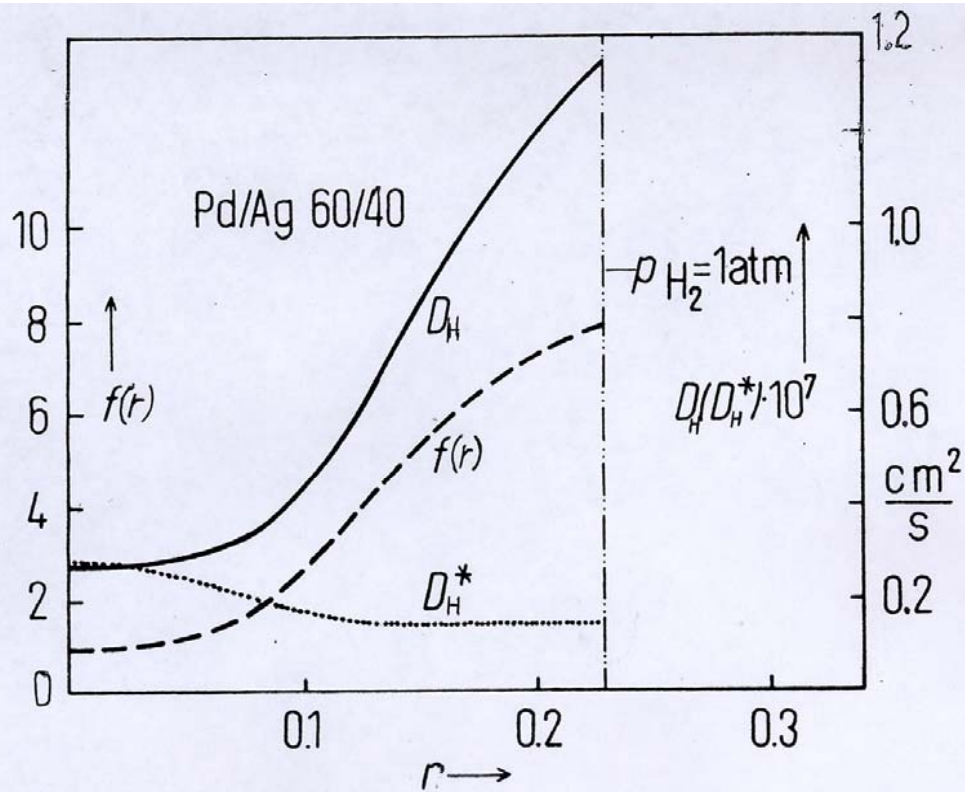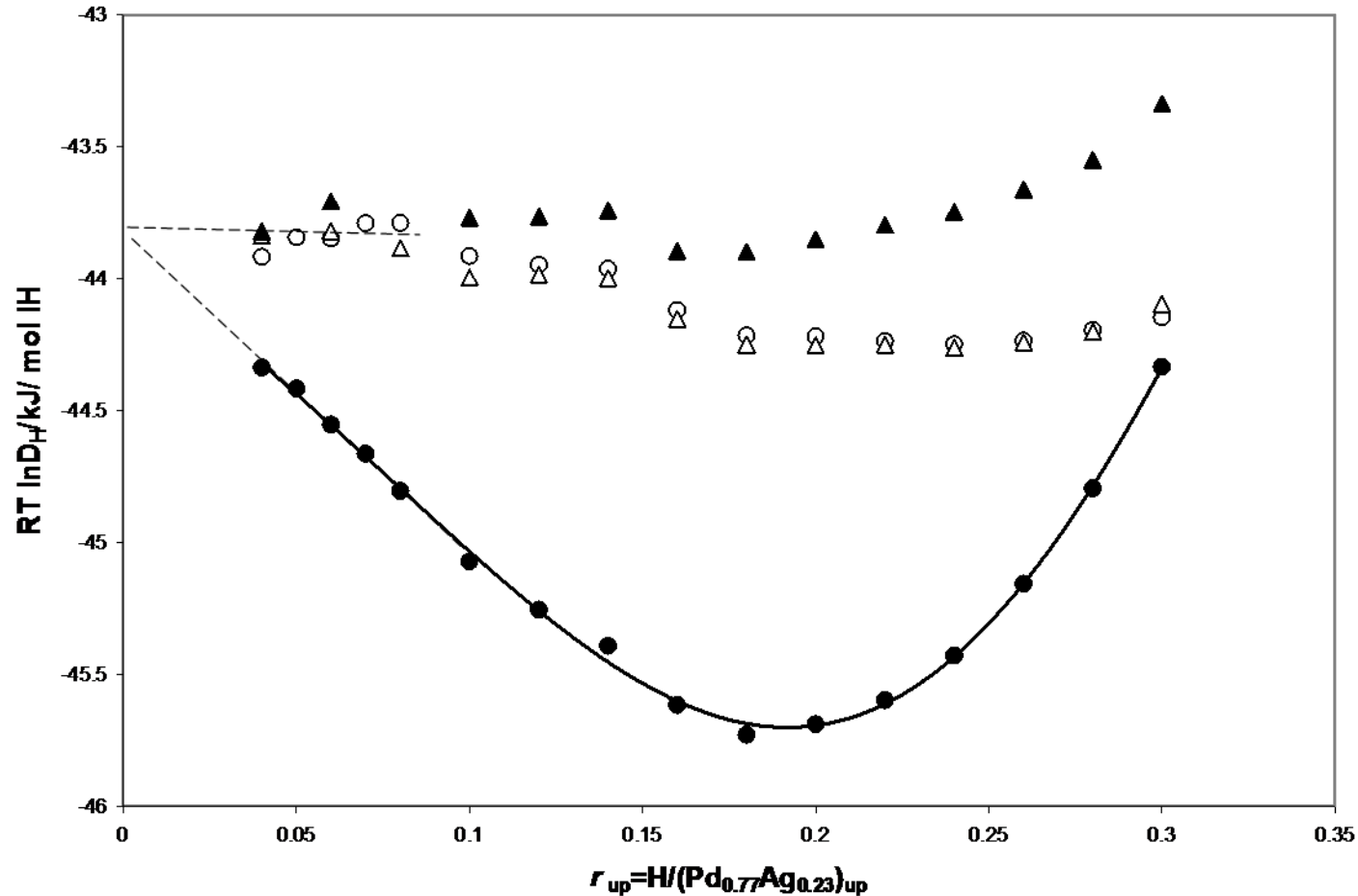
Dependence of Fick's (D_H) and Einstein's (D_H^*) diffusion coefficients
and thermodynamic factor f on atomic ratio H/Me (r) (303 K)
from Züchner and Boes (Ber. Bunsenges Physik. Chem.
1976)

Plot of RTln D_H *vs* r_{up} (423 K) $Pd_{0.77}Ag_{0.23}$ Alloy

Effect of r_{up} on D_H°

For Pd and *Pd*-M alloys (with X_M not too large), h_1 is more negative than g_1. Since $g_1 = h_1 - Ts_1$, $s_1 = (h_1 - g_1)/T$, and therefore s_1 must be negative. (This is found experimentally for Pd-H, e.g., at 473 K, $h_1 = -83$ kJ/mol H, $g_1 = -43$ kJ/mol H (Kuji et al, J. Phys. F: Met. Phys. 13 (1983) 1785)

From $\ln D_H^\circ = \ln D_H^{\circ *} - s_1 r_{up}/2R$, it follows that D_H° must increase with r_{up} for these systems at low H contents, i.e., there is a compensation effect operating, when r_{up} increases, E_D increases (decreases D_H) and $\ln D_H^\circ$ increases (increases D_H).

$$(D_H = D_H^\circ \exp(-E_D/RT))$$